Fossil methane source dominates Cariaco Basin water column methane geochemistry

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[1] Natural radiocarbon measurements on methane (^{14}C-CH_4) extracted from the Cariaco Basin water column show that 98% of the methane in Cariaco Basin waters is derived from fossil (radiocarbon-free) sources. Previous work on Cariaco Basin methane (CH_4) considered only a diagenetic sediment source. Similar measurements of sediment ^{14}C-CH_4 indicate that sediment CH_4 is produced from modern particulate material; thus the sediment and water column CH_4 have distinct sources. Using time-dependent CH_4 geochemical box models which include a fossil seep CH_4 source term, we estimate 1) 0.024–0.028 Tg y^{-1} of seep CH_4 are added to the Cariaco Basin water column, 2) the water column CH_4 will reach a steady-state concentration by the year 2065, and 3) the seep CH_4 inputs possibly began in 1967, following the July 30 Caracas earthquake. Oxidizing this CH_4 to dissolved inorganic carbon does not appear to affect Cariaco Basin ^{14}C chronologies. **Citation:** Kessler, J. D., W. S. Reeburgh, J. Southon, and R. Varela (2005), Fossil methane source dominates Cariaco Basin water column methane geochemistry, *Geophys. Res. Lett.*, *32*, L12609, doi:10.1029/2005GL022984.

1. Introduction

[2] The Cariaco Basin has been an ideal site for studies of anoxic geochemistry and, because the sediments are unbioturbated, for paleoclimatic studies. The Cariaco Basin is located on the continental margin of Venezuela (10°30′N, 65°W), is almost 1400 m deep, and is separated from the tropical Atlantic by 150 m sills. Anoxic conditions are maintained below a depth between 250–300 m by thermal stratification and high flux of organic matter to the deep basin. High sedimentation rates, plus lack of bioturbation due to anoxia, have led to the extensive use of Cariaco Basin sediment cores for developing high-resolution paleoclimate records [*Hughen et al.*, 1996b; *Lin et al.*, 1997; *Hughen et al.*, 2000; *Peterson et al.*, 2000; *Haug et al.*, 2001] and ^{14}C calibration chronologies [*Hughen et al.*, 2000, 2004].

[3] Anoxic conditions in the Cariaco Basin were discovered by L. V. Worthington in 1954 and were followed by studies on the stoichiometry of anaerobic degradation of organic matter [*Richards and Vaccaro*, 1956]. Steady-state vertical advection-diffusion models were used to explain silica, sulfide, phosphate [*Fanning and Pilson*, 1972], and methane (CH_4) [*Reeburgh*, 1976] distributions. Temporal changes in the hydrography, depth of the anoxic/oxic interface, and concentration of several constituents (including CH_4) in the Cariaco Basin water column led to the development of a time-dependent box model [*Scranton et al.*, 1987; *Scranton*, 1988] of the anoxic region of the Cariaco Basin. Methane modeling studies [*Reeburgh*, 1976; *Scranton*, 1988] showed that the CH_4 geochemistry could be explained with a diagenetic sediment CH_4 source, no water column CH_4 production, and water column anaerobic CH_4 oxidation. *Ward et al.* [1987] measured Cariaco Basin water column aerobic and anaerobic CH_4 oxidation rates using ^{14}C-labelled CH_4. Although there are written and anecdotal reports of natural gas releases in this region [*von Humboldt*, 1900], this previous work gave no indication that seeps were an important Cariaco Basin CH_4 source.

2. Experimental

[4] Here we present the first natural radiocarbon measurements on Cariaco Basin water column and sediment methane (^{14}C-CH_4). Water and sediment samples were collected from January 21–24, 2004 on board the B/O *Hermano Gines* 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 [*Scranton et al.*, 2001; *Astor et al.*, 2003].

[5] Seawater CH_4 concentration analyses were conducted by filling 160 mL serum vials directly from Niskin bottles and inserting a 13 mL helium (He) headspace. Sediment CH_4 concentration analyses were conducted by making a slurry of 3 mL of sediment and 6 mL of He purged water in 37.5 mL serum vials. All vials were poisoned with a saturated mercuric chloride solution and sealed with blue butyl rubber stoppers and crimp caps. After the samples were allowed to equilibrate, three aliquots of the headspace were removed for concentration analysis with gas chromatography (GC) and flame ionization detection. The results have been corrected for the amount of CH_4 still dissolved in solution [*Yamamoto et al.*, 1976].

[6] Shipboard extraction of CH_4 for radiocarbon analysis was conducted using Lamont radon stripping boards (J. D. Kessler and W. S. Reeburgh, Preparation of natural methane samples for stable isotope and radiocarbon analysis, submitted to *Limnology and Oceanography: Methods*, 2005, hereinafter referred to as Kessler and Reeburgh, submitted manuscript, 2005). Evacuated 20 L glass carboys are filled with 19 L of seawater directly from Niskin bottles, connected to the stripping

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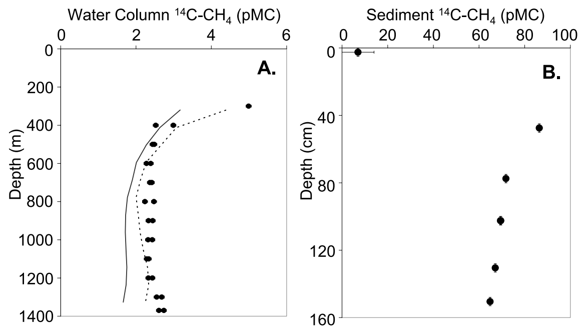

Figure 1. (a) Natural radiocarbon results for Cariaco Basin water column and (b) sediment methane (^{14}C-CH_4) expressed as percent Modern Carbon (pMC). Note the differences in horizontal and vertical scales between the water column (Figure 1a) and sediment (Figure 1b). Error bars are ±1 σ. The dashed and solid lines in Figure 1a are predicted ^{14}C-CH_4 profiles based on models with and without mid-depth intrusions, respectively. The main difference between the model results is attributed to different eddy diffusion coefficients.

boards [*Mathieu et al.*, 1988], and purged with He to extract the dissolved CH_4. The extracted CH_4 is trapped in a U-trap at liquid nitrogen temperature. The U-traps were fabricated with electropolished stainless steel tubing (3/8″ OD, 2 feet long) bent in a "U" shape, filled with a molecular sieve (HiSiv 3000 in the 1/16″ pellet form), and equipped with nonrotating-stem needle valves with PEEK stem tips (Swagelok D-Series). HiSiv 3000 (UOP Molsiv Adsorbents) was chosen as the trapping medium due to its trapping efficiency, lack of isotopic fractionation, and ability to quantitatively trap CH_4 at −172°C. The traps are reusable and are reactivated between each use (He flow at 0.5 L min^{-1}, 275°C) with an oven designed to heat the traps without damaging the valves.

[7] In order to extract, purify, and oxidize the CH_4 collected in the U-traps, a two-stage purification-oxidation vacuum line has been developed at UC Irvine (Kessler and Reeburgh, submitted manuscript, 2005). The first stage of this vacuum line is a continuous loop designed to extract the CH_4 from the U-traps and pass it through traps designed to remove H_2O, CO_2, CO, and non-CH_4 hydrocarbons. Analysis of our purified sample gas with Quadrupole Mass Spectroscopy at the National Institute of Standards and Technology [*Currie et al.*, 2000] showed no detectable traces of carbonaceous impurities. Next, the purified CH_4 is injected into an adjoining oxidation loop on the same vacuum line which continuously circulates the purified CH_4 through a 975°C CuO furnace converting it to CO_2 and H_2O.

[8] An aliquot of the CO_2 produced from CH_4 oxidation was converted to graphite with hydrogen reduction catalyzed by iron [*Vogel et al.*, 1984] and analyzed with ^{14}C Accelerator Mass Spectrometry (AMS) at the Keck Carbon Cycle AMS facility at UC Irvine. We have shown that these procedures are quantitative, do not cause isotope fractionation, and that the blanks are small ($0.47_7 \pm 0.24$ μmoles of CH_4; ^{14}C-CH_4 = 96.1 ± 0.3 pMC (percent Modern Carbon)) [*Stuiver and Polach*, 1977; Kessler and Reeburgh, submitted manuscript, 2005].

[9] At water depths ≤ 300 m, the CH_4 concentration was too low to collect enough CH_4 carbon for a conventional AMS measurement. Small sample AMS measurements were conducted at these depths (6 μmoles of carbon instead of the conventional 83 μmoles of carbon). At depths ≤ 250 m, the amount of CH_4 carbon collected required dilution with ^{14}C-devoid CO_2 to conduct a successful AMS measurement [*Currie et al.*, 2000]. Diluted samples have been back corrected.

3. Results

[10] Since previous work suggested a diagentic sediment source of CH_4 to the water column, the ^{14}C-CH_4 results (Figure 1a) were unexpected; most of the Cariaco Basin water column CH_4 is almost completely devoid of radiocarbon (2.5 pMC), though the ^{14}C content increases above 400 m. In contrast, the sediment CH_4 contains significant amounts of ^{14}C (86.4 pMC at 45 cm depth) indicating the CH_4 is derived from relatively modern particulate carbon (Figure 1b). Since the turnover time of CH_4 in the Cariaco Basin water column is short (50–60 years), as calculated from our CH_4 concentration data and specific CH_4 oxidation rates [*Ward et al.*, 1987], these measurements clearly indicate the presence of a large fossil source of CH_4. Since the temperature of the Cariaco Basin is too high (16.9°C) for hydrate formation, this fossil CH_4 is most likely from previously unknown seeps.

[11] Primarily to quantify the input of seep CH_4, we modified Scranton's time-dependent Cariaco box model [*Scranton*, 1988] to include seeps. We adhered to the measured specific anaerobic CH_4 oxidation rates [*Ward et al.*, 1987]. Using a procedure similar to *Scranton* [1988], the diffusive diagenetic sedimentary flux was calculated as 0.20 μmoles cm^{-2} y^{-1} from our measured sediment CH_4 concentration data (17.97 μM at 2 cm depth) and was held constant over the entire basin.

[12] The model was initiated with a water column CH_4 concentration profile measured in February 1974 [*Reeburgh*, 1976; *Wiesenburg*, 1975] that was intercalibrated with other data sets by *Scranton* [1988]. The time-dependent model then predicted a seep-source profile, which shows large seep inputs at 870 m and at 1370 m (Figure 2). With this seep profile, the model predicts a 2004 CH_4 concentration profile that agrees with the measured 2004 profile to better than 1% below 650 m depth. (The GC CH_4 concentrations agree with those calculated from the stripped and trapped CH_4 within 3 % on average below 300 m depth. If a homogeneous distribution of CH_4 inputs is modeled similar to *Scranton* [1988], the agreement between the measured and modeled 2004 CH_4 concentration profiles decreases to between 30.5–42.3 % on average below 650 m depth.) Above 650 m, the model over-predicts the measured concentration profile (Figure 2). Higher specific CH_4 oxidation rates than those reported by *Ward et al.* [1987], as well as increased vertical resolution, are needed to achieve better agreement; this was also observed by *Scranton* [1988].

[13] Scranton's vertical time-dependent box model [*Scranton et al.*, 1987; *Scranton*, 1988] has been superceded in a strict sense by subsequent research documenting

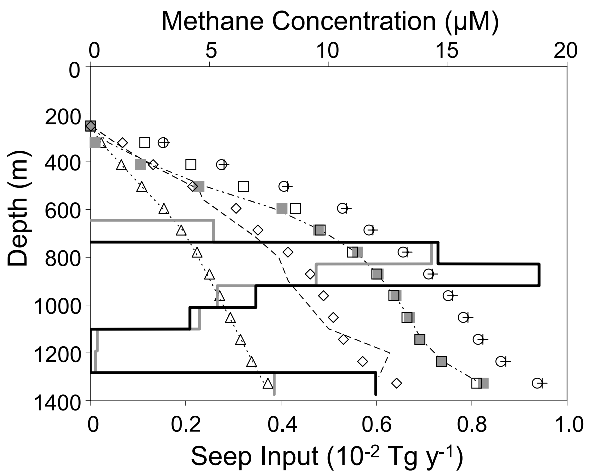

Figure 2. Modeled water column methane concentration distributions excluding mid-depth intrusions unless otherwise noted: (triangles) 1974, (diamonds) 1986, (open squares) 2004, (shaded squares) 2004 (including mid-depth intrusions), (circles) 2050, (pluses) 2065. Measured water column methane concentration distributions: (dotted line) February 1974 [*Reeburgh*, 1976; *Wiesenburg*, 1975], (dashed line) February to March 1986 [*Ward et al.*, 1987], (dash-dotted line) January 2004. The solid gray and black lines represent the model-predicted seep methane input profiles with and without mid-depth intrusions, respectively. The main difference between the seep inputs is attributed to different eddy diffusion coefficients. Each box is 92 m deep.

intrusions. However the seep source is so dominant that the effects of episodic intrusions are overwhelmed and the original model can be modified to quantify the seep input. *Holmén and Rooth* [1990] found that in order to jointly explain temperature, salinity, and tritium distributions in the Cariaco Basin, the model presented by *Scranton et al.* [1987] must be modified to include injection of warm hypersaline shelf waters which reach the bottom of the basin and input of Caribbean thermocline waters at the sill. *Scranton et al.* [2001] observed water with sufficient density to reach the basin bottom north of the Eastern sill, however they did not observe hypersaline shelf waters reaching the bottom of the basin. Instead they proposed that a turbidity current associated with a July 1997 earthquake transported oxidized iron into the deep basin decreasing H_2S concentrations. No CH_4 decrease was observed with this event and the CH_4 concentration followed approximately a linear increase over a 30 year period [*Scranton et al.*, 2001] as predicted by the original time-dependent model [*Scranton*, 1988]. *Scranton et al.* [2001] and *Astor et al.* [2003] documented episodic mid-depth (250–350 m) intrusions of oxygenated water ($\leq$30 μM). These oxygen intrusions may increase the CH_4 oxidation rate in the upper box (242–366 m) of the time-dependent model [*Scranton*, 1988] beyond what was measured by *Ward et al.* [1987]. The highest specific CH_4 oxidation rate measured by *Ward et al.* [1987] was 2.5×10^{-3} day^{-1} at 240 m depth, possibly corresponding to an oxygen intrusion, but decreased rapidly to 1.5×10^{-4} day^{-1} averaged over the upper box. As an upper estimate on the effects of episodic mid-depth oxygen intrusions, we doubled the highest specific oxidation rate measured in the entire water column and applied it continuously to the upper box; the agreement between the measured and modeled 2004 water column CH_4 concentration profiles decreased to only 3.6 % on average below 650 m depth. We did not model intrusions to the deep basin, because *Scranton et al.* [2001] showed that CH_4 concentration has not responded to deep basin intrusions.

[14] The model is more sensitive to the values of the eddy diffusion coefficients. If the eddy diffusivities are changed from 0.49–4.08 cm^2 s^{-1} [*Scranton*, 1988] to 0.6–2.0 cm^2 s^{-1} [*Holmén and Rooth*, 1990], the agreement between the measured and modeled 2004 water column CH_4 concentration profiles decreases to 23.7 % on average below 650 m depth. Even increasing the oxidation rate in the upper box to model oxygen intrusions, the seep CH_4 fluxes must decrease by 15 % in order to cause 1 % agreement (Figure 2). We can use the sediment and seep CH_4 inputs to model ^{14}C-CH_4 profiles (Figure 1a). Both modeled profiles agree well with the measured ^{14}C-CH_4 profile.

4. Discussion

[15] Averaged over the anoxic region of the basin, our results indicate that 0.024–0.028 Tg y^{-1} (0.14–0.17 mole m^{-2} y^{-1}) of seep CH_4 and 3×10^{-4} Tg y^{-1} of sediment CH_4 are being added to the water column, while 0.01 Tg y^{-1} of CH_4 are removed by anaerobic oxidization. Since CH_4 oxidation in year 2004 only consumes one-third of the source, the bottom water CH_4 concentration has more than doubled since 1974 (Figure 2). Since CH_4 oxidation follows pseudo-first order kinetics [*Ward et al.*, 1987], oxidation rates will increase; both models (with and without intrusions) forecast that the Cariaco Basin will reach a steady-state (<0.01% increase y^{-1}) CH_4 concentration by year 2065 (Figure 2). Hindcasting with the models indicates the seep inputs began sometime between 1958 and 1967. If the seep inputs are initiated in 1967, then the model predicts water column CH_4 concentrations that agree well with the measured 1974, 1986, and 2004 CH_4 concentration profiles (Figure 2). Coincidentally, a moderate-sized earthquake (M_w = 6.6), whose epicenter was in the Caribbean Sea, 70 km NNW of Caracas (the Caracas earthquake of 1967), occurred on July 30, 1967 [*Suárez and Nábělek*, 1990]. This event could have initiated the release of fossil CH_4 into the Cariaco Basin. The projected paths of the El Pilar and San Sebastián faults are parallel to the major axis of the Cariaco Basin [*Audemard et al.*, 2005; *Suárez and Nábělek*, 1990], however, their exact locations within the basin are unknown. The hindcasting results could also be interpreted as the result of a complete basin flushing event in the mid-1900s.

[16] Could oxidation of this fossil source to dissolved inorganic carbon (DIC) influence Cariaco Basin DIC ^{14}C distributions and bias the marine reservoir correction used in Cariaco Basin radiocarbon chronologies [*Hughen et al.*, 2004, 2000]? Present evidence indicates that any bias is negligible. Measured modern (prebomb) Cariaco Basin reservoir corrections [*Guilderson et al.*, 2005; *Hughen et*

al., 1996a] are similar to open ocean values [*Druffel et al.*, 1989], as are surface DIC concentrations and $\delta^{13}C$ values [*Deuser*, 1973; *Druffel et al.*, 1989]. Reservoir-corrected Cariaco Basin sediment foraminifera ^{14}C data show excellent agreement with the INTCAL98 tree ring ^{14}C calibration [*Hughen et al.*, 2000; *Stuiver et al.*, 1998] over a 2000 year overlap from 10.5 to 12.5 kA ^{14}C BP (thousand radiocarbon years Before Present).

[17] Methane fluxes could have had a greater influence in the Pleistocene, when lowered sea levels sharply reduced water exchange between the basin and the Caribbean. The $\delta^{13}C$ of the CH_4 DIC source is about 60‰ lighter than atmospheric CO_2, so these episodes would leave a distinctive stable isotope signature. The planktonic foraminifera species *G. bulloides* and *G. ruber* have $\delta^{13}C$ values that are 0.2–0.5‰ lighter than mean Holocene values for the period 14–20 kA ^{14}C BP [*Lin*, 1992]. Ignoring any contribution to these offsets from whole-ocean glacial-interglacial $\delta^{13}C$ shifts, this corresponds to a fossil CH_4 contribution to the surface Cariaco Basin DIC pool of just 0.3–0.8%, and would bias ^{14}C ages by less than 65 years.

[18] In conclusion, our radiocarbon results indicate that a large (0.024–0.028 Tg CH_4 y^{-1}) and previously unknown seep source of CH_4 dominates Cariaco Basin water column CH_4 distributions. If this seep source is localized, the possibility exists that carbonate structures, similar to those found in the Black Sea [*Michaelis et al.*, 2002], could also occur in the Cariaco Basin.

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