Deep Sediment-Sourced Methane Contribution to Shallow Sediment Organic Carbon: Atwater Valley, Texas-Louisiana Shelf, Gulf of Mexico

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Abstract: Coastal methane hydrate deposits are globally abundant. There is a need to understand the deep sediment sourced methane energy contribution to shallow sediment carbon relative to terrestrial sources and phytoplankton. Shallow sediment and porewater samples were collected from Atwater Valley, Texas-Louisiana Shelf, Gulf of Mexico near a seafloor mound feature identified in geophysical surveys as an elevated bottom seismic reflection. Geochemical data revealed off-mound methane diffusion and active fluid advection on-mound. Gas composition (average methane/ethane ratio ~11,000) and isotope ratios of methane on the mound (average $\delta^{13}$C$_{CH_4(g)} = -71.2\%$; $\Delta^{14}$C$_{CH_4(g)} = -961\%$) indicate a deep sediment, microbial source. Depleted sediment organic carbon values on mound ($\delta^{13}$C$_{SOC} = -25.8\%$; $\Delta^{14}$C$_{SOC} = -930\%$) relative to off-mound ($\delta^{13}$C$_{SOC} = -22.5\%$;
Δ^{14}C_{SOC} = −629‰) suggest deep sourced ancient carbon is incorporated into shallow sediment organic matter. Porewater and sediment data indicate inorganic carbon fixed during anaerobic oxidation of methane is a dominant contributor to on-mound shallow sediment organic carbon cycling. A simple stable carbon isotope mass balance suggests carbon fixation of dissolved inorganic carbon (DIC) associated with anaerobic oxidation of hydrate-sourced CH$_4$ contributes up to 85% of shallow sediment organic carbon.

**Keywords:** methane; advection; geochemistry; carbon isotopes; sediment carbon

1. Introduction

Sediment organic carbon (SOC) composition and provenance have been extensively studied in the Gulf of Mexico (GoM). Generally, inputs of terrestrially-derived organic carbon (OC) dominate near shore sediments and decrease with distance offshore [1–5]. Terrestrial-derived OC in surficial sediments of the GoM shifts from C3 plant material near shore to highly degraded, soil-derived material offshore [1–3]. Surface sediments on the slope (365–2270 m water depth) have Δ$^{14}$C values between −309.1‰ and −228.6‰ corresponding to 64% to 78% modern carbon [3]. Mayer et al. [4] calculated that surficial SOC on the slope is 41% to 46% of marine origin. Carbon isotope signatures typical for marine phytoplankton have been measured in surface sediments at water column depths from 74 to 2250 m (mean δ$^{13}$C value = −20.8‰; [6]). In the same study, depleted (δ$^{13}$C = −24.1‰) sedimentary organic matter was observed at a cold seep site (688 m water depth) that suggested a contribution of seep hydrocarbons to sediment organic matter.

Methane hydrate deposits are abundant in deep sediments along the Texas-Louisiana Shelf [7,8]. Hydrate-sourced CH$_4$ may contribute to the sediment OC pool and should be considered in investigations of carbon cycling and regional carbon mass balance calculations. During anaerobic oxidation of methane (AOM), bacteria utilize seawater-sourced sulfate (SO$_4^{2−}$) as a terminal electron acceptor to oxidize methane as an energy source, and produce sulfide (H$_2$S) and dissolved inorganic carbon (DIC) in the process [9,10]. During this oxidation porewater DIC sourced from downward seawater diffusion, upward deep system advection or diffusion, and AOM is incorporated into microbial biomass [11–14]. This is a contrast to aerobic CH$_4$ assimilation, where methane-derived carbon is directly incorporated into microbial biomass [15]. Deep sediment hydrocarbons, including CH$_4$, have been shown to contribute to carbon cycling in shallow sediments and the water column [16–21]. However, the indirect contribution of hydrate-sourced CH$_4$ to shallow sediment carbon pools through AOM and subsequent carbon dioxide (CO$_2$) fixation has not been thoroughly evaluated.

Shallow sediment CH$_4$ in Atwater Valley, Gulf of Mexico has been shown to be dominated by biogenic gas from deep sediments [17]. In this study, two sites in Atwater Valley were contrasted: A sediment mound with active fluid advection and high vertical CH$_4$ flux and an off-mound site exhibiting steady-state CH$_4$ diffusion [22,23]. Gas speciation and δ$^{13}$C values at both sites indicate that the shallow sediment gas is primarily biogenic-sourced CH$_4$, absent of higher molecular weight gases [22]. In this study a carbon budget is constructed for each site using hydrocarbon gas concentrations and stable carbon isotope (δ$^{13}$C) and radiocarbon isotope (Δ$^{14}$C) signatures of the
organic and inorganic carbon pools in solid phase sediment and pore water. The hypothesis is that dissolved inorganic carbon (DIC) assimilated during AOM is a dominant contributor to on-mound shallow sediment organic carbon cycling.

2. Materials and Methods

2.1. Study Location

Atwater Valley is a shallow trough in the Mississippi Canyon, Gulf of Mexico (Figure 1a). This underwater trough is part of the Mississippi Fan Fold-belt with sediment features including basinward-verging anticlines and underlain southern verging thrust faults across a 300 km long and 50 km wide region. Fold strata were formed during Late Jurassic to Miocene geologic periods resulting in formation of substantial salt tongues and sheets [24]. Canyon fill through the gas hydrate stability zone (HSZ) is comprised of fine-grained sediments, mostly interbedded debris flows and hemipelagic sediments overlain by a fine Holocene pelagic drape [25]. The area is characterized by seafloor mounds and basins formed through vertical advection of hydrocarbons, minerals, and CH4-rich fluids [26].

Figure 1. (a) Atwater Valley, Gulf of Mexico, Texas-Louisiana Shelf coring location (provided by Google Earth); (b) Sediment floor contours through the sample region, with sites on- (cores 3,7,8) and off-mound (core 2), the solid line represents the seismic data transect through the coring locations; (c) Core sites selected for this study were over a strong sediment bottom reflection (BSR) off-mound and on the mound observed with an elevated BSR and vertical seismic blanking above the BSR mound.

A 4 m high seafloor mound, at a water column depth between 1296 and 1300 m, was chosen as a study site based on previous seismic and geochemical studies conducted in May 2004 [22,23,27]
(Table 1). A key mound feature (Figure 1b) is a shallowing bell-shaped bottom simulating reflection (BSR) that raises approximately 200 m relative to off-mound BSR at 240 mbsf (Figure 1c, Table 1). At this location, heat flow elevates from a background signature off-mound of 40 to 160 mW·m$^{-2}$ on-mound (Table 1). These geophysical conditions on mound were interpreted to be a thermal perturbation to the HSZ base, creating vertical fluid fluxes [23].

Porewater chloride (Cl$^-$) concentrations on-mound averaged 934 ± 74 mM, well above the seawater background, indicating active vertical advection of higher salinity porewaters (Table 1) and a rise in the BSR (Figure 1c). This interpretation is supported with the observation of Late Jurassic to Miocene salt tongues and salt diapirism in this region that would reduce deep sediment hydrate stability [24]. An advective CH$_4$ flux of 3250 mM·m$^{-2}$·year$^{-1}$ was estimated on the mound (Table 1). In contrast, 750 m off-mound (Figure 1b) a moderate diffusive CH$_4$ flux of 20.6 mM·m$^{-2}$·year$^{-1}$ was observed (Table 1). Off-mound, sediment porewater SO$_{4}^{2-}$ concentrations were observed to decrease linearly from near seawater values at the sediment-water interface to below detection limits at 410 centimeters below the sea floor (cmbsf). Below 410 cmbsf, sediment headspace methane concentrations increased linearly, indicating a sulfate methane-transition (SMT) supported by the anaerobic oxidation of methane (AOM). Vertical fluid advection limited downward SO$_{4}^{2-}$ diffusion on-mound (Table 1).

Table 1. Review of previously published data for core sites on- and off-mound. Where data is general for the mound and not located at specific stations it is listed under C7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>C2 Off Mound</th>
<th>C7 Mound</th>
<th>C3 Off Mound</th>
<th>C8 Mound</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitude</td>
<td>89°16′49.696</td>
<td>89°16′49.696</td>
<td>89°16′49.696</td>
<td>89°16′49.696</td>
<td>[27]</td>
</tr>
<tr>
<td>Water Column Depth (m)</td>
<td>1300</td>
<td>1296</td>
<td>1301</td>
<td>1296</td>
<td>[27]</td>
</tr>
<tr>
<td>Core Pentetration (cmbsf)</td>
<td>470</td>
<td>867</td>
<td>515</td>
<td>370</td>
<td>[27]</td>
</tr>
<tr>
<td>SMT (cmbsf)</td>
<td>410</td>
<td>no SMT</td>
<td>no SMT</td>
<td>59</td>
<td>[22]</td>
</tr>
<tr>
<td>Methane Flux (mM CH$_4$ m$^{-2}$·year$^{-1}$)</td>
<td>20</td>
<td>3250</td>
<td>ND</td>
<td>167</td>
<td>[22]</td>
</tr>
<tr>
<td>Average Cl$^-$ (mM)</td>
<td>551 ± 6</td>
<td>934 ± 44</td>
<td>911 ± 79</td>
<td>770 ± 102</td>
<td>[22]</td>
</tr>
<tr>
<td>Heat Flow (mW·m$^{-2}$)</td>
<td>40</td>
<td>160</td>
<td>-</td>
<td>-</td>
<td>[22]</td>
</tr>
<tr>
<td>BSR depth (mbsf)</td>
<td>240</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>[23]</td>
</tr>
</tbody>
</table>

Close proximity in spatial variation of downward SO$_{4}^{2-}$ diffusion and inferred vertical CH$_4$ flux observed in previous studies on this mound makes it a unique study site to investigate CH$_4$ contribution to shallow sediment carbon cycling [22]. Porewater and sediment inorganic and organic carbon concentration and carbon isotope ratio data from an off-mound core (C2) are compared to an on-mound core (C7). Results from two additional sediment mound cores (C3 and C8) located near C7 are used to provide additional data for interpretation of CH$_4$ contribution to sediment carbon pools (Table 1).

2.2. Sediment Core Collection and Processing

Piston cores C7, C3, and C8 were collected on-mound (water depth = 1296 m) and C2 was collected off-mound (water depth = 1300 m, Figure 1b,c). For on-mound cores C7 was located near the
center, while C3 and C8 were near the mound edge, 150 and 70 m, respectively, from C7. Sediment cores were collected and processed shipboard as described in Coffin et al. [22]. Briefly, sediment cores were obtained using a 10 m piston coring system with 2.75 polycarbonate core liners. Cores ranged in length from ~300 to 800 cm and were processed immediately onboard the ship.

Core liners were inspected for gas pockets and gas expansion voids. At void spaces, the liner was drilled and gas sampled with a 60 mL polypropylene syringe fitted with a modified 3-way stopcock. Gas samples were then transferred to 30 mL pre-evacuated, glass serum vials fitted with a gastight stopper and aluminum seal. Subsequently, sediment plugs were collected from regular intervals along the core using a 3 mL polypropylene syringe with the tip cut off, transferred to pre-weighed 20 mL serum vials, and capped with gastight stoppers and aluminum seals to determine sediment headspace light hydrocarbon concentrations; (CH₄ through C₃H₈) as well as δ¹³C(CH₄(g)) ratios.

For additional sampling, core liners were removed and cut in 10 cm sections within an interval of 25–45 cm. Wet sediment from each section was frozen in snap-tight Petri-dishes for laboratory measurements of sediment porosity and percent organic carbon. Porewater pressed from sediment using 70 mL Reeburgh-style PVC press containers pressurized to 400 KPa (60 psi) by a low-pressure air on a latex sheet between core sections and press gas inflow was collected into 60-mL polypropylene syringes [28]. Porewater was filtered from syringes through ashed Whatman GF-F filters into ashed 20 mL vials and subsequently distributed into appropriate vials for each analysis; 2 mL in a 5 mL glass serum vial for [DIC]; 1 mL in a 2 mL glass serum vial for δ¹³CDIC, and; 2 mL in a 5 mL glass screw-top vial for dissolved organic carbon concentration [DOC] and δ¹³CDOC. Pressed sediment for inorganic and organic carbon concentration and isotope analyses was wrapped in ashed aluminum foil, sealed in Whirlpack bags, and stored frozen at −20 °C for analyses at the land-based laboratory.

### 2.3. Shipboard Analyses

To extract volatile hydrocarbons from sediment into vial headspace for gas analysis, 3 mL of nitrogen sparged, deionized water was injected through the septum of the serum vial and vial was shaken for 3 min. After this extraction, the headspace sample was removed from the vial and injected into a sampling loop on a Shimadzu GC-14A gas chromatograph-flame ionization detector (GC-FID) with a Hayesep-Q packed column (Alltech, Deerfield, IL, USA) to measure CH₄, ethane (C₂H₆), and propane (C₃H₈) concentrations. Sediment CH₄ concentrations were corrected for atmospheric background in the vials (95% extraction efficiency was assumed). Core gas pocket C₁-C₃ alkane concentrations were also measured using the GC-FID. Analytical precision was within 0.1 mM, based on replicate analyses. The limit of detection for methane was 0.009 mM and where concentrations were lower data are presented as 0.0 mM.

Porewater DIC concentrations were determined using a UIC CO₂ coulometer (UIC, Inc., Joliet, IL, USA) standardized to a certified seawater reference material (University of California, San Diego, CA, USA). Replicate variability was less than 0.15 mM.

### 2.4. Post-Cruise Laboratory Analyses

Sediment total carbon and OC (%TC, %SOC) concentrations and δ¹³C values were determined on a Fisons EA 1108 C/H/N analyzer in line with a Thermo Electron Delta Plus XP Isotope Ratio Mass
Spectrometer (IRMS) interface via a Conflo II (Thermo Scientific, Waltham, MA, USA). Pressed sediment was dried at 80 °C, ground with a mortar and pestle, then 15 to 20 mg of sediment was weighed in tin capsules for TC analysis. For SOC analysis, sub-samples were weighed in silver capsules, treated with an excess of 10% HCl and dried in an oven at 70 °C overnight to remove inorganic carbon. Sediment inorganic carbon (%CaCO₃) concentrations were determined from the difference between TC and SOC. A concentration calibration curve for carbon concentration analysis was generated daily by analyzing an acetonilide standard. For sediment δ¹³C_SOC values, IAEA-C₈ (oxalic acid), IAEA-CH-6 (sucrose) and USGS 40 (l-glutamic acid) were used as calibration standards. Acetonilide standards (USGS-40 and IAEA-C₈) were also used as check standards during analysis. Allδ¹³C data presented in this work are in per mil units (‰) and referenced to the Vienna Pee Dee Belemnite (VPDB) scale. Errors were based on triplicate runs. Error for % SOC was within ±0.03%, %CaCO₃ varied by less 0.2%, and δ¹³C_SOC varied by less than 0.2‰.

Sediment δ¹³C_CaCO₃, pore water δ¹³C_DIC, and gas pocket and sediment δ¹³C_CH₄ ratios were determined using a Thermo Electron Trace GC equipped with a Varian Porapak-Q column and GC-CIII combustion interface in-line with the Delta Plus XP IRMS (Thermo Scientific, Waltham, MA, USA) [22]. For δ¹³C_CaCO₃ analysis, 250 mg of sediment in a serum vial was treated with 2 mL of 10% HCl. For δ¹³C_DIC analysis, 2 mL porewater samples were treated with 200 μL of 85% H₃PO₄. In both cases, CO₂ was extracted from the vial headspace and injected into the GC via a split/splitless inlet in split mode. All δ¹³C_CaCO₃ and δ¹³C_DIC values were normalized through analysis of CO₂ and C₁-C₅ alkanes in NIST RM 8560 (natural gas, petroleum origin). Samples for δ¹³C_CH₄ analysis were introduced via an in-line cryogenic focusing system according to the method of Plummer et al. [29]. A separate δ¹³C normalization curve was generated for C₁-C₄ alkanes and used to normalize δ¹³C_CH₄ data. Replicate δ¹³C_CaCO₃ values varied by less than 0.2‰, δ¹³C_DIC by less than 0.5‰, and δ¹³C_CH₄ by less than 1.0‰.

Porewater DOC was measured on an OI Analytical 1010 total organic carbon analyzer (OI Analytical, College Station, TX, USA) using a heated persulfate oxidation method modified for seawater analyses [30]. The samples were kept frozen until ready for analysis, then acidified and nitrogen sparged in the lab prior to analysis to remove DIC. The total organic carbon analyzer was interfaced with the Delta Plus XP IRMS. A DOC calibration curve was generated using standards of potassium hydrogen phthalate. Measured δ¹³C_DOC values were normalized to the VPDB scale by analyzing solutions of IAEA-CH-6 (= −10.449 ± 0.033‰) and USGS 40 (−26.389 ± 0.042) standards. Using triplicate analyses, DOC concentrations varied by less than 0.02 mM, and δ¹³C_DOC varied by less than 0.2‰.

2.5. Radiocarbon Isotope Analysis

Graphite sample preparation for Δ¹⁴C analysis of CH₄ and SOC are described in detail by Pohlman et al. [31]. Targets were prepared in the U.S. Naval Research Laboratory (NRL) Graphite Lab. Targets were then analyzed at the NRL accelerator mass spectrometer (AMS) facility using an AMS equipped with a high intensity cesium sputter source for ¹⁴C analysis [32]. Data analysis was according to standard procedures described in Tumey et al. [33]. Samples were measured against OX II standards and blanks distributed throughout loadings of the sample wheel. On average, each wheel contained 2 AMS blanks for tuning the accelerator, three processing blanks appropriate for the samples on the wheel, and 7 OX II standards. δ¹³C results were obtained from GC-IRMS analysis of the samples.
These values were used to calculate the δC fractionation correction for each sample. The Δ^{14}C data were calculated as:

\[ Δ^{14}C = \left( \frac{R_{sn}}{R_{abs}} - 1 \right) \times 1000 \quad (\text{‰}) \] (1)

where \( R \) is \(^{14}C/^{13}C\) or \(^{14}C/^{12}C\), \( R_{sn} \) represents the sample with normalization to a standardized δ\(^{13}C\) and \( R_{abs} \) represents oxalic acid standards normalized to a δ\(^{13}C\) standard and the standardized atmospheric \(^{14}C\) level in 1950 [34–36]. To compare the influence of C cycling with aging of deposited sediment, Δ^{14}C was converted to conventional radiocarbon age (CRA) where:

\[ t = -8033 \ln \left( \frac{Δ^{14}C}{1000} + 1 \right) + \lambda (y - 1950) \] (2)

In this equation, \( t \) is the CRA in years before present (1950), using the Libby half-life for \(^{14}C\) \((t/2 = 5568 \text{ years})\). To obtain actual calendar years, a standardized conversion was applied. The Δ^{14}C term is the value obtained after the \(^{13}C\) correction is applied, \( λ \) is the \(^{14}C\) constant \((1/8267 \text{ years})\), and \( y \) is the year of measurement. Thus, for Δ^{14}C of 0, \( t \) would be 0 for a measurement performed in 1950 and 1955 for 2007, when the measurement was performed [33].

2.6. δ\(^{3}C\) Data Interpretation

The relative contribution of CH\(_4\) to the shallow sediment carbon pools on-mound with a high advection and off-mound with a moderate diffusion assumes microbial assimilation of DIC during AOM [37]. Methane contribution at these different flux rates is summarized at specific core depths or averages through the sulfate methane transition zone. Accounting for isotope fractionation during assimilation, DIC contribution to organic carbon pools is estimated using a simple, two end-member isotope mass balance [38]:

\[ R_x = R_{PD}C_{PD} + R_{DIC}C_{DIC} \] (3)

where \( R_x \) represents δ\(^{13}C\) of SOC or DOC and the isotopic composition of marine phytodetritus (PD) and DIC are represented by \( R_{PD} \) and \( R_{DIC} \), respectively. The variables \( C_{PD} \) and \( C_{DIC} \) represent the corresponding fractional contributions of marine PD and DIC such that:

\[ C_{PD} + C_{DIC} = 1 \] (4)

The percent contribution of DIC to each carbon pool (%\( X \)) can then be derived from Equations (3) and (4):

\[ %X = \frac{R_x - R_{PD}}{R_s - R_{PD}} \times 100 \] (5)

where \( R_x \) represents the isotopic composition of DIC. Consideration of isotope fractionation during DIC assimilation is presented in the Discussion.

3. Results

Results focus on a comparison of off-mound (C2) and on-mound (C7) CH\(_4\) contribution to organic carbon in gas, porewater and sediment samples. Core C3 provides supplementary data for assessing the
on-mound CH₄ flux and cycling. Core C8, located near the edge of the mound, shown to have active vertical CH₄ diffusion [22], is also used in data interpretation.

3.1. Radiocarbon

The Δ¹⁴C(CH₄) values measured in gas pockets of near-mound cores C3 and C8 taken close to the primary mound core are presented in Figure 2 and Table 2. The gas pockets in core C8 were slightly enriched in ¹⁴C relative to gas pockets in core C3. On-mound SOC in core C7 was substantially more ¹⁴C-depleted than SOC in off-mound core C2 (Figure 2). In each core, the shallowest sediments had a more modern radiocarbon age, however, there was a large difference in the Δ¹⁴C(SOC) data between the cores. To estimate a change in apparent sediment age caused by the presence of CH₄, a sedimentation rate of 0.037 ± 0.022 cm·year⁻¹ [3] and natural radiocarbon decay starting at shallow sediment off-mound Δ¹⁴C value (~283‰) was applied to data to construct a conservative age line (Figure 3). CRA in off-mound and on-mound SOC did not conform to the predicted conservative age line. In the shallow section of the off-mound core, carbon age was older than predicted aging line down to approximately 300 cm and was younger below 300 cm. On-mound sediment CRA was older than the age line through the core.

![Figure 2. Δ¹⁴C(CH₄) of free gas and SOC at on-mound and off-mound sites.](image)

![Figure 3. Conventional radiocarbon age of SOC for cores taken off- and on-mound. The conservative aging line shown was calculated using estimates of annual sedimentation rate for this region.](image)
3.2. Solid Phase Sediment Profiles

An overview of all carbon pool concentration and $\delta^{13}$C data is presented in Table 2. A complete data set is available in Supplementary. Sediment OC concentrations were higher in off-mound C2 core than on-mound C7 core (Figure 4a, Table 2). On-mound $\delta^{13}$SOC values showed strong $^{13}$C-depletion near the seawater interface (SWI, Figure 4b). Off-mound SOC was more $^{13}$C-enriched with higher values near surface above the SMT of 410 cmbsf (Figure 4b, Table 1). Profiles of CaCO3 (Figure 4c) and $\delta^{13}$CCaCO3 (Figure 4d) also were substantially different when compared on- and off-mound. CaCO3 as a percentage of total sediment mass was substantially higher on-mound (average = 11.4 ± 1.1%, $n = 16$) than off-mound (average = 4.1 ± 3.0%, $n = 19$). Sediment $\delta^{13}$CCaCO3 values were generally $^{13}$C-enriched on-mound (average = $-2.7 \pm 2.8\%$, $n = 16$) relative to off-mound (average = $-4.5 \pm 2.4\%$, $n = 19$). However, at the SWI, on-mound $\delta^{13}$CCaCO3 value was $^{13}$C-depleted while off-mound $\delta^{13}$CCaCO3 was $^{13}$C-enriched.

**Figure 4.** Sediment profiles at on-mound and off-mound sites: (a) Percent sediment organic carbon (SOC); (b) $\delta^{13}$SOC; (c) percent CaCO3; and (d) $\delta^{13}$CCaCO3.
Table 2. Summary of C pool concentrations and $\delta^{13}$C, with minimum, maximum and average values for each core. The full data set for each core is available in Supplementary.

<table>
<thead>
<tr>
<th>Core ID</th>
<th>Gas</th>
<th>Porewater</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}$C$_{\text{CH}_4}$</td>
<td>$\Delta$C$_{\text{CH}_4}$</td>
<td>CH$_4$ (mM)</td>
</tr>
<tr>
<td>C2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Min</td>
<td>ND</td>
<td>ND</td>
<td>LOD</td>
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<tr>
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<td>ND</td>
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<td>ND</td>
<td>ND</td>
<td>5.3 ± 5.5</td>
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<td>C3</td>
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</tr>
<tr>
<td>Min</td>
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<td>-963</td>
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<tr>
<td>AVG ± SD</td>
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<td>-960 ± 3</td>
<td>4.2 ± 1.8</td>
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<tr>
<td>C7</td>
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<td>Min</td>
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<td>ND</td>
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<td>5.64 ± 3.62</td>
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</table>
3.3. Gas Sources and Sediment and Porewater Carbon Profiles

Through the discussion we assume that shallow CH$_4$ originates from deep sediment CH$_4$ fluxes; deep CH$_4$ is based on on-mound core liner gas pocket data. Assuming void gas from core liner pockets is a deeper source is supported with depleted $\Delta^{14}$C$_{\text{CH}_4}$ data (see Section 3.1. Radiocarbon), coupled with observation of elevated Cl$^-$ profiles (Table 1) indicating deep vertical advection to the shallow system. Further support for this interpretation is presented below with on-mound porewater DIC data. This $\delta^{13}$C$_{\text{CH}_4}$ value is compared to sediment headspace methane (CH$_4$(g)) to assess shallow sediment cycling (Table 2). Measured $\delta^{13}$C$_{\text{CH}_4(g)}$ values from on-mound core C7 and near-mound core C3 showed little variation within and between cores. Variation of $\delta^{13}$C$_{\text{CH}_4(g)}$ was greater and moderately depleted in $^{13}$C in near-mound core C8. For all cores with gas pockets in which ethane was detected, the C$_1$/C$_2$ ratios were high ([27]; average 11,000, $n = 13$). As a note, all CH$_4$ concentrations shown in Table 2 are relative (headspace) measurements and underestimate actual sediment methane concentrations as a result of pressure changes during core retrieval from the ocean floor resulting in degassing [21].

Off-mound (C2) CH$_4$ concentrations were highest below the apparent SMT at 410 cmbsf (Table 2) and near the limit of detection above the SMT (Figure 5a). On-mound CH$_4$ concentrations were higher in shallow sediments (C3, C7, and C8), relative to off-mound, and showed a general decrease toward the sediment-water interface (SWI). On-mound sediment $\delta^{13}$C$_{\text{CH}_4}$ was relatively uniform through the profile except for $^{13}$C depletion at the SWI (Figure 5b). Mound core C3 had a similar profile with moderate $^{13}$C depletion through the profile. More variation was observed in on-mound core C8, with $^{13}$C-depletion observed at 50 cmbsf (Figure 5b). Off-mound sediment CH$_4$ was $^{13}$C-enriched in shallow sediments up to 260 cmbsf and was depleted deeper than 300 cmbsf (Figure 5b). Off-mound $\delta^{13}$C$_{\text{CH}_4}$ data are not presented above 260 cmbsf because CH$_4$ concentrations were below the limits of detection for carbon isotope analyses.

On-mound (C7) porewater DIC concentrations increased from the SWI to 34 cmbsf, and subsequently decreased towards the core base (Figure 6a). Off-mound (C2) porewater DIC concentrations gradually increased from a SWI minimum to a maximum at 350 cmbsf and then declined rapidly toward the core base. On-mound, $\delta^{13}$C$_{\text{DIC}}$ values decreased to most depleted $^{13}$C value at 34 cmbsf where concentration increased; below this point $\delta^{13}$C$_{\text{DIC}}$ values increased and remained uniform (Figure 6b). Off-mound $\delta^{13}$C$_{\text{DIC}}$ values showed a similar pattern with the minimum value at 330 cmbsf.

While on-mound and off-mound porewater DOC concentration ranges were similar, notable differences in vertical profiles were observed (Figure 7a). Off-mound DOC concentrations in porewaters were lowest in near surface sediments and generally increased with depth. On-mound porewater DOC concentrations were relatively consistent throughout the profile, except for a low value near surface. On-mound porewater $\delta^{13}$C$_{\text{DOC}}$ values showed little variation, however, porewater DOC was substantially $^{13}$C-depleted throughout the core with a minimum value at 34 cmbsf (Figure 7b). In contrast, off-mound porewater $\delta^{13}$C$_{\text{DOC}}$ values varied substantially and were generally $^{13}$C-enriched; $\delta^{13}$C$_{\text{DOC}}$ values were elevated in samples taken less than 100 cmbsf and depleted below 100 cmbsf (Figure 7b).
Figure 5. (a) Sediment CH₄ concentrations; and (b) δ¹³C(CH₄) values measured for on-mound (C7) and off-mound (C2) core locations. On-mound cores include cores 3 and 8 that are used for estimating the C isotope values for source CH₄ and interpretation of mound C cycling.

Figure 6. (a) Sediment pore water dissolved inorganic carbon (DIC) concentrations; and (b) δ¹³C(DIC) values measured on-mound and off-mound.
4. Discussion

4.1. Shallow Sediment Carbon

Shallow sediment carbon cycling in Atwater Valley was investigated assuming marine phytodetritus and AOM carbon fixation are the primary sources to SOC and DOC. The difference in $\Delta^{14}C_{SOC}$ values between cores on- and off-mound is likely a result of AOM incorporation of isotopically-depleted DIC into OC [11,12,37], with a substantially greater CH$_4$ influence on-mound (Figures 2 and 3). There is a pronounced $^{14}$C-depletion in SOC on-mound (−955‰ to −890‰) with a slightly more modern signature in surface sediments. Elevation in $\Delta^{14}$C observed in on-mound (C8) surface sediment results from more modern seawater DIC fixation during AOM, further discussed below. Note that on mound $\delta^{13}C_{DIC}$ was relatively uniform near 0‰ (Figure 6b) and represents a deep sourced signature associated with the fluid advection observed in the mound $\delta^{13}C_{CH_4}$ (Figure 5b). An alternate interpretation of on-mound aged carbon data could be sediment erosion resulting in uncovering relic SOC. While erosion could contribute to the aged carbon pattern on-mound, elevated CaCO$_3$ concentrations relative to off-mound values indicate active AOM, resulting in over saturated
DIC and subsequent precipitation (Figure 4). In contrast to on-mound data, off-mound SOC was substantially more modern (−678‰ to −283‰, Figure 3) implying a lower contribution of AOM DIC fixation to carbon cycling. Gordon and Goñi [3] reported surface sediment $\Delta^{14}C_{SOC}$ ranging from −309.1‰ to −228.6‰ in the same general sampling area, with water column depths of 365 to 2270 m. In this study, similar $\Delta^{14}C_{SOC}$ on- and off-mound profiles with more $^{14}C$-depletion observed on-mound does indicate depleted radiocarbon DIC contribution to carbon cycling (Figures 2 and 3). The near-constant vertical CRA of the sediments sampled in this study, especially off-mound, suggests sediment mixing or rapid deposition, perhaps created by a shelf slump (Figure 3). Subsequent diagenesis of organic matter with different contributions of $^{14}C$-depleted CH$_4$ between core locations is evident with differences in CRA between on-mound and off-mound cores. $\delta^{13}C$ data in this study provides an estimate of the DIC fixation driven by the AOM of deep sourced CH$_4$ in shallow sediment carbon cycling. Other investigators have shown that Mississippi River particulate organic carbon (POC) changes from a terrigenous ($\delta^{13}C = −28\%o\text{ to } −26\%o$) to phytoplankton source ($\delta^{13}C = −19\%o$) near the river mouth [1,3,39,40]. In a previous study, POC-$\delta^{13}C$ reported well offshore near Atwater Valley ranged from −22.5‰ to −18.7‰, [41], in the range of phytodetritus [42,43]. For our study off-mound $\delta^{13}C_{SOC}$ values (−20.5‰ at the surface to −23‰ near the core bottom, Figure 4) were characteristic of SOC dominated by phytodetritus. In contrast, on-mound $\delta^{13}C_{SOC}$ ranged from −25.0‰ down core to −28.2‰ near surface, indicating an alternate carbon source.

A common interpretation in $^{13}C$-depleted isotope signatures in coastal waters is carbon sourced from terrestrial plants [39]. However, more recent studies show $^{13}C$-depleted $\delta^{13}C_{SOC}$ values observed in these sediments likely results from carbon assimilated into bacterial biomass during CH$_4$ cycling [22,37]. In anoxic sediments bacterial biomass is incorporated and preserved in solid phase sediments [44,45] and through time can constitute a significant portion of the SOC pool [46,47]. While our data indicate SOC is initially derived from marine phytoplankton, once deposited it is subject to diagenesis which includes incorporation of deep sediment CH$_4$ into solid phase sediment and pore water carbon pools.

Several additional observations pertaining to sediment carbon pools support interpretation of CH$_4$ contribution to carbon cycling. In the presence of sediment anaerobic CH$_4$ oxidation DIC oversaturation results in formation of CaCO$_3$ [48,49]. On-mound where $^{13}C$ depleted SOC was observed, CaCO$_3$ concentrations were 3 to 4 times higher than off-mound (Figure 4c). On-mound and off-mound data also suggest CH$_4$ contribution to pore water DOC. On-mound core porewater $\delta^{13}C_{DOC}$ values ranged from −27.6‰ to −24.8‰ with $^{13}C$-depletion in shallower sediments, though porewater DOC concentrations showed little variation (Figure 7). The shift to lower $\delta^{13}C_{DOC}$ values in shallow on-mound sediments coincided with a decrease in pore water SO$_4^{2−}$ concentrations and apparent AOM [22]. Off-mound porewater DOC concentrations below the SMT were similar to those on-mound and had depleted $\delta^{13}C_{DOC}$ (−26.2‰; Figure 7) indicating a CH$_4$ contribution to porewater DOC. In off-mound surface sediments above the SMT, porewater DOC concentrations were lower with an increase in $\delta^{13}C_{DOC}$ (−20.1‰) more typical of a marine phytoplankton source. Here it is assumed that DO$^{13}C$ depletion is not a result of diagenesis or selective metabolism during heterotrophic microbial carbon cycling that would result in isotopic fractionation of the total DOC pool [50,51].
4.2. Methane Source and Cycling

Composition and isotopic signatures of gas pocket samples on-mound indicate a microbial CH$_4$ source with average C$_1$/C$_2$ = 11,000 (methane/ethane) and $\delta^{13}$C$_{CH_4(g)} = -71.2$‰ (Table 2) [8,52–54]. While data interpretation is contingent on piston core depths, there are indications that on-mound CH$_4$ originates from deep sediment; (1) $\Delta^{14}$C$_{CH_4(g)}$ depletion measured in on-mound (C3) (−961‰) is a value characteristic of CH$_4$ that originates in from a deep system [55]; and (2) SO$_4^{2-}$ not observed below the SWI in cores C3 and C7 suggests active advection of deep sediment CH$_4$ to the surface [22]. In contrast, $^{14}$C-enrichment indicated by $\Delta^{14}$C$_{CH_4(g)}$ values in on-mound (C8, −903‰, Figure 2) and presence of a shallow SMT (59 cmbsf) suggests modern seawater DIC is being reduced to CH$_4$ during methanogenesis. A biogenic CH$_4$ source, absent of higher molecular weight gases and oil products that are present in a thermogenic source [53], presents an opportunity to study deep sediment CH$_4$ contribution to shallow sediment carbon cycling. On mound core C3 gas pocket carbon isotope ratios is used as a CH$_4(g)$ end-member to estimate CH$_4$ contribution to organic carbon pools, presented below.

Strong difference in shallow sediment CH$_4$ cycling was observed within and between cores. Measured on-mound sediment headspace $\delta^{13}$C$_{CH_4}$ values (−70.4‰) deeper than 100 cmbsf were similar to the $\delta^{13}$C$_{CH_4(g)}$ value indicating little microbial CH$_4$ consumption or production (Figure 5b). In contrast, in the top 100 cm on-mound, sediment headspace $\delta^{13}$C$_{CH_4}$ values were depleted 11‰ relative to $\delta^{13}$C$_{CH_4(g)}$ values (Figure 5, Table 1). The $^{13}$C-enrichment indicated by $\delta^{13}$C$_{CH_4(g)}$ values in C8 (−65.8‰) at 240 cmbsf likely results from isotopic fractionation during AOM [22,56]. Where the upward CH$_4$ flux due to active vertical fluid advection (such as C7 and C3) impedes downward SO$_4^{2-}$ diffusion into sediment, AOM or methanogenesis will not occur and there is not a change in the $\delta^{13}$C$_{CH_4(g)}$ ratio. Depleted $\delta^{13}$C$_{CH_4}$ values on-mound near surface and corresponding enriched $\delta^{13}$C$_{DIC}$ values do indicate active methanogenesis [57,58]. Methanogenesis typically occurs in marine sediments below AOM [59,60]. However, with advection on-mound, $\delta^{13}$C$_{DIC}$ data indicate shallow methanogenesis near the SWI (Figure 5b). While enriched $\delta^{13}$C$_{CH_4}$ and an associated SMT was not observed there is potential for seawater SO$_4^{2-}$ to support AOM at the SWI (Figure 5b).

Active CH$_4$ cycling was also observed in the off-mound core. Above the BSR (Figure 1) there was greater variation in the $\delta^{13}$C$_{CH_4}$ profile with lowest value (−86.9‰), potentially resulting from methanogenesis at a mid-core depth (Figure 5b), just below the SMT (Table 1). Note in a recent study carbon isotope equilibration at the point of sulfate-limited anaerobic oxidation was observed and may account for this depleted $\delta^{13}$C$_{CH_4}$ [61]. Above the SMT, decreased CH$_4$ concentrations and enriched sediment headspace $\delta^{13}$C$_{CH_4}$ values up to −48.8‰ result from AOM through the SO$_4^{2-}$ gradient (Figure 5). A corresponding depletion in $\delta^{13}$C$_{DIC}$ values to −47.1‰ (330 cmbsf) and a subsequent increase to −10.5‰ towards the core base (Figure 6) is characteristic of AOM through the SMT located above the zone of methanogenesis [57,62].

4.3. Estimation of CH$_4$ Contribution to the Shallow Organic Carbon

The relative contributions of phytodetritus and AOM to shallow sediment carbon cycling on-mound and off-mound can be estimate using a simple carbon budget calculation (Equation (5)). We assume sediment CH$_4$ is primarily oxidized during AOM for energy and DIC is assimilated into cellular
biomass [11–13] with an isotopic fraction of 3.75‰, a value recently applied in a study on the Hikurangi Margin [37] and an intermediate (2.0‰ to 5.5‰) for isotopic fractionation during DIC assimilation in the reversed tricarboxylic acid cycle [63–65]. For estimating the DIC contribution to SOC during AOM it is assumed $\delta^{13}C_{PD}$ end-member (Equation (5)) was $-20.5\%o$, the off-mound signature in surface sediments with the most modern $\Delta^{14}C_{SOC}$ value (Figure 2). Use of this $\delta^{13}C_{PD}$ end-member is supported by other studies on the TX-LA Shelf where offshore to nearshore sediment $\delta^{13}C$ values ranged from $-21.7\%o$ to $-19.7\%o$ [1,3,40]. On the Gulf of Mexico abyssal plain, with no substantial terrestrial inputs, $\delta^{13}C_{SOC}$ measured values were $-20.6\%o$ [66]. The average porewater $\delta^{13}C_{DIC}$ value measured on-mound, through the SMT (between 34 and 144 cm) was $-29.5\%o$. Adjusting this value for fractionation during DIC fixation (3.75‰, [37]) provides a $\delta^{13}C_{DIC}$ end member of $-25.8\%o$. On-mound, with a $\delta^{13}C_{SOC}$ average of $-25.0\%o$, results in an AOM-DIC contribution to SOC of 85% (Equation (5), Figure 8). We assume, with on-mound advection, AOM occurs at the sediment water column interface where $SO_4^{2-}$ is available and this signature is buried through time. This observation of high CH₄ contribution to shallow sediment carbon cycling is supported with a comparison of regional sedimentation rates and on-mound vertical CH₄ flux. Phytodetritus contribution to SOC in this region is estimated on the basis of a sedimentation rate near this location of 0.005 cm·year⁻¹ [1], sediment density of 2.6 gm·cm⁻³ [67], and SOC mineralization of shallow off-mound sediment relative to deep on-mound sediment of 37% [22,68] to be 40.8 mM·C·m⁻²·year⁻¹. This suggests a small contribution of carbon relative to CH₄ at 3250 mM·C·m⁻²·year⁻¹ (Table 1). Applying this approach to off-mound sediment $\delta^{13}C_{SOC}$ values below 35 cmbsf averaged $-22.7\%o$ and results in a 42% contribution of AOM-derived DIC incorporation to SOC (Figure 8).

Porewater DOC concentrations and $\delta^{13}C_{DOC}$ also indicate different carbon sources between on- and off-mound cores (Figure 7). In this analysis we do assume that porewater bacterial production, cell DOC excretion, and degradation of SOC contribute to porewater DOC. Assuming DIC is fixed into bacterial carbon and subsequently cycled to DOC (Figure 8), the contribution of AOM to DOC (Equation (5)) can be estimated using the phytodetritus end-member $\delta^{13}C_{PD}$ of $-20.5\%o$ and $\delta^{13}C_{DIC}$ of $-25.8\%o$. The $\delta^{13}C_{DOC}$ average off-mound ($-24.3\%o$), suggests 72% of DOC below the SMT is AOM derived (Figure 8). The on-mound average $\delta^{13}C_{DOC}$ value of $-25.6\%o$ through the entire C7 core indicates an indirect contribution of AOM to porewater DOC of 96%. The production of DOC via AOM in sediment may result in significant contribution relative to phytoplankton derived carbon. It is important to note that patterns in $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ depletion were similar in the vertical core profiles and with high porewater DOC concentrations organoclastic degradation of DOC and subsequent production from light DIC from further AOM can result in an overestimate of AOM related DOC production. Furthermore acetogenesis can contribute to the observation of depleted $^{13}$C in the DOC [69]. Also, it is interesting that this observation is similar to a recent study off the coast of New Zealand where AOM contribution to porewater DOC was estimated to be up to 71% at a location with lower vertical CH₄ flux rates [37].
5. Conclusions

Diffusive and advective fluxes of deep sediment CH$_4$ contribute significantly to shallow sediment carbon cycling in Atwater Valley, Gulf of Mexico. Deep salt diapirs at this study location are predicted to result in destabilization of CH$_4$ hydrates and result in an elevated vertical methane flux [22,23]. This prediction is supported in the observation of a substantial rise in the BSR (Figure 1c). The upward flux of deep sediment CH$_4$ via fluid advection on-mound supports a substantial fraction of sediment carbon production (up to 85%), whereas marine phytoplankton sourced carbon contributes ~50% where there is a low diffusive CH$_4$ flux (Figure 8). Consistent $^{13}$C-enriched $^{13}$CDIC values deeper than 100 cmbsf and the $^{14}$C-depleted $^{14}$CSOC and $^{14}$CH$_4$ values measured in gas pockets on-mound can be interpreted as long-term mound formation driven by active advection that supported shallow sediment carbon cycling driven by AOM near the SWI where SO$_4^{2-}$ is abundant. The cycling of CH$_4$ via AOM is reflected in the organic and inorganic carbon pools. The variation in CH$_4$ cycling in an advection dominated on-mound sediment and a diffusion dominated sediment off-mound is evident in the same sediment carbon pools. Observed $^{13}$C$_{DIC}$ profiles followed changes in $^{13}$C$_{CH4}$ values, as did $^{13}$C$_{CaCO3}$ values, indicating oxidation of CH$_4$ during AOM was occurring in the sediment pore fluids on the mound. Mass balances using $^{13}$C of CH$_4$ and SOC showed a large difference in the estimated contribution of deep sediment CH$_4$ to the shallow sediment carbon pools off and on-mound relative to marine phytoplankton. The DOC pool in sediment porewaters also reflected a significant contribution (up to 96%) from deep sediment CH$_4$. In another study on the TX-LA Shelf, petroleum seeps were found to contribute 40% to 60% to the total organic C in a shallower slope region [17].
This study suggests a need for global consideration of the distribution of deep sediment CH$_4$, especially hydrate bound methane, and the flux of carbon from this globally-significant carbon pool to shallow sediments. More estimates of deep sediment CH$_4$ and petroleum contributions to shallow sediments and the water column will help refine marine carbon cycling models and budget estimates and improve predictions of the impacts of climate change on these reservoirs. The current estimate for the world coastal CH$_4$ hydrate distribution is $21 \times 10^{15}$ m$^3$ of CH$_4$ at standard temperature and pressure [8]. A more thorough understanding of the potential for fixation of CH$_4$ into organic carbon and carbonate phases in shallow sediments will assist in evaluating deep sediment sourced CH$_4$ fluxes through the shallow sediments to the water column and the atmosphere.

**Supplementary Materials**


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**Conflicts of Interest**

The authors declare no conflict of interest.

**References**


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