Abstract: Moderate elevated vertical methane (CH$_4$) flux is associated with sediment accretion and raised fluid expulsion at the Hikurangi subduction margin, located along the northeast coast of New Zealand. This focused CH$_4$ flux contributes to the cycling of inorganic and organic carbon in solid phase sediment and pore water. Along a 7 km offshore transect across the Porangahau Ridge, vertical CH$_4$ flux rates range from 11.4 mmol·m$^{-2}$·a$^{-1}$ off the ridge to 82.6 mmol·m$^{-2}$·a$^{-1}$ at the ridge base. Stable carbon isotope ratios ($\delta^{13}$C) in pore water and sediment were variable across the ridge suggesting close proximity of heterogeneous
carbon sources. Methane stable carbon isotope ratios ranging from $-107.9\%$ to $-60.5\%$ and a C1:C2 of 3000 indicate a microbial, or biogenic, source. Near ridge, average $\delta^{13}C$ for pore water and sediment inorganic carbon were $^{13}C$-depleted ($-28.7\%$ and $-7.9\%$, respectively) relative to all core subsamples ($-19.9\%$ and $-2.4\%$, respectively) suggesting localized anaerobic CH$_4$ oxidation and precipitation of authigenic carbonates. Through the transect there was low contribution from anaerobic oxidation of CH$_4$ to organic carbon pools; for all cores $\delta^{13}C$ values of pore water dissolved organic carbon and sediment organic carbon averaged $-24.4\%$ and $-22.1\%$, respectively. Anaerobic oxidation of CH$_4$ contributed to pore water and sediment organic carbon near the ridge as evidenced by carbon isotope values as low as to $-42.8\%$ and $-24.7\%$, respectively. Carbon concentration and isotope analyses distinguished contributions from CH$_4$ and phytodetrital carbon sources across the ridge and show a low methane contribution to organic carbon.

**Keywords:** coastal sediment; carbon cycling; methane; phytodetritus; convergence forcing; stable isotopes

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1. **Introduction**

The majority of coastal sediment carbon cycling studies have focused on contributions from autochthonous photosynthetic marine and allochthonous terrigenous inputs [1–3]. However, hydrocarbons produced within deep sediment through thermochemical and microbiological conversions can significantly contribute to cycling of carbon, especially in shallower sediments and water column [4–9]. Stable carbon isotope ratios ($\delta^{13}C$) indicative of petroleum and methane (CH$_4$) origins are found in bacterioplankton biomarkers [4]. In a related study in the Northeastern Pacific Ocean, it has been estimated that sediment methane contributes about 28% of the carbon to the water column dissolved organic carbon (DOC) pool [10,11] and is a significant energy resource for biological activity in many coastal regions worldwide [10,12–14]. Methane also contributes to carbon pools within shallow sediments [13,15,16].

Vertical CH$_4$ flux in shallow sediments is predominantly controlled by anaerobic oxidation of methane (AOM) which occurs at the sulfate-methane transition (SMT) zone [17–20]. Equation (1) shows the net biochemical reaction for AOM in marine sediments:

$$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \quad (1)$$

Comparison of SMT depths in CH$_4$-rich sediments through different marine environments suggests a wide range in vertical CH$_4$ flux rates that are dependent on CH$_4$ concentrations and physical settings [16,21–23].

Natural abundance carbon isotopes have been useful for studying microbial cycling of hydrocarbons in marine environments [4,5,24–27]. Stable carbon isotope analysis ($\delta^{13}C$) of CH$_4$ has been successfully used to distinguish between thermogenic and biogenic CH$_4$ sources [28,29]. Furthermore, $\delta^{13}C$ values of pore water dissolved inorganic carbon (DIC) and calcium carbonate (CaCO$_3$) can provide an assessment of AOM and/or CH$_4$ reduction through methanogenesis [14,30–32]. Vertical CH$_4$ fluxes combined
with carbon isotope analysis of organic and inorganic carbon pools in coastal ocean regions will help to quantify the contribution of CH₄ to the shallow sediment carbon pools.

Along the Hikurangi Margin, the Pacific Plate subducts beneath the Australian Plate at a rate of 40–45 mm·year⁻¹ [33]. On the southern margin, sediment accretion occurs at a rate of approximately 12 mm·year⁻¹ [34] and subduction creates a focused vertical fluid flux from deep within the accretionary wedge and underthrust sediments [35]. In this study, the relative contribution of CH₄ from subducting sediments and pelagic phytodetritus to shallow sediment is examined using δ¹³C values of solid phase sediment and pore water carbon pools (Figure 1). Focused fluid advection, observed immediately adjacent to the landward flank of the ridge, may contribute to carbon shallow sediment carbon cycling, along with ex situ pelagic derived organic matter (terrestrial and pelagic sources) [35–37]. This study provides further assessment of previous seismic data interpretation. We test the hypothesis that the different sources of carbon, CH₄ and pelagic detritus, partition between dissolved and particulate carbon pools with CH₄ as the primary contributor to pore water dissolved carbon and pelagic detritus the dominant contributor to sediment carbon (Figure 2).

**Figure 1.** Sediment core locations across the Porangahau Ridge on the Hikurangi Margin, east of northern New Zealand.

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**2. Methods**

**2.1. Regional Description**

The Hikurangi Plateau is an igneous province within the Pacific Plate, undergoing oblique subduction below the Australian Plate [33], leading to formation of an accretionary wedge 20–25 Ma ago [34]. The central Hikurangi subduction margin contains a 150 km wide imbricated frontal wedge that is poorly drained and over pressured with low taper thrust systems concurrent with a smooth subducting
plate, a thick trench sedimentary sequence, and weak basal décollement with a convergent rate of approximately 40 mm·a\(^{-1}\) [38]. The Porangahau Ridge is located south on this subduction margin on the outer accretionary wedge (Figure 1). Sediment geology at this location is driven by the accretionary wedge growing at a rapid rate, filling with turbidites and mudstones [34].

Bottom simulating reflections (BSR) in seismic profiles through large areas of this study region indicate the presence of gas hydrates [39,40]. A local heatflow anomaly based on upwarping of BSRs was interpreted as an indication of fluid expulsion from the subduction interface on the Porangahau Ridge [35]. Previous work suggests that gas from beneath the Porangahau Basin in the accretionary wedge is transported along with fluids that undergo a compaction during sediment subduction and possibly transform from a smectite to illite (Figure 2). Fluid is interpreted to migrate horizontally along a décollement that transition to a vertical pattern through a thrust fault upon downward décollement stepping or vertical hydrofracturing [40]. A high-resistivity anomaly on the western landward side of the ridge if due to gas hydrates would provide further evidence for elevated fluid flow [36].

**Figure 2.** Sediment and pore water carbon pools studied across the Porangahau Ridge to determine the relative contribution of phytodetritus and vertical CH\(_4\) flux to shallow sediment. Sediment organic and inorganic carbon concentrations (SOC and CaCO\(_3\)) and \(^{\delta 13}\)C (SOC and TIC) and pore water dissolved organic and inorganic carbon (DOC and DIC) are summarized to compare spatial variation in these carbon sources. Data interpretation suggests phytodetritus dominates contribution to solid phase sediment carbon while AOM has a more significant contribution to the dissolved carbon cycling which, subsequently, contributes to the solid phase pool.
Seismic data retrieved during hydrocarbon exploration across the Porangahau Ridge displayed strong reflections above the predicted regional BSR; profiles were interpreted as free gas beneath a locally upwarped base of gas hydrate stability zone. These data were used to focus piston coring locations for this study. The coring area is seaward of a Cretaceous to Palaogene base believed to create a deforming tectonic buttress for a frontal accretionary wedge comprised of underlying Plio- to Pleistocene accreted turbidites that are near slope basins formed the Miocene to recent times [38,41]. Six cores were collected in June 2006 across the ridge in an offshore transect (Figure 1) [36,37]. Data were interpreted to compare variation in the contribution of CH4 and pelagic detritus to shallow system carbon pools across the ridge with previous indications of fluid expulsion at specific locations along this transect [35] (Figure 2).

2.2. Sample Collection and Analysis

Sediment was collected using a 6.5 m piston core with an average of 15 subsamples taken from each core; cores ranged in length from 206 to 480 centimeters below sea floor (cmbsf). Pore water was obtained using Reeburgh style presses pressurized to ~400 kPa (~60 psi) [36,37].

For determination of sediment CH4 and higher molecular weight gas concentrations, a sediment plug was collected from the core using a 3 mL syringe with the end removed and sealed a in 20 mL serum vial. Gas was extracted [42] and measured on-board using a Shimadzu GC-FID GC-14A gas chromatograph equipped with a 6 foot Hayesep-Q 80/100 mesh column (Alltech, Deerfield, IL, USA) and quantified with certified gas standards (Scott Gas, Plumbsteadville, PA, USA). Limit of detection (LOD) for CH4 concentrations was 0.009 mM; values below LOD are presented as 0.0 mM.

A Dionex DX-120 ion chromatograph (Thermo Scientific, Waltham, MA, USA) was used on-board to measure pore water SO4^{2−} concentrations. Samples were diluted 1:50 (vol:vol−1) prior to analysis and measured against IAPSO (International Association for the Physical Sciences of the Ocean) standard seawater (28.9 mM SO4^{2−}). The SO4^{2−} LOD was 0.6 mM; values below LOD are reported as 0.0 mM.

Total dissolved sulfide (TDS) concentrations were measured on-board using a Turner spectrophotometer [43]. LOD was 0.05 mM; values below LOD are reported as 0.0 mM.

Concentrations of DIC were measured on-board using a coulometer (UIC, Inc., Joliet, IL, USA) that was standardized with a certified reference material (CRM #68, Scripps, La Jolla, CA, USA). LOD for DIC was 0.23 mM. DIC concentrations in all samples were above LOD.

Sediment samples were stored frozen in pre-weighed snap-tight Petri dishes. Porosity was determined from wet and dry mass of sediment. Concentrations and stable carbon isotopic compositions of sediment organic carbon (SOC) and total carbon (TC) were determined with a Thermo Delta Plus XP IRMS (Thermo Scientific, Waltham, MA, USA) in-line with a Costech EA using a Conflo III interface and helium carrier gas. Fifteen to 20 mg of dry, homogenized sediment was analyzed in triplicate. For SOC, sediments were weighed into silver capsules, acidified with excess 10% HCl to remove inorganic carbon, and dried at 60 °C. For TC, sediments were weighed into tin capsules and analyzed with no further treatment. Percent calcium carbonate (%CaCO3) was determined by subtracting %SOC from the %TC. Sediment δ^{13}C_{TIC}, was calculated using a mass and isotopic balance.

Stable carbon isotope ratios (δ^{13}C) were measured on TC, SOC, CH4, dissolved organic carbon (DOC) and DIC. δ^{13}C_{CH4} was measured from the same samples used for CH4 concentrations; samples
with concentrations less than 2 μM are similar to the atmospheric background and are not reported. A sufficient volume of headspace was first cryogenically concentrated [44], and subsequently introduced into a Thermo Trace gas chromatograph (GC) equipped with a Varian Porapak-Q column, interfaced via a GC-C III combustion interface to a Thermo Delta Plus XP IRMS.

The same GC-C-IRMS system, with a split/splitless inlet instead of the cryofocusing unit, was used to measure δ<sup>13</sup>C<sub>DIC</sub> [13]. One mL of pore water was sealed in a 2 mL serum vial, then acidified with 20 μL of 85% phosphoric acid to convert the DIC to CO<sub>2</sub>, which was then extracted into the headspace and injected into the GC.

δ<sup>13</sup>C<sub>DOC</sub> was analyzed using an OI Analytical 1010 wet chemical oxidation system (OI Analytical, College Station, TX, USA) in line with the IRMS [45]. All δ<sup>13</sup>C data are presented in per mil units (‰), and referenced to the PeeDee Belmenite standard.

2.3. Carbon Pool Data Interpretation

Data was evaluated assuming that carbon cycling associated with AOM is oxidation of CH<sub>4</sub> to CO<sub>2</sub> and fixation of CO<sub>2</sub> into microbial biomass [46]. AOM contribution to sediment carbon pools was studied assuming mixing between two end-members: phytodetritus (C<sub>PD</sub>) and CH<sub>4</sub> (C<sub>CH4</sub>). The spatial variation in the CH<sub>4</sub> contribution to sediment carbon pools through the study region is evaluated with mass and isotopic balances summarized by Equations (2) and (3):

\[ C_x = C_{PD} + C_{CH4} \]  
\[ \delta^{13}C_x = \delta^{13}C_{PD}C_{PD} + \delta^{13}C_{CH4}C_{CH4} \]

where \( C_x \) = concentration of the carbon pool (CaCO<sub>3</sub>, SOC, DOC and DIC) and \( \delta^{13}C_x \) = the stable isotopic composition of the respective component. During diagenesis of organic matter with the initial components \( C_{PD(i)} \) and \( C_{CH4(i)} \), mass and isotopic changes of carbon pools are represented by Equation (4):

\[ \delta^{13}C_xC_x = \delta^{13}C_{PD(i)}C_{PD(i)} + \delta^{13}C_{CH4(i)}C_{CH4(i)} + \delta^{13}C_A\Delta C \]

where \( \Delta C \) = net change in carbon pool concentration and \( \delta^{13}C_A = \) net change in isotopic composition during diagenesis. When \( \delta^{13}C_{PD}C_{PD} \) (or \( \delta^{13}C_{CH4}C_{CH4} \)) = constant or zero and \( \Delta C_x \neq 0 \), Equation (5) becomes:

\[ \frac{d(\delta^{13}C \times C)}{dC} = \delta^{13}C_A + \frac{d(\delta^{13}C_A)}{dC} \Delta C \]

where linear slopes of \( \delta^{13}C_A \) versus \( C_x \) estimate the net isotopic signal of carbon lost or gained through vertical sediment profiles during diagenesis [47–50].

The relative contribution of AOM to carbon pools at key depths, through each sediment core, was calculated using a two end-member isotope mass balance [51]:

\[ R_X = R_{PD}C_{PD} + R_{CH4}C_{CH4} \]  

where \( R_X \) represents the isotopic composition (δ<sup>13</sup>C) of the C pools: DIC, TIC, DOC and SOC, \( R_{PD} \) and \( R_{CH4} \) represent the isotopic composition of marine phytodetritus (PD) and CH<sub>4</sub> respectively, and \( C_{PD} \) and \( C_{CH4} \) represent their corresponding fractional contributions such that:
Percent contribution of CH₄ to each C pool (%X) is derived from Equations (6)–(8):

\[
\%X = \frac{R_X - R_{PD}}{R_s - R_{PD}} \times 100
\]  

where \( R_s \) represents the isotopic composition of CH₄ or DIC.

3. Results

Measured CH₄ concentrations ranged from LOD to 11.4 mM (Figure 3). The lowest concentrations were furthest off the ridge in both the landward and seaward direction, whereas the highest were at the landward ridge base (C17). All CH₄ profiles had lowest concentrations in shallowest core sections. Concentrations in ridge cores (C17 and C7) showed rapid increases at mid core depths (Figure 3). \( \delta^{13}C_{CH4} \) values ranged from −107.9‰ to −60.5‰ (Figure 3). Generally, \( \delta^{13}C_{CH4} \) profiles were more positive (\(^{13}C\)-enriched) in shallow sediment and more negative (\(^{13}C\)-depleted) down core. Strong \(^{13}C\)-depletion occurred mid depth in C4, C17, and C7 (Figure 3). Average C1:C2 was 3000 (\( n = 23 \)) and combined with the range of \( \delta^{13}C_{CH4} \) values, indicates a biogenic CH₄ source in this region.

Pore water SO₄²⁻ concentrations ranged from the LOD in mid to deep core sections to 29.3 mM in near surface sediments (Figure 4). Minimum SO₄²⁻ concentration in each core was observed at different depths, with C17 and C7 having SO₄²⁻ depletion at the most shallow depths. TDS ranged from LOD to 11.9 mM (Figure 4). TDS was not detected in surface sediments and increased down core in the presence of rapid shifts in CH₄ and SO₄²⁻ profiles. Highest H₂S concentrations were observed in C17 and C7.

Pore water DIC values ranged from 2.5 mM to 21.5 mM (Figure 5). Except in C3, profiles showed low concentrations in surface samples and rapid non-conservative concave up increases at mid core depths (Figure 5). In C3, collected closest to shore, average DIC concentrations were lowest overall. In all cores \( \delta^{13}C_{DIC} \) values ranged from 3.0‰ to −47.6‰ with consistent \(^{13}C\)-enrichments in surface sediments (Figure 5). Seaward off the ridge (C5 and C14) \( \delta^{13}C_{DIC} \) profiles were linear with down core shifts to minimum values: −27.6‰ and −31.6‰, respectively. In contrast, \( \delta^{13}C_{DIC} \) profiles for C4, C17 and C7 were sharply \(^{13}C\)-depleted to a minimum of −45.1‰ (C7, Figure 5). In C3 there was a smaller range in \( \delta^{13}C \) values between the shallow and deep pore water samples (−5.3‰ to −20.1‰).

Sediment CaCO₃ concentrations ranged from 5.9% to 32.3% (Figure 6). With the exception of C17 and C7, all cores had relatively uniform CaCO₃ profiles with a range of 5.9% to 17.0% coupled with slight variation in \( \delta^{13}C_{TIC} \) profiles (−3.5‰ to 1.3‰). In contrast, in C17%CaCO₃ ranged from 5.9% to 32.3%, with the highest percentage 156 cmbsf (Figure 6). Concomitant with the CaCO₃ increase in C17, there was \(^{13}C\) depletion (Figure 6).

Sediment porosity ranged from 0.477 to 0.766 and averaged 0.604 ± 0.059 (\( n = 53 \)). Across the ridge core, %SOC ranged from 0.24% to 0.85% (Figure 7) and was lowest in cores closest to the ridge (C17 and C7). The \( \delta^{13}C_{SOC} \) values ranged from −19.0‰ to −24.7‰ and were generally enriched in surface sediment and depleted at depth toward the SO₄²⁻ minimum; a trend that was most apparent in C17 (Figure 7).

Pore water DOC concentrations ranged from 0.3 mM to 5.2 mM, with core average concentrations lowest in C17 and highest in C4 and C14 (Figure 8). Pore water \( \delta^{13}C_{DOC} \) values ranged from −42.8‰...
to $-21.1\%$, suggesting variation in DOC sources. In C3, C7 and C5, $\delta^{13}$C$_{DOC}$ varied approximately $\pm 2\%$ through the profiles (Figure 8).

**Figure 3.** Profiles of sediment CH$_4$ concentrations and $\delta^{13}$C values relative to centimeters below seafloor (cmbsf) from piston cores collected across the Porangahau Ridge. Graphs are listed by location relative to the ridge with the first column westward moving to the ridge and the second column eastward moving off the ridge.
**Figure 4.** Profiles of pore water $\text{SO}_4^{2-}$ (●) and TDS (○) concentrations in piston cores relative to centimeters below seafloor (cmb sf) collected across the Porangahau Ridge. Lines are drawn through the linear portion of the $\text{SO}_4^{2-}$ profile that were used to estimate the sulfate-methane transition (SMT) depth (cmb sf) and the diffusive $\text{SO}_4^{2-}$ (and CH$_4$) flux (mmol $\text{SO}_4^{2-}$·m$^{-2}$·a$^{-1}$). Graphs are listed by location relative to the ridge with the first column westward moving to the ridge and the second column eastward moving off the ridge.
Figure 5. Profiles of pore water dissolved inorganic carbon (DIC) concentrations and $\delta^{13}$C values relative to centimeters below seafloor (cmbsf) in piston cores collected across the Porangahau Ridge. Graphs are listed by location relative to the ridge with the first column westward moving to the ridge and the second column eastward moving off the ridge.
Figure 6. Profiles of sediment percent CaCO₃ and δ¹³C values of the total inorganic carbon (CaCO₃) relative to centimeters below seafloor (cmbsf) in piston cores collected across the Porangahau Ridge. Graphs are listed by location relative to the ridge with the first column westward moving to the ridge and the second column eastward moving off the ridge.
Figure 7. Profiles of percent (%C) and δ$^{13}$C values of sediment organic carbon (SOC) relative to centimeters below seafloor (cmbsf) in piston cores collected across the Porangahau Ridge. Graphs are listed by location relative to the ridge with the first column westward moving to the ridge and the second column eastward moving off the ridge.
**Figure 8.** Profiles of pore water dissolved organic carbon (DOC) concentrations and δ\(^{13}\)C values relative to centimeters below seafloor (cmbsf) in piston cores collected across the Porangahau Ridge. Graphs are listed by location relative to the ridge with the first column westward moving to the ridge and the second column eastward moving off the ridge.
4. Discussion

4.1. Methane Source, Vertical Flux and Cycling

Measured stable carbon isotope ratios and gas compositions are typical of biogenic CH$_4$ ($\delta^{13}$C$_{CH_4} = -107.9$ to $-60.5$‰; average C1:C2 = 3000, [29]). In general, CH$_4$ concentrations decrease with distance away from the ridge (Figure 3). Concentration profiles reflect active CH$_4$ consumption via AOM at mid core depths and CH$_4$ production below this zone (Figures 3 and 4). Elevated TDS and DIC concentrations coincide with increasing CH$_4$ and decreasing SO$_4^{2-}$ concentrations which suggest AOM is the principle process controlling sediment CH$_4$ profiles (Equation (1), Figures 4 and 5). Isotopic fractionation during AOM and methanogenesis is evident in the $\delta^{13}$C$_{CH_4}$ and $\delta^{13}$C$_{DIC}$ profiles. During AOM $^{13}$C-depleted CO$_2$ is produced and subsequent reduction of this CO$_2$ results in a $\delta^{13}$C$_{CH_4}$ minimum at the SMT as observed in C4, C17 and C7 ([21,52–54]; Figure 3; Figure 5). AOM signature is most prominent in C4, C17 and C7 where $\delta^{13}$C$_{DIC}$ values are more $^{13}$C-depleted. Furthermore, the bacterial phylotypes commonly observed to participate in sulfate dependent AOM were observed in these sediments [37].

SMT depth is primarily a function of vertical CH$_4$ flux [18]. Although sediment did appear to contain low SOC concentrations (Figure 7) there is potential for organoclastic SO$_4^{2-}$ reduction in the shallow sediment where small changes in concentrations were observed (Figure 4; [55]). Linear portions of SO$_4^{2-}$ profiles indicated consumption of CH$_4$ by AOM (Figure 4). An absence of TDS in shallow sediments may occur because of oxidation by bio-irrigation, but there is a clear pattern of TDS production correlated with linear declines in pore water SO$_4^{2-}$ concentrations through the SMT resulting from AOM (Figure 4). Linear SO$_4^{2-}$ profiles were extrapolated to estimate SMT depth and indicated that C17 and C7 had shallowest SMT zones at 183 and 211 cmbsf, respectively (Figure 4). Deepest SMT (1287 cmbsf) was in nearshore C3, well off the ridge. In the other cores, SMT zones were at intermediate depths (364–443 cmbsf).

Assuming steady state consumption and the reaction stoichiometry of AOM (Equation (1)), CH$_4$ fluxes were estimated using SO$_4^{2-}$ profiles and Fick’s First Law [17,56]. Highest CH$_4$ fluxes were on the ridge in C17 and C7 (86.2 and 74.2 mmol m$^{-2}$·a$^{-1}$, respectively). Off ridge CH$_4$ flux rates were lower, ranging from 11.4 to 61.5 mmol m$^{-2}$·a$^{-1}$, with higher values offshore (Figure 4). Methane fluxes across Porangahau Ridge are moderate relative to values reported for other coastal regions. Similar ranges have been reported for passive sediment regions in the Bering, Kara, Chukchi and White Seas with maximum values at 25.3 and 47.4 mmol CH$_4$ m$^{-2}$·a$^{-1}$ [21,22]. However, regions in the Beaufort Sea with past accumulation of scoured sediment show elevated CH$_4$ fluxes at 154.8 mmol CH$_4$ m$^{-2}$·a$^{-1}$ [16]. Higher diffusion rates at 249 mmol CH$_4$ m$^{-2}$·a$^{-1}$, reported across a mound in Atwater Valley on the Texas-Louisiana Shelf, may be the result of deep sediment hydrate instability caused by salt diapirs [13]. On the mid Chilean Margin, with extreme plate subduction, geochemical profiles at a seismic blanking region showed an elevated flux at 362 mmol CH$_4$ m$^{-2}$·a$^{-1}$ [15]. While seismic data and presence of a high-resistivity anomaly on the western side of the Porangahau Ridge indicates fluid migration resulting from décollement or vertical hydrofracturing [35,36], geochemical estimates of deep CH$_4$ migration to shallow sediments suggest lower CH$_4$ hydrate loading relative to other coastal locations.
4.2. Inorganic Carbon Pools in Porangahau Ridge Sediments

Solid phase sediment and pore water inorganic carbon concentrations and $\delta^{13}$C values are influenced by microbial processes (AOM, OSR, and methanogenesis) and physical properties (downward diffusion and carbon pool solubility). In deeper core sections, increases in DIC concentration associated with decreases in $\text{SO}_4^{2-}$ concentration are attributed to elevated AOM rates (Figure 4). DIC profiles were generally concave up at mid core depths, being most pronounced in C17 (Figure 5). Concave up concentration profiles suggest that DIC production from AOM is greater than DIC losses from diffusion and carbonate precipitation [57]. These data support the conservative interpretation of observed vertical CH$_4$ fluxes and AOM.

DIC concentrations and $\delta^{13}$CDIC profiles reflect variation in vertical CH$_4$ flux across the ridge (Figure 5). Steepest gradients in DIC concentrations and the most $^{13}$C-depleted $\delta^{13}$CDIC values were near the ridge in C17 and C7 and also in C4, landward further from the ridge. Vertical CH$_4$ flux is most rapid at C17 relative to other locations. Minimum $\delta^{13}$CDIC values at the SMT (−43.3‰ to −47.5‰) that are more $^{13}$C-depleted than resident organic matter (−24.5‰ ± 0.5‰, Figure 7) are unequivocal evidence of AOM [58–60]. In addition, there is a mid-profile, rapid enrichment in $^{13}$C that we assume results from shallow sediment CH$_4$ production (Figure 5). Slight decreases in DIC concentrations are associated with shifts in the $\delta^{13}$CDIC at C7 and C17.

Authigenic CaCO$_3$ concentrations and $^{13}$C-depleted pore water DIC suggest elevated AOM rates at the SMT [46,58]. $^{13}$C-enriched DIC in C4, C17 and C7, below the SMT results from isotopic fractionation during CO$_2$ reduction [54,61]. In C3 $\delta^{13}$CDIC values range from −5.3‰ (a near seawater value) to −20.2‰ at the greatest core depth. $\delta^{13}$C values of sediment organic matter are conserved during microbial respiration to DIC [27,31,61,62]. Average $\delta^{13}$CSOC value through C3 is −21.7‰ ± 0.3‰ ($n = 12$, Figure 7). Such a shift in $\delta^{13}$CDIC may result from mixing between seawater and microbially-respired phytodetritus. This location is used later in this discussion as a phytodetritus end-member for calculating the CH$_4$ contribution to DIC pools across the ridge.

Active CH$_4$ cycling is also reflected in CaCO$_3$ and $\delta^{13}$CTIC profiles in near ridge cores C17 and C7 (Figure 6). Increased carbonate alkalinity as a result of AOM precipitates CaCO$_3$ and incorporates $^{13}$C-depleted DIC into this pool [30]. Calcium carbonate ranged 5.9% to 32% of solid phase sediment. Off ridge cores (C3, C4, C14, and C5) had relatively uniform CaCO$_3$ and $\delta^{13}$CTIC profiles with depth in the sediment. A strong contrast to this was observed in C17 with a maximum CaCO$_3$ concentration (32.3% at 156 cmbsf) and a minimum $\delta^{13}$CTIC value at the same depth (−43.8‰). Similar CaCO$_3$ and $\delta^{13}$CTIC profiles were observed at C7. These CaCO$_3$ and $\delta^{13}$CTIC profiles highlight locations where CH$_4$ contribution to bulk carbon pools is greatest.

4.3. Organic Carbon Pools in Porangahau Ridge Sediments

Methane cycling is not reflected to the same extent in SOC profiles (Figure 7). Sediment organic carbon concentrations were lowest in ridge cores (C17 and C7) and increased off the ridge. Range of $\delta^{13}$CSOC values across the ridge suggests two carbon sources: phytodetritus and CH$_4$ (−19.0‰ to −24.7‰). In the most landward core (C3), $\delta^{13}$CSOC profiles were relatively uniform and had values characteristic of phytodetritus (−22.5‰ to −18.7‰, [27,63,64]). In other cores, $\delta^{13}$CSOC values were
generally $^{13}$C-enriched in surface sediments and $^{13}$C-depleted at depth. A recent study nearby on southern Wairarapa Ridge reported $\delta^{13}$C$_{SOC}$ values in near surface sediment (<10 cmbsf) ranging from $-22.8\%$ to $-22.3\%$ in seep locations and non-seep (control) sites [63]. This illustrates that despite high CH$_4$ fluxes in this region, CH$_4$ was not appreciably incorporated into the SOC pool.

In this study, phytodetritus is the predominant source of SOC in most cores. However, an alternate source of SOC was observed in deep sections of C4 and C17 with a minimum $\delta^{13}$C$_{SOC}$ value at C17 ($-24.7\%$). Although these values approach terrestrial-derived carbon signatures [62], considering the distance offshore, overlying $^{13}$C-enriched SOC, pore water DIC concentration and $\delta^{13}$C$_{DIC}$ profiles, this is likely from CH$_4$ cycling. Note that $^{13}$C-depletion of SOC is concomitant with lower SOC concentrations in C17 suggesting decreased organic carbon production associated with CH$_4$ cycling. Similar shifts in $\delta^{13}$C$_{SOC}$ values with depth were not observed in a location close to our study site [63]; however, this may be a function of their sampling depth ($\leq$10 cm) relative to the SMT depth.

Pore water DOC concentrations showed similar patterns to SOC with the lowest concentrations in C17 and higher in C4 (Figure 8). In C17, lower CH$_4$ concentration corresponded to pronounced $^{13}$C-depletion in $\delta^{13}$C$_{DOC}$ ($-42.8\%$). Of note is the disparate range of $\delta^{13}$C$_{DOC}$ values encountered in surface sediment across the ridge and $^{13}$C-depletion in DOC at mid depths in C17. In the case of C4 and C14, an increase in concentration was accompanied by a $^{13}$C-enrichment in DOC. In C17, DOC was significantly $^{13}$C-depleted near and at the SMT (156 cmbsf, respectively) where DOC concentrations were lower.

Other studies indicate CH$_4$ contributes to pore water DOC. At a Gulf of Mexico site with advective CH$_4$ flux ($-3250$ mM m$^{-1}$ a$^{-1}$), there was substantial depletion of $\delta^{13}$C$_{DOC}$ ($-27.6\%$) which reflected influence of AOM in this carbon pool [13,65]. In contrast, on the Cascadia Margin, average $\delta^{13}$C$_{DOC}$ values were $-21.6\% \pm 1.3\%$ in a region with active advective methane fluxes [32]. Enriched $\delta^{13}$C$_{DOC}$ suggests advection of CH$_4$ prohibits AOM and subsequent production of DOC. However, a sediment CH$_4$ source to the Cascadia Margin water column contributed 28% of water column DOC in a region with an advective flux [10].

4.4. Methane Contribution to Shallow Sediment Carbon Pools

Carbon mass and isotope balances in each vertical core profile indicate CH$_4$ contribution to carbon cycling varies across the ridge (Equations (2)–(5); Figure 2). Linear slopes of $\delta^{13}$C$_{C_{x}}$ versus $C_{x}$ reflect the net isotopic signature of carbon lost or gained at each site in the various pools. Sites at the ridge base have $^{13}$C-depleted values, consistent with AOM and methanogenesis (Table 1). Net isotopic value ($\delta^{13}$C$_{A}$) of pore water DIC ranged from $-31.4\%$ to $-35.0\%$ off the ridge. Near the ridge, $\delta^{13}$C$_{A}$ values of DIC were lower below the SMT in C4 and C7 ($-49.2\%$ to $-41.3\%$), and through the entire C17 profile ($-48.8\%$). For TIC, $\delta^{13}$C$_{A}$ values ranged from 0.0% to 1.1% off the ridge at C3, C4, C14 and C5. Near the ridge at C17 and C7, $\delta^{13}$C$_{A}$ values ranged from $-58.0\%$ to $-22.6\%$, with the most $^{13}$C-depleted values in C17 suggesting a substantial AOM contribution to the carbon pool. Although AOM contribution to inorganic carbon pool is clearly evident, SOC $\delta^{13}$C$_{A}$ values ranged from $-21.2\%$ to $-17.1\%$, indicating phytodetritus was the dominant source of sediment organic carbon. Pore water DOC $\delta^{13}$C$_{A}$ values ranged from $-40.9\%$ to $-21.1\%$. In C17, a $^{13}$C-depleted value of $-40.9\%$ suggests CH$_4$ contributed to the DOC pool below the SMT; above the SMT there was a moderate contribution
from phytodetritus with a slight $^{13}$C-enrichment ($\sim$36.5‰). $\delta^{13}$C value for DOC was also depleted in C3 on the near shore, landward side of the ridge. However, $\delta^{13}$C$_{DIC}$ values and CH$_4$ flux estimates do not indicate a significant CH$_4$ contribution at this site. Here the $^{13}$C-depleted value may indicate a recalcitrant source of terrestrial organic matter.

**Table 1.** Net isotopic values ($\delta^{13}$C$_{\Delta}$) calculated for dissolved inorganic carbon (DIC), organic carbon (DOC) and total inorganic carbon (CaCO$_3$) and sediment organic carbon (SOC) derived from the slopes of the plots $\delta^{13}$C$_{x}$ vs C$_{x}$ (Equation (5)). Data from C4, C17 and C7 were plotted above (A) and below (B) the SMT. Values for C3, C4 and C5 were generated from full core profiles.

<table>
<thead>
<tr>
<th>Station</th>
<th>DIC</th>
<th>DOC</th>
<th>CaCO$_3$</th>
<th>SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3</td>
<td>$-31.4$</td>
<td>$-26.5$</td>
<td>$0.0$</td>
<td>$-20.8$</td>
</tr>
<tr>
<td>C4 A</td>
<td>$-31.6$</td>
<td>$-22.6$</td>
<td>$1.0$</td>
<td>$-19.5$</td>
</tr>
<tr>
<td>B</td>
<td>$-41.3$</td>
<td>$-22.3$</td>
<td>$1.1$</td>
<td>$-20.2$</td>
</tr>
<tr>
<td>C17 A</td>
<td>$-48.8$</td>
<td>$-36.5$</td>
<td>$-56.6$</td>
<td>$-17.8$</td>
</tr>
<tr>
<td>B</td>
<td>$-49.2$</td>
<td>$-40.9$</td>
<td>$-58.0$</td>
<td>$-17.1$</td>
</tr>
<tr>
<td>C7 A</td>
<td>$-33.4$</td>
<td>$-22.8$</td>
<td>$-22.6$</td>
<td>$-21.2$</td>
</tr>
<tr>
<td>B</td>
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<td>$-21.6$</td>
</tr>
<tr>
<td>C14</td>
<td>$-35.0$</td>
<td>$-21.1$</td>
<td>$0.8$</td>
<td>$-20.6$</td>
</tr>
<tr>
<td>C5</td>
<td>$-31.4$</td>
<td>$-22.6$</td>
<td>$0.0$</td>
<td>$-20.3$</td>
</tr>
</tbody>
</table>

Further examination of CH$_4$ contribution to sediment carbon cycling was conducted with a two-end-member isotope mass balance [51]. It was assumed that CH$_4$ is not directly assimilated, but is first oxidized via AOM and the CO$_2$ (DIC) produced in this reaction is fixed into biomass [46]. This assumption is supported by research showing the AOM community only assimilates 1% of the CH$_4$ with the other 99% being oxidized to CO$_2$. Subsequently, a significant proportion of CH$_4$ sourced CO$_2$ is assimilated by the AOM community [66–68]. Assimilation of CH$_4$ carbon through AOM contrasts with aerobic CH$_4$ oxidation where 60% of CH$_4$ carbon is assimilated into biomass [69].

AOM contribution to SOC, CaCO$_3$, DOC and DIC was estimated in C4, C17 and C7, where an SMT was observed, using a carbon isotope mass balance (Equations (6)–(8)). CH$_4$ contribution to each carbon pool was estimated at the SMT (i.e., the maximum contribution in each core). Regarding SOC, a $^{13}$C isotopic fractionation of $-3.75\%$ during CO$_2$ fixation was assumed, a midpoint for the 2.0‰ to 5.5‰ range expected for the reversed tricarboxylic acid cycle (rTCA) [70–72]. This assumption is based on extensive data gathered for rTCA in laboratory and field research where bacterial biomass results in $\delta^{13}$C values to be $-2.0\%$ to $-12.0\%$ depleted relative to the substrate through a temperature range of 30–100 °C and varying growth conditions [70–74]. Characterization of the microbial community diversity in sediments supports the assumption that the primary CO$_2$ fixation cycle is rTCA [75,76]. Selection of an intermediate value ($-3.75\%$) is based on core samples taken from sediment profiles at points where AOM was active and low isotope fractionation during CO$_2$ assimilation is expected. To evaluate AOM contribution to SOC (%SOC$_{CH_4}$), the average $\delta^{13}$C$_{SOC}$ value of C3 as the C$_{PD}$ end-member was used ($\sim$21.7‰, Table 2). This value is within the expected range of water column phytoplankton: $-22.5\%$ to $-18.7\%$ [27,63,64,77,78]. Low CH$_4$ concentrations and a near conservative
DIC concentration and $\delta^{13}$C$_{DIC}$ profiles suggest minimal CH$_4$ contribution to carbon cycling in this core and support the use of this end-member. For C17, with assumptions stated above, the $\delta^{13}$C$_{end-members}$ for DIC ($-47.6\%$) and phytodetritus ($-21.7\%$) and minimum $\delta^{13}$C$_{SOC}$ value in the SMT ($-24.7\%$) AOM contribution to SOC is $8\%$. Using the same approach for C4 and C7 and end members listed in Table 2, the contributions of AOM to SOC are $12\%$ and $8\%$, respectively (Table 3).

**Table 2.** $\delta^{13}$C values (‰) used in carbon isotope mass balance calculations to estimate CH$_4$ contribution to sediment organic carbon (SOC), dissolved inorganic carbon (DIC), total inorganic carbon (TIC) and dissolved organic carbon (DOC). Sample data are the minimum values observed in the sulfate-methane transition zone. End-members used are phytodetritus (PD), methane (CH$_4$) and dissolved inorganic carbon (DIC). Note: * indicates values to which the $-3.75\%$ fractionation was applied for isotopic mass balance calculations.

<table>
<thead>
<tr>
<th>Core</th>
<th>SOC</th>
<th>CaCO$_3$</th>
<th>DOC</th>
<th>DIC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>End members</td>
<td>Samples</td>
<td>End members</td>
<td>Samples</td>
</tr>
<tr>
<td></td>
<td>PD</td>
<td>DIC</td>
<td>SOC</td>
<td>PD</td>
</tr>
<tr>
<td>C4</td>
<td>-21.7</td>
<td>-41.5</td>
<td>-24.4</td>
<td>-0.3</td>
</tr>
<tr>
<td>C17</td>
<td>-21.7</td>
<td>-47.6</td>
<td>-24.7</td>
<td>-0.3</td>
</tr>
<tr>
<td>C7</td>
<td>-21.7</td>
<td>-38.5</td>
<td>-23.4</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

To estimate AOM contribution to CaCO$_3$, it was assumed that there was no isotopic fractionation during DIC precipitation to form CaCO$_3$ [79]. $\delta^{13}$C$_{TIC}$ profile in C3 did not vary with depth, showed no evidence of CH$_4$ and had a relatively conservative DIC profile. Thus, we used the average $\delta^{13}$C$_{TIC}$ value from C3 ($-0.3\%$) as the phytodetritus end-member for estimating contribution of CH$_4$ to the CaCO$_3$ pool. The CH$_4$ end-member is the average $\delta^{13}$C$_{CH_4}$ value below the SMT from all cores ($-83.3\%$). For C17, the minimum $\delta^{13}$C$_{TIC}$ value ($-43.9\%$, Table 2) observed through the SMT represents a 55% contribution from AOM (Table 3). In C7, the AOM contribution to CaCO$_3$ was estimated to be 19% based on a $\delta^{13}$C$_{TIC}$ of $-15.0\%$. Moving landward to C4, the minimum $\delta^{13}$C$_{TIC}$ value of $-2.5\%$ resulted in a CH$_4$ contribution to CaCO$_3$ of 3%.

**Table 3.** Percent CH$_4$ contribution to dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), calcium carbonate (CaCO$_3$), and sediment organic carbon (SOC) at core locations observed to have a SMT (C4, C17, C7).

<table>
<thead>
<tr>
<th>Core</th>
<th>DIC</th>
<th>DOC</th>
<th>CaCO$_3$</th>
<th>SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>32%</td>
<td>7%</td>
<td>3%</td>
<td>12%</td>
</tr>
<tr>
<td>C17</td>
<td>47%</td>
<td>71%</td>
<td>55%</td>
<td>8%</td>
</tr>
<tr>
<td>C7</td>
<td>33%</td>
<td>24%</td>
<td>19%</td>
<td>8%</td>
</tr>
</tbody>
</table>

For CH$_4$ contribution to sediment pore water carbon pools, it was assumed that phytodetritus-derived $\delta^{13}$C$_{DOC}$ was $-21.7\%$ and that DOC is produced during DIC fixation; therefore the same DIC end-members as in SOC calculations were used (Table 2). With these end-members and a $\delta^{13}$C$_{DOC}$ value of $-42.8\%$, maximum AOM contribution to DOC is 71% in C17 (Table 3). Moving seaward to C7, contribution of AOM to pore water DOC was estimated to be 24%. Landward in C4, the AOM contribution to DOC was 7%.
To calculate CH$_4$ contribution to pore water DIC, the CH$_4$ end-member presented above for CaCO$_3$ (−83.3‰) was used with no isotopic fractionation. The phytodetritus end-member was estimated using C3 pore water δ$^{13}$C$_{DIC}$ profile (Figure 4). δ$^{13}$C$_{DIC}$ values in C3 represent mixing of seawater DIC (−0‰) and DIC derived from SOC degradation (−21.7‰) were used, with no contribution from CH$_4$. For C17 and C7, the phytodetritus end-member is the δ$^{13}$C$_{DIC}$ value in C3 at respective depths of the SMT (C17 = −15.9‰ at 183 cmbsf; C7 = −16.5‰ at 211 cmbsf). Using the same approach for C4 and extrapolating the C3 profile to 443 cmbsf (the depth of the SMT in C4) resulted in a δ$^{13}$C$_{DIC}$ value that cannot be representative of mixing between DIC derived from seawater and that derived from SOC degradation (−32.2‰). Therefore, −21.7‰ was used for the phytodetritus end-member, a reasonable value for DIC produced during SOC decomposition. In C17 the minimum δ$^{13}$C$_{DIC}$ value in the SMT was −47.6‰; CH$_4$ was estimated to contribute 47% to the DIC pool (Table 3). In C7, δ$^{13}$C$_{DIC}$ at the SMT is −38.5‰ resulting in a 33% contribution from CH$_4$ to DIC. In C4, maximum contribution from AOM is 32% to pore water DIC.

5. Conclusions

Relative contribution of phytodetritus and deep biogenic CH$_4$ to shallow sediment carbon pools varies across the Porangahau Ridge. Estimated CH$_4$ fluxes across the ridge ranged from 11.4 to 86.2 mmol CH$_4$ m$^{-2}$·a$^{-1}$ with the highest value on the westward side of the ridge where heat flow, seismic and controlled source electromagnetics data indicate elevated vertical fluid migration [35,36]. While seismic and geophysical parameters do show high fluid migration, CH$_4$ flux at this study site is moderate relative to previous studies [13,15]. These data do show need for a combination of seismic and geochemical data for a thorough assessment of vertical methane flux levels. A carbon mass and isotope evaluation through core profiles [47,48] showed strong variation in contribution of CH$_4$ to SOC, CaCO$_3$, DOC and DIC (Table 1). A key observation for this assessment is the westward ridge elevated CH$_4$ contribution to CaCO$_3$ and DIC but not to SOC. A large contribution to CaCO$_3$ but not SOC results from low microbial biomass production relative to CH$_4$ oxidation. There was CH$_4$ contribution to pore water DOC, but DOC concentrations are 3-fold lower than SOC resulting in a low contribution to the total carbon. At locations with an observed SMT (C4, C17 and C7) a more thorough evaluation of the CH$_4$ contribution to shallow sediment carbon cycling is completed with a two end-member isotope mass balance [51]. At the landward ridge location (C17), CH$_4$ contribution to CaCO$_3$ and DIC was 55% and 47%, respectively showing a high respiration of CH$_4$ to inorganic carbon pools during AOM (Table 3). There was a large contribution of AOM to pore water DOC at this location (71%); however, as stated above, this is small fraction of total sediment carbon. The CH$_4$ contribution to SOC in this location was only 8%. In contrast, at C4 CH$_4$ contribution to CaCO3 and DIC was 3% and 32%, indicating lower values of CH$_4$-sourced carbon precipitating to inorganic phases. CH$_4$-sourced pore water DOC at this location was an order of magnitude less (7%). Off ridge sediment is dominated by phytodetritus. This study examines shallow sediment carbon cycling and highlights the need to assess deep sediment CH$_4$ contribution to coastal models. In addition, the combination of sediment geochemical profiles, seismic data [35], CSEM, and estimates of vertical fluid migration [36] provides strong predictive tools of for deep sediment CH$_4$ hydrate loadings.
Acknowledgments

Acknowledgment is made to the New Zealand Foundation of Research, Science and Technology, Office of Naval Research and Department of Energy, National Energy Technology Laboratory for financial support of this research. We express sincere appreciation for support from the RV Tangaroa crew for support during this expedition.

Author Contributions

All authors have contributed to writing and revisions of this manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References


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