Anaerobic methane oxidation in low-organic content methane seep sediments

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Abstract

Sulfate-dependent anaerobic oxidation of methane (AOM) is the key sedimentary microbial process limiting methane emissions from marine sediments and methane seeps. In this study, we investigate how the presence of low-organic content sediment influences the capacity and efficiency of AOM at Bullseye vent, a gas hydrate-bearing cold seep offshore of Vancouver Island, Canada. The upper 8 m of sediment contains <0.4 wt.% total organic carbon (OC) and primarily consists of glacially-derived material that was deposited 14,900–15,900 yrs BP during the retreat of the late Quaternary Cordilleran Ice Sheet. We hypothesize this aged and exceptionally low-OC content sedimentary OM is biologically refractory, thereby limiting degradation of non-methane OM by sulfate reduction and maximizing methane consumption by sulfate-dependent AOM. A radiocarbon-based dissolved inorganic carbon (DIC) isotope mass balance model demonstrates that respired DIC in sediment pore fluids is derived from a fossil carbon source that is devoid of 14C. A fossil origin for the DIC precludes remineralization of non-fossil OM present within the sulfate zone as a significant contributor to pore water DIC, suggesting that nearly all sulfate is available for anaerobic oxidation of fossil seep methane. Methane flux from the SMT to the sediment water interface in a diffusion-dominated flux region of Bullseye vent was, on average, 96% less than at an OM-rich seep in the Gulf of Mexico with a similar methane flux regime. Evidence for enhanced methane oxidation capacity within OM-poor sediments has implications for assessing how climate-sensitive reservoirs of sedimentary methane (e.g., gas hydrate) will respond to ocean warming, particularly along glacially-influenced mid and high latitude continental margins.

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1. INTRODUCTION

The sulfate-methane transition (SMT), the redox zone in methane-containing marine sediments where sulfate reduction is coupled to the anaerobic oxidation of methane (AOM), has been a subject of intense investigation for over four decades (Reeburgh, 1976; Alperin et al., 1988; Hoehler et al., 1994; Hinrichs et al., 1999; Boetius et al., 2000;
Alperin and Hoehler, 2009). Sulfate-dependent AOM is an oxidative process mediated by sulfate reducing bacteria and Anaerobic Methane oxidizing archaea (ANME) (Eq. (1))

\[
\text{SO}_{4}^{2-} + \text{CH}_4 \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \tag{1}
\]

Consumption of methane by AOM in near-seafloor marine sediments significantly limits methane emissions from the seafloor. Reeburgh et al. (1993) estimated that nearly 90% of the \(~85 \text{Tg CH}_4 \text{ yr}^{-1}\) produced globally in marine and freshwater systems is consumed before reaching the atmosphere, but did not delineate consumption by AOM. Hinrichs and Boetius (2002) utilized available AOM rate data and calculated that \(~382 \text{Tg CH}_4 \text{ yr}^{-1}\) are consumed globally in continental margin sediments by AOM. This estimate is about five times the global methane consumption term estimated by Reeburgh et al. (1993) and equivalent to \(~60\%\) of the net modern atmospheric methane flux (Kvenvolden and Rogers, 2005). As part of the global AOM budget, 78 Tg CH4 yr⁻¹ are consumed at methane seeps (Hinrichs and Boetius, 2002). Bowles et al. (2011b) calculate a substantially lower global seep AOM consumption rate of 3.5 Tg CH4 yr⁻¹, but that estimate is based on \text{ex situ} pressure incubations that yield rates 6–10 times slower than \text{in situ} pressure incubations (Bowles et al., 2011a).

Despite uncertainties in the global AOM budget, there is strong evidence that AOM, in combination with aerobic oxidation in sediments (Sommier et al., 2006) and the overlying water column (Valentine et al., 2001), presently limits the ocean’s contribution to \(~2\%\) of the annual atmospheric methane flux (Reeburgh, 2007). However, methane mobilized from marine sediments may have been a more prominent component of the global carbon cycle during punctuated episodes in the geologic past (e.g., Dickens et al., 1995; Zachos et al., 2005). Additionally, if current trends in ocean warming continue (e.g., Westbrook et al., 2009; Biastoch et al., 2011), oceanic methane emissions may become increasingly important in the future, particularly at high-latitudes where climate warming is most pronounced. Therefore, a better understanding of the factors regulating methane release at cold seeps, the primary conduits for transmitting methane from the seafloor (Judd, 2004), is necessary to constrain the current and future global methane budget.

The primary energy source driving all microbially-mediated carbon transformations at methane seeps is OM deposited on the seafloor (represented as CH₂O in Fig. 1). OM deposited at the sediment surface is initially degraded to carbon dioxide (CO₂) by aerobic respiration. Once oxygen is consumed, respiration proceeds by anaerobic processes. Within anaerobic sediments, fermentation of OM releases hydrogen and short-chain organic compounds that support organoclastic sulfate reduction (SR) in the sulfate zone (SZ) and methanogenesis at greater depths (Valentine, 2001). Methane seeps are distinct from other ocean floor settings because tectonic forces and geologic conduits channel methane to the seafloor, supporting AOM rates that exceed non-seep sediments (Bowles et al., 2011b and references therein). When the methane flux exceeds the capacity of AOM (e.g., Niemann et al., 2006b), excess methane is either oxidized aerobically near the sediment–water interface (Sommier et al., 2006) or emitted into the ocean. SR is coupled to OM degradation and AOM via interspecies hydrogen transfers. Thus, SR occupies a central role in the carbon cycle of methane seeps. How sulfate...
is partitioned between the processes of OM oxidation and AOM is a key factor influencing how much methane may be consumed by AOM.

In the present study, we investigate how sedimentary OM bioavailability influences the biogeochemistry of Bullseye vent, a methane seep located on the glacially-influenced northern Cascadia margin offshore of British Columbia, Canada (Fig. 2). We demonstrate that the upper 8 m of sediment at Bullseye vent are comprised of low OM-content glacial-marine material deposited during the termination of the last glacial maximum. We hypothesize that Bullseye vent and methane seeps having similarly OM-poor sediment content allocate a smaller proportion of sulfate to the oxidation of sedimentary OM than OM-rich seep sediments with similar methane fluxes and electron acceptor availability. A radiocarbon-based mass balance model for pore water dissolved inorganic carbon (DIC) provides compelling evidence that remineralization of non-fossil OM by sulfate reduction is not a significant process in Bullseye vent sediments. Instead, production of pore water DIC is dominated by fossil carbon sources that most likely include methane, deeply buried sedimentary OM and dissolved organic carbon (DOC). These findings have implications for predicting how other glacially-influenced methane seeps and sediments may respond to enhanced methane emissions from climate-sensitive sedimentary methane reservoirs, including gas hydrate.

2. SITE DESCRIPTION AND SLOPE SEDIMENTATION

Bullseye vent, located on the continental margin offshore of Vancouver Island, Canada (Fig. 2a), is a seafloor depression located on a topographic high formed by thrust faulting within the northern Cascadia margin accretionary prism (Fig. 3a). The vent site is underlain by bedded sediments that gradually thin into the footwall side of uplifted thrust faults (Fig. 3a) (Riedel et al., 2006b). Several of these features, described as ‘chimneys,’ are present along the inner margin of the landward thrust fault (Riedel et al., 2006b). Seismic blanking results from acoustic scattering associated with free gas, shallow carbonates or gas hydrate accumulations (Riedel et al., 2002; Wood et al., 2002; Züblsdorff and Speiß, 2004). Gas hydrate recovered from Bullseye vent contains microbial methane with δ13C values that range from −64.6‰ to −63.2‰ and a near-fossil δ14C value of −985 ± 2.6‰ (Pohlman et al., 2009). Methane constitutes at least 99.7% of the total hydrocarbons recovered from gas hydrate samples at this site (Pohlman et al., 2009).

Sediments from the upper 50 meters below the seafloor (msbf) along the northern Cascadia margin are comprised of Late Pleistocene (10–50 ka BP) and Holocene-aged mater-
Late Pleistocene sedimentation along the northern Cascadia margin was dominated by glacial-marine sediment transport and deposition during the advance and retreat of the Cordilleran Ice Sheet (Bornhold and Barrie, 1991; Cosma and Hendy, 2008). As the ice sheet advanced and subsequently retreated from ~30 ka BP until ~10 ka BP, terrestrial organic and lithogenic material was rapidly deposited (up to 463 cm ka$^{-1}$) on the continental slope (McKay et al., 2004; Cosma and Hendy, 2008). At the termination of glaciation during the Bølling–Allerød interstadial (~14.7 ka BP) and continuing throughout the Holocene, marine primary production increased and sediment with organic matter of marine origin has accumulated, albeit at greatly reduced rates (~5 cm ka$^{-1}$) (McKay et al., 2004).

### 3. METHODS

#### 3.1. Sample collection and processing

Sediment piston cores for this study were obtained during cruises PGC01-03 and PGC02-08 on board the CCGS John P. Tully. Four cores (identified as A, B, C and D in Fig. 2b) were collected during cruise PGC01-03. Data reported from these four cores are limited to sulfate concentrations and sulfate reduction rates. During PGC02-08, seven cores were collected along an 850 m transect that crosses Bullseye vent and extends upslope toward the eastern slope basin (Fig. 2b, Table 1). Core 5 was collected from within the depression of the vent site where gas hydrate is present and chemosynthetic biological communities are living at the seafloor (Riedel et al., 2006b). Cores 2 and 3 are from the edge of the depression and overlie the acoustically defined gas hydrate cap (solid blue line in Fig. 2b) and a zone of seismic blanking (dashed grey line in Fig. 2b), which has been associated with underlying free gas (Riedel et al., 2002; Wood et al., 2002; Zühlendorf and Spieß, 2004). Core 6 was also collected from above the seismic blanking zone, but not above the hydrate cap. Cores 4, 1 and 7 extend from 150 to 450 m away from the seep down the antcline of the accreted ridge.

Samples for methane concentration measurements were collected at 3 cm intervals as 2 cm$^3$ sediment plugs and stored in 20 mL serum vials sealed with 1-cm-thick butyl rubber septa. Pore waters were extracted by pressure-squeezing (~3 bar) and were filter-sterilized with 0.45 μm acrodisc polyethersulphone (PES) syringe filters (Pall Corporation). Sediment samples for radiocarbon analysis were collected from samples adjacent to those processed for pore water analysis. Higher resolution solid phase elemental and stable carbon isotope vertical profiles (25–40 cm intervals) were obtained from the sediment processed for pore water extraction. Sediment samples were freeze-dried and split into fractions for isolation of foraminifera and analysis of TOC and bulk carbonate. The sediment samples for foraminifera were disaggregated by sonication for 1 h in a dilute Calgon®

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Fig. 3. Bullseye vent seepage area. (a) Black line indicates location of seismic reflection profile ODP-2 shown in panel B. Blue circles indicate location of piston cores used in this study. Dotted yellow line indicates location of ~225 m high east facing escarpment which separates the mini-basin underlying Bullseye vent from the broad slope basin to the northeast. (b) Seismic reflection profile ODP-2 shows strong continuous reflections from the basin sediments. The escarpment is believed to be a fault scarp that vertically isolates the slope basin from the Bullseye area. The dashed lines indicate seismic reflections that may be of common stratigraphic origin. The bottom simulating reflector (BSR), an indication of free gas near the base of the gas hydrate stability zone, is evident beneath the uplifted mini-basin and the accreted ridge, but is more difficult to identify beneath the slope basin. TWT (s): two way travel time, in seconds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
solution and the >125 μm size fraction was rinsed and separated by wet sieving. After drying for 24 h at 50 °C, 7–10 mg of mixed planktonic foraminifera (primarily *Neogloboquadrina* spp. and *Globigerinoides* spp., the dominant species in the study area for the past 50 ka (Kennett and Ingram, 1995)) were handpicked. Bulk samples for TOC and carbonate measurements were ground with mortar and pestle and stored in glass vials until analyzed.

### 3.2. Pore water analyses

Dissolved concentrations of methane, sulfate and DIC, and stable carbon isotopes of DIC were measured as described by Pohlman et al. (2008). Briefly, methane concentrations were determined by the headspace equilibration technique and gas-chromatography (GC) flame-ionization detection using a Shimadzu GC 14-A. Sulfate concentrations were measured by ion chromatography using a Dionex DX-120 ion chromatograph equipped with a 4 mm AS-9HC column. DIC concentrations were determined coulometrically using a model 5011 UIC carbon dioxide coulometer. The stable carbon isotope composition of pore water DIC was measured using a Thermo Finnigan Delta S isotope ratio mass spectrometer (IRMS). Stable carbon isotope values are reported relative to Vienna PeeDee Belemnite (VPDB) in the standard δ-notation.

### 3.3. Bulk sediment analyses

The stable carbon isotopic composition (δ¹³C) of the TOC and bulk carbonate was determined with a Thermo Finnigan Delta Plus XP IRMS. Prior to isotope analysis, TOC samples were weighed in silver cups with a microbalance, acidified with 10% HCl to remove carbonate, dried at 105 °C for 24 h and then combusted on-line with a Fisons EA-1100 Elemental Analyzer (EA) interfaced to the IRMS. Samples for bulk carbonate stable isotopes were prepared for IRMS analysis by injecting 200-μL of 85% phosphoric acid saturated with CuSO₄ to precipitate sulfides into 2 mL serum vials containing approximately 0.2 g sediment. After heating the vials at 50 °C for 24 h, headspace gas from the vials was injected into a Thermo Finnigan Trace gas chromatograph (GC) where gases were separated isothermally (50 °C) on a Poraplot-Q capillary column (30 m, 0.32 mm ID) and then transferred to the IRMS through an open split. The ¹³C/¹²C ratios are expressed in conventional δ-notation relative to the VPDB standard. The total peak area from masses 44 and 45, normalized to an acetonitrile standard, was used to calculate the TOC concentration.

### 3.4. Radiocarbon sample preparation and analysis

Foraminifera and bulk carbonate were converted to CO₂ in an evacuated quartz carbonate digester by adding a solution of 85% H₃PO₄ saturated with CuSO₄ to dissolve the carbonate and precipitate sulfides evolved during the digestion/extraction process (Boehme et al., 1996). DIC was extracted as CO₂ from pore water samples by adding 1 mL of a 10% H₃PO₄ solution saturated with CuSO₄ into the serum vials and stripping the solution with UHP He for 30 min. Sediment for TOC analysis was acidified with a 10% solution of HCl to remove inorganic carbon, rinsed thoroughly with distilled water, freeze dried and then placed in ¼” Vycor® tubes with ~200 mg copper oxide and a grain of silver. The tubes were evacuated and placed in a 900 °C muffle furnace for 6 h to convert sedimentary OM to CO₂ (Pohlman et al., 2000).

Carbon dioxide from bulk carbonate, foraminifera, DIC and TOC samples was purified cryogenically by a series of vacuum distillations using the radiocarbon sample distillation and graphite preparation system described by Pohlman et al. (2000). Approximately 1 mg of sample carbon, as purified CO₂, was transferred into graphite production reactors. The remaining CO₂ from the foraminifera, bulk carbonate and TOC samples was collected in Vycor® tubes and analyzed by dual-inlet IRMS. δ¹³C values for four foraminifera samples lost during shipping were estimated by regression analysis of paired foraminifera and bulk carbon samples from Table 2 ($r^2 = 0.97; P < 0.001; n = 6$). For radiocarbon analyses, the CO₂ from each sample was catalytically reduced to graphite with hydrogen and 3 mg of iron at 600 °C for 6 h (Vogel et al., 1984; Pohlman et al., 2000).

Graphite targets were analyzed for radiocarbon at the Naval Research Lab (NRL) accelerator mass spectrometry (AMS) facility. The NRL AMS is a 3 MV Pelletron tandem accelerator with an MC-SNICS ion source (Grabowski et al., 2000). All radiocarbon results include fully propagated internal errors from samples, standards and blanks (Tuney et al., 2004). In this study, the δ¹³C notation is used for calculating conventional radiocarbon ages (Stuiver and Polach, 1977) and when performing mass balance corrections that account for precipitation of methane.

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**Table 1**

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<th>Station</th>
<th>Latitude (N)</th>
<th>Longitude (W)</th>
<th>Water depth (m)</th>
<th>Core length (m)</th>
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Table 2

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<th>Bulk carbonate</th>
<th>TOC</th>
<th>TIC</th>
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<td>AMS ID</td>
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<td>15950 ± 150</td>
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</table>

a Values extrapolated by regression of $\delta^{13}C$ data from paired foram and TIC samples (see text for details). Values include the propagated errors.

\[
\text{SR rate} = \frac{[\text{SO}_4^{2-}] \cdot \frac{\phi \cdot z}{I} \cdot \frac{H_2^{35}S}{35\text{SO}_4^{2-} \text{(added)}}}{1}
\]

where $[\text{SO}_4^{2-}]$ is the pore water sulfate concentration (nmol cm$^{-3}$), $\phi$ is sediment porosity, $z$ is the fractionation factor (1.04, Jørgensen, 1978), $I$ is the incubation time (in days), $H_2^{35}S$ is the radioactivity of sulfide determined by an acidic chromium reduction method (Albert et al., 1995) and $35\text{SO}_4^{2-} \text{(added)}$ is radioactivity of the radioisotope added to the incubation. The limit of detection is 0.2 nM d$^{-1}$. All depths were run in duplicate, and the standard deviation of these duplicates ranged from 9 to 78 nM/day.

3.6. Diffusive methane fluxes

Diffusive methane fluxes from the SMT to the sediment water interface (SWI) were calculated according to Fick’s first law (Berner, 1980) as:

\[
J = -\phi \cdot D_s \frac{dC}{dz}
\]

where $J$ is the diffusive flux (μmol m$^{-2}$ yr$^{-1}$), $\phi$ is the average sediment porosity above the SMT (0.7), $D_s$ is the sediment diffusion coefficient for methane (0.50 × 10$^{-5}$ cm$^2$ s$^{-1}$) corrected for temperature and porosity effects (Iversen and
Jørgensen, 1993), $C$ is the pore water concentration of methane ($\mu$mol L$^{-1}$) between the SMT and the sediment water interface, and $z$ is sediment depth (cmbsf).

4. RESULTS

4.1. Pore water geochemical profiles

In general, sulfate concentrations decrease with depth to the SMT, while methane concentrations increase with depth below the SMT (Fig. 4). With the exception of Core 5, where sulfate concentrations average 2.6 ± 0.8 mM ($n = 9$) throughout, sulfate concentrations decrease from seawater values (~29 mM) near the seafloor to values generally <0.1 mM below the SMT (Fig. 4). Methane concentrations range from 0.001 to 0.018 mM above the SMT and increase dramatically near and below the SMT (Fig. 4). Including Core 5, which was collected at an active seep, methane concentrations below the SMT range from 0.3 to 9.7 mM. However, because the solubility of methane at 1 bar and 4 °C is ~1.8 mM (Yamamoto et al., 1976), the samples from below the SMT likely lost methane during core recovery and sampling.

Dissolved inorganic carbon concentrations increase from seawater values (~2.4 mM) near the seafloor to concentrations that range from 14.5 to 23.0 mM at the SMT (Fig. 5). Below the SMT, DIC concentrations generally remain constant or increase slightly with increasing depth. Minimum $\delta^{13}$C-DIC values occur at the SMT, ranging from $47.5\%_{oo}$ to $43.3\%_{oo}$ (Fig. 4). $\delta^{13}$C values of DIC increase with distance from the SMT (both upcore and downcore) in all cores (Fig. 4) except for Core 5, where the SMT is at the seafloor. The $\Delta^{14}$C-DIC values above the SMT ($-860_{oo}$ to $-470_{oo}$) are highest near the seafloor and decrease with depth to the SMT (Fig. 5, see Electronic Annex for actual values). The $\Delta^{14}$C-DIC values below the SMT...
4.2. TOC and bulk carbonate concentration and $\delta^{13}C$

The $\delta^{13}C$ and wt.% of TOC are relatively uniform with depth throughout all of the cores (Fig. 6). All but three of the 74 samples analyzed for $\delta^{13}C$-TOC range from $-26.4\%$ to $-23.0\%$ and the overall average is $-24.5 \pm 0.5\%$. The outlier values (all from the seep Core 5) range from $-32.3$ to $-28.1\%$. The wt.% TOC ranges from 0.22% to 0.67% and averages 0.36 $\pm$ 0.10 wt.% (Fig. 6). $\delta^{13}C$ values of the bulk carbonate range from $+2.5\%$ to $-27.0\%$ with an average value of $-6.0 \pm 5.8\%$ (Fig. 7).

4.3. Radiocarbon age and $\delta^{13}C$ of planktonic foraminifera, TOC and bulk carbonate

Average radiocarbon ($^{14}C$) ages of the planktonic foraminifera, TOC and bulk carbonate are 15,600 $\pm$ 500, 18,460 $\pm$ 1920 and 25,750 $\pm$ 3450 $^{14}C$ yr BP, respectively (Table 2; Fig. 8). The sediment profiles do not display obvious age relationships with depth. However, the ages among the different sediment components are distinct. In nearly all cases, the radiocarbon age of planktonic foraminifera is youngest, the TOC is intermediate in age and bulk carbonate is oldest (Fig. 8). Average $\delta^{13}C$ values for the planktonic foraminifera, TOC and bulk carbonate samples analyzed for radiocarbon are $-3.3 \pm 1.4\%$, $-24.8 \pm 0.5\%$, and $-8.1 \pm 5.6\%$, respectively (Table 2).

4.4. Ex situ sulfate reduction rates

The four cores from Cruise PGC03-01 were measured for sulfate concentrations (Fig. 9a) and sulfate reduction rates (Fig. 9b). Sulfate concentrations for Cores A and B (located outside the gas hydrate cap, Fig. 2b) are near those of overlying seawater (28 mM) and decrease to $24\text{mM}$ by 400 cmbsf (Fig. 9a), where the SMT is inferred to reside. Sulfate reduction rates for Core A are 2.1–2.2 nmol cm$^{-3}$ d$^{-1}$ within the upper 200 cm and 0.25 nmol cm$^{-3}$ d$^{-1}$ at 300 cm (Fig. 9b). For Core B, rates are 1.7–2.5 nmol cm$^{-3}$ d$^{-1}$ within the top 100 cmbsf, and 3.0 nmol cm$^{-3}$ d$^{-1}$ near or within the SMT (452 cmbsf) (Fig. 9b). Below the SMT in Cores A and B, sulfate reduction rates are 0.35 nmol cm$^{-3}$ d$^{-1}$ or less. Sulfate concentrations for Cores C and D (located beneath the gas hydrate cap) are $\leqslant 6\text{mM}$ at all depths (Fig. 9a). The SMT depth for these cores is likely less than 1 mbsf. Sulfate reduction rates in Cores C and D are $\leqslant 1.4\text{nmol cm}^{-3}\text{d}^{-1}$ (Fig. 9b) with an average rate of 0.4 nmol cm$^{-3}$ d$^{-1}$.
5. DISCUSSION

5.1. Evidence for the anaerobic oxidation of methane (AOM) at Bullseye vent

Geochemical data (Fig. 4) indicate AOM is active along the entire Bullseye vent transect and that elevated methane fluxes are concentrated above the seismic blanking features associated with gas and gas hydrate (Fig. 2b). Evidence for AOM is provided by δ\(^{13}\)C-DIC values at the SMT that range from \(-47.5\)\(^{\circ}\) to \(-43.3\)\(^{\circ}\) (Fig. 4) and are substantially more \(^{13}\)C-depleted than the bulk sediment OM (\(-24.5\)\(^{\circ}\) ± 0.5, Fig. 6). The only known mechanism for generating the observed DIC values at the SMT is oxidation of \(^{13}\)C-depleted methane by AOM (Claypool and Kaplan, 1974; Suess and Whiticar, 1989; Malinverno and Pohlman, 2011). SMT depths from cores overlying the 0.1 km\(^2\) gas and gas hydrate-associated blanking features (Cores 2, 3, 5 and 6; bound by the dashed grey line in Fig. 2b) are shallower than those distal to the seep (Cores 1, 4 and 7, Fig. 2b), suggesting elevated methane fluxes near the seep. Core 7, located at the greatest distance from the seep, has a SMT of 580 cmbsf, similar to the regional SMT depth for this portion of the northern Cascadia margin (500 cmbsf at IODP Site U1327; Riedel et al., 2006a). Thus, the coring transect captured the spatial distribution of enhanced methane flux at Bullseye vent.

Among 19 piston cores from Bullseye vent for which sulfate and methane profile data are available (Fig. 2b; 11 from Riedel et al., 2006b; 1 from Briggs et al., 2011; and 7 from this study), only Core 5 from this study contained methane near the sediment–seawater interface. We now consider how the sedimentary origins and burial history of Bullseye vent have enhanced the current methane oxidizing capacity of this seep.

5.2. Delineating sediment origins and deposition at Bullseye vent

5.2.1. Incorporation of methane carbon in sedimentary carbon pools

Using stable (\(^{13}\)C) and radiocarbon (\(^{14}\)C) isotope ratios of sedimentary carbon pools to infer OM sources and deposition rates at methane seeps may be confounded by the incorporation of methane carbon released by AOM. Terrigenous and marine OM sources in continental margin sediments offshore of Vancouver Island are distinguished by \(^{13}\)C values of \(-22\)\(^{\circ}\) to \(-20\)\(^{\circ}\) for marine OM and \(-27\)\(^{\circ}\) for terrigenous OM (Meyers, 1997; McKay et al., 2004; Kaneko et al., 2010). Sediment deposition rates are based on the extent of radioactive decay of \(^{14}\)C since death and burial of planktonic foraminifera (e.g., McKay et al., 2004). However, \(^{13}\)C-depleted (Whiticar, 1999) and \(^{14}\)C-depleted (Pohlman et al., 2009) methane carbon assimilated into the host sediment may obscure the \(^{13}\)C-based origins and \(^{14}\)C-based ages of carbonate and sediment (e.g., Paull et al., 1989). To properly utilize \(^{13}\)C and \(^{14}\)C based isotope proxies for sedimentary source and depositional rate studies in methane seeps, the extent to which the AOM-derived carbon alters various sedimentary carbon pools must be determined.

With the exception of three samples from the SMT of Core 5 (Fig. 6), the \(^{13}\)C-content of the TOC (\(-24.5\)\(^{\circ}\) ± 0.5) is constant and reflects a simple mixture of terrigenous OM (\(-27\)\(^{\circ}\)) and marine phytoplankton (\(-21\)\(^{\circ}\)) (McKay et al., 2004; Kaneko et al., 2010). By contrast, the \(^{13}\)C values of the bulk carbonate (\(-27.0\)\(^{\circ}\) to +2.5\(^{\circ}\)) are, for the most part, substantially more \(^{13}\)C-depleted than the regional range (\(-1\) to +1\(^{\circ}\)) for biogenic carbonate (Ortiz et al., 1996) (Fig. 7). Thus, while the
Table 3
Planktic foram mass balance radiocarbon ($^{14}$C) correction inputs and outputs.

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth (cmbsf)</th>
<th>Percent authigenic carbonate</th>
<th>Measured $D^{13}$C$_{in}$</th>
<th>Corrected $D^{13}$C$_{in}$</th>
<th>Corrected $^{14}$C age</th>
<th>$\Delta$-Age</th>
<th>Calendar age</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGC02-08-05</td>
<td>70</td>
<td>7.2 ± 1.0</td>
<td>−863 ± 3</td>
<td>−800 ± 3</td>
<td>15800 ± 160</td>
<td>150</td>
<td>17.78±0.66</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>11.6 ± 1.3</td>
<td>−864 ± 4</td>
<td>−858 ± 5</td>
<td>16650 ± 260</td>
<td>400</td>
<td>17.57±0.91</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.4 ± 1.1</td>
<td>−864 ± 4</td>
<td>−861 ± 4</td>
<td>15850 ± 250</td>
<td>300</td>
<td>17.90±0.71</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>10.5 ± 1.2</td>
<td>−865 ± 4</td>
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<td>15750 ± 270</td>
<td>350</td>
<td>17.73±0.95</td>
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<tr>
<td>PGC02-08-06</td>
<td>120</td>
<td>9.2 ± 1.1</td>
<td>−842 ± 5</td>
<td>−836 ± 5</td>
<td>14550 ± 250</td>
<td>300</td>
<td>15.94±0.75</td>
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<tr>
<td></td>
<td>200</td>
<td>12.0 ± 1.3</td>
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<td>−844 ± 7</td>
<td>14950 ± 380</td>
<td>350</td>
<td>16.49±1.13</td>
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<tr>
<td></td>
<td>330</td>
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<td>−845 ± 3</td>
<td>15000 ± 140</td>
<td>50</td>
<td>16.54±0.51</td>
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<tr>
<td></td>
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<td>−853 ± 3</td>
<td>15400 ± 170</td>
<td>100</td>
<td>17.17±0.67</td>
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<tr>
<td></td>
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<td>−863 ± 3</td>
<td>15950 ± 150</td>
<td>50</td>
<td>18.13±0.57</td>
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<tr>
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<td>3.4 ± 0.9</td>
<td>−845 ± 6</td>
<td>−843 ± 6</td>
<td>14900 ± 310</td>
<td>100</td>
<td>16.46±0.90</td>
</tr>
</tbody>
</table>

$^{a}$ Calculated by Eq. (5) (includes propagated error).
$^{b}$ Calculated according to Stuiver and Polach (1977).
$^{c}$ Calculated according to Eq. (6).
$^{d}$ Calculated according to Eq. (7) using the corrected $D^{14}$C value (includes propagated error).
$^{e}$ Calculated as the difference between the corrected $^{14}$C age and the measured $^{14}$C age (Table 2).
$^{f}$ Calibrated calendar age using the corrected $^{14}$C age, the CALIB 5.0 program (Stuiver and Reimer, 1993) and the Marine04 calibration data (Hughen et al., 2004).

$^{13}$C-based evidence for methane incorporation to TOC is limited, it is strong for bulk carbonate.

Radioisotope ages of the TOC and bulk carbonate are both older than the planktonic foraminifera (Fig. 8). For TOC, the age offset from the planktonic foraminifera is most likely related to contributions from pre-aged terrigenous OM (Raymond and Bauer, 2001; Olkhouchi et al., 2002). For bulk carbonate, the offset reflects incorporation of methane carbon with a reported $\Delta^{14}$C value of −985‰ (Pohlman et al., 2009); equivalent to a radiocarbon age of ~34,000 yrs. Planktonic foraminifera, the sediment component most frequently used to calculate sediment accumulation rates in marine sediments, possess the youngest radiocarbon ages among the paired samples (Fig. 8). However, $\delta^{13}$C values as low as −5.2‰ for the planktonic foraminifera (Table 2) imply that precipitation of methane-derived authigenic carbonate (AC) might also have influenced the measured radiocarbon ages. This observation is consistent with previous studies where the primary biogenic signal of living and dead foraminiferal tests in hydrate-bearing cold seeps was altered by methane-derived AC (Torres et al., 2003; Hill et al., 2004).

5.2.2. Mass balance-corrected sedimentation rates

To obtain an accurate chronologic stratigraphy for Bullseye vent, isotopic alterations caused by precipitation of methane-derived AC on planktonic foraminifera tests are corrected through a series of isotope mass balances using a general 2-source isotope mixing model (Eq. (4)) as

$$X_{\text{foram}} = (X_{\text{DIC}} \ast f_{AC}) + (X_{\text{biogenic}} \ast (1 - f_{AC})),$$

where $X$ is the measured $\delta^{13}$C or $D^{14}$C of the foraminifera ($X_{\text{foram}}$), pore water DIC ($X_{\text{DIC}}$) or pure biogenic calcite ($X_{\text{biogenic}}$). Because AC forms when components of DIC generated during AOM (Eq. (1)) precipitate at the SMT ($^{13}$C values as low as −5.2‰ for the planktonic foraminifera ($X_{\text{foram}}$) are those $D^{14}$C values as: $D^{14}$C$_{\text{DIC}}$ = $D^{14}$C$_{\text{DIC}}$ − $D^{14}$C$_{\text{biogenic}}$

where $f_{AC}$ is the fractional contribution of AC (Table 3), $D^{14}$C$_{\text{DIC}}$ is the $D^{14}$C of pore water DIC nearest the SMT (Fig. 5; see Electronic Annex for actual values), and $D^{14}$C$_{\text{foram}}$ is the measured $D^{14}$C of planktonic foraminifera [Kulm et al., 1986; Paull et al., 1992; Aloisi et al., 2002], the isotopic signature of AC is represented by the measured isotopic signature of DIC ($X_{\text{DIC}}$) at the SMT. This approach assumes the isotopic composition of the measured DIC is similar to when the carbonate precipitated on the foraminiferal tests. The pure biogenic calcite component ($X_{\text{biogenic}}$) is the calculated isotopic signature for unaltered planktonic foraminifera.

The fraction of AC ($f_{AC}$) present in foraminifera is calculated by rearranging Eq. (4) and inserting appropriate $\delta^{13}$C values as:

$$f_{AC} = \frac{(\delta^{13}C_{\text{foram}} - \delta^{13}C_{\text{biogenic}})}{(\delta^{13}C_{\text{DIC}} - \delta^{13}C_{\text{biogenic}})}$$

where the $\delta^{13}$C for pure biogenic calcite ($\delta^{13}C_{\text{biogenic}}$) is 0.0 ± 0.5‰ (Ortiz et al., 1996), $\delta^{13}$C for DIC ($\delta^{13}C_{\text{DIC}}$) is the pore water $\delta^{13}$C-DIC value at the SMT for each core (Fig. 4), and $\delta^{13}$C values for planktonic foraminifera ($\delta^{13}C_{\text{foram}}$) are those directly measured or estimated (Table 2). Model results (Table 3) indicate that post-depositional accumulation of AC accounts for ~3–12% of carbonate in planktonic foraminifera. These findings are similar to those from Hydrate Ridge where AC comprised of 3–20% of foraminiferal tests (Torres et al., 2003).

The biogenic $D^{14}$C values ($D^{14}$C$_{\text{biogenic}}$) for planktonic foraminifera are calculated by rearranging Eq. (5) and inserting appropriate $D^{14}$C values (Eq. (6)) as

$$D^{14}$C$_{\text{biogenic}} = \frac{D^{14}$C$_{\text{foram}} - (D^{14}$C$_{\text{DIC}} \ast f_{AC})}{(1 - f_{AC})}$$

where $f_{AC}$ is the fractional contribution of AC (Table 3), $D^{14}$C$_{\text{DIC}}$ is the $D^{14}$C of pore water DIC nearest the SMT (Fig. 5; see Electronic Annex for actual values), and $D^{14}$C$_{\text{foram}}$ is the measured $D^{14}$C of planktonic foraminifera.
5.2.3. Bullseye vent: a glacial-marine sediment methane seep

The corrected planktonic foraminalifer ages from Cores 5, 6 and 7 range from 14,550 to 15,950 radiocarbon (14C) yrs BP, or 15,940 to 18,130 calendar yrs BP (Table 3). That time interval corresponds with the late glacial period of the last glacial maximum (LGM) (Cosma and Hendy, 2008). The maximum extent of glaciation on the continental slope offshore of Vancouver Island during the last glacial maximum occurred ~19 ka BP. Retreat of the ice sheet began ~17 ka BP (Blaise et al., 1990). From the peak of glaciation until approximately 14.6 ka BP – a period that entirely encompasses the age of material recovered in cores from Bullseye vent – large quantities of sediment comprised of glacially-derived lithogenic sediment and predominantly terrigenous OM (McKay et al., 2004; Cosma and Hendy, 2008) were deposited along the continental margin (Clague and James, 2002). Sedimentation rates reported for this continental slope during this time period are 160 cm ka⁻¹ (Blaise et al., 1990), ~47 cm ka⁻¹ (McKay et al., 2004) and ~110–480 cm ka⁻¹ (Cosma and Hendy, 2008) (see Fig. 2a for the core locations). The average calculated sedimentation rate interpolated from the age-depth profile from Core 6 (166 cm ka⁻¹, Fig. 10) is within the range of these studies. Thus, the dated sediments, ranging in depth from 70 to 573 cmbsf, were unequivocally deposited during the period of deglaciation following the LGM.

δ¹³C-TOC data from our 74 samples represents a more extensive vertical range (5–818 cmbsf) and resolution than the radiocarbon dataset, and provides an opportunity to further delineate the Bullseye vent sediment origins. Calculations using a 2-source isotope mass balance equation (Eq. (4)) with a marine end member value of −21δR, a terrigenous end member value of −27δR, and the measured value for each TOC sample, indicate that 63 ± 9% of the TOC from all Bullseye vent profiles (Fig. 6) is terrigenous in origin. Consistent with this calculation, terrestrial OM contributions for sites located 14 km (McKay et al., 2004) and 37 km (Cosma and Hendy, 2008) from Bullseye vent were estimated to range from 50% to 70% for the same time interval. Similarly high levels of terrigenous contributions to the northern Cascadia margin are only documented for late-glacial and early-deglacial periods of the LGM, which strongly suggests the entire upper 8 m of sediment at Bullseye vent was deposited before 14.6 ka BP, when rapid warming began during the Bolling (McKay et al., 2004) and terrigenous and lithogenic contributions decreased (McKay et al., 2004; Cosma and Hendy, 2008).

5.3. Tectonic control of sedimentation at Bullseye vent

Although glacial marine sediments accumulated rapidly over large areas offshore of Vancouver Island during the last deglaciation, the absence of Holocene-aged sediment at Bullseye vent is distinct from nearby non-seep slope sites investigated by McKay et al. (2004) and Cosma and Hendy (2008), where 3.5 and 5.0 m, respectively, of post-glacial sediment with OM of predominant marine origin is present (see Fig. 2a for core locations). The depositional history at Bullseye vent is related to the tectonic framework of the margin, as described below.

Multichannel seismic (MCS) data show that Bullseye vent overlies minibasin deposits that have been uplifted by ~225 m relative to a landward slope basin (Fig. 3b). Two discontinuous and vertically offset turbidite sequences visible in seismic profiles of the mini-basin and the slope-basin (dashed lines in Fig. 3b) may have been a continuous stratigraphic unit prior to uplift. The prominent ~225 m eastward-facing fault scarp (Fig. 3b) that formed during uplift now isolates Bullseye vent from down-slope sedimentation by turbidity currents and exposes it to bottom water currents that have starved the platform of hemipelagic sedimentation since at least the Early Holocene (see Section 5.2.3). Thick deposits of glacial-marine sediments on this turbidite-isolated ridge suggest the ice sheet that melted in this area during the Late Pleistocene resulted in the deposition of sediments on this platform. Indeed, the Cordilleran Ice Sheet advanced onto the continental shelf to within 45 km of Bullseye vent 16.7 ka BP (Blaise et al., 1990), which is within the 2000 yr period when more than 5 m of sediment was deposited at Bullseye vent (Fig. 10).

\[ 14^C_{\text{age}} = -8033 \times \ln \left( 1 + \frac{14^C_{\text{cosmoc}}}{1000} \right) \]
Exposure of the uplifted ridge to bottom water currents may also have caused the seafloor to erode. The ages of planktonic foraminifera from within the Bullseye vent depression (Core 5) are older than foraminifera from shallower sediment depths outside the depression (Core 6) (Fig. 10). Older sediment within the seep depression is consistent with sediment loss resulting from gas and fluid seepage (Hovland and Judd, 1988), erosion caused by ocean currents (Hammer et al., 2009) or some combination of both. Furthermore, because authigenic carbonate forms in the subsurface as a by-product of AOM at cold seeps (Kulm et al., 1986; Paull et al., 1992; Aloisi et al., 2002), methane-derived authigenic carbonate outcropping the seafloor is additional evidence for seafloor erosion (Paull and Ussler, 2008).

5.4. Evidence for coupled AOM and sulfate reduction

We hypothesize that the organically lean, aged and weathered surface sediment at Bullseye vent is recalcitrant and therefore unlikely to support significant organoclastic SR. If so, AOM and sulfate reduction coupled by the 1:1 stoichiometry in Eq. (1) is the expected dominant sink for sulfate. To test our hypothesis, we compare sulfate reduction rates from Bullseye vent to those from other seeps to establish general relationships between SR rates and the availability of OM at seeps. We then utilize a radiocarbon-based DIC isotope mass balance model to identify the OM sources and processes contributing DIC to pore fluids at Bullseye vent.

5.4.1. Sulfate reduction rates

The AOM component of SR rates from ex situ incubations is greatly underestimated because methane (substrate for AOM) escapes during sample recovery (Bowles et al., 2011a). Sample depressurization does not, however, reduce substrate availability for organoclastic SR. Thus, SR rate differences among sites with similar methane availability may be attributed to the OM-based SR rate component with OM-poor seeps being expected to have lower total SR rates because methane-based SR is inhibited by substrate loss and OM-based SR is limited by substrate availability. Accordingly, volumetric SR rates from the Bullseye vent depression (0.1–3.0 nmol cm⁻³ d⁻¹; Fig. 9b) are equal to or less than the lowest SR rates from studies of other active seeps in the GoM (Joye et al., 2004; Orcutt et al., 2010; Bowles et al., 2011b), Southern Hydrate Ridge (Treude et al., 2003), Gulf of Cadiz (Niemann et al., 2006a) and the Haakon Mosby mud volcano (Niemann et al., 2006b). Indeed, the maximum SR rates from seeps with abundant non-methane OM sources in the GoM and on Hydrate Ridge are often three or more orders of magnitude greater than the Bullseye vent SR rates. By contrast, the maximum SR rates from Bullseye vent are similar to maximum rates from the OM-poor Woodland Basin near Papua New Guinea in the Pacific Ocean (1.3–4.8 nmol cm⁻³ d⁻¹; Wellsbury et al., 2002) and are comparable to Gulf of Cadiz mud volcanoes (15–25 nmol cm⁻³ d⁻¹) where TOC content is <0.35 wt.% TOC (Niemann et al., 2006a). Although some OM-rich continental margin settings have similar SR rates as Bullseye vent (e.g., Treude et al., 2005; Niewoehner et al., 1998), rates of SR at OM-poor seeps are, in general, low relative to OM-rich seeps. We suggest this observation is related to limited sedimentary OM bioavailability at OM-poor seeps.

5.4.2. DIC-based radiocarbon (¹⁴C) mass balance model

To assess the relative contributions of OM and methane as substrates for SR at Bullseye vent, we employ an isotope mass balance model to calculate the ¹⁴C-content of DIC added to pore fluids since burial. From that, we determine the contribution from OM decomposition within the SZ. This approach takes advantage of the differing ¹⁴C-content of sediment TOC (Δ¹⁴C = –923‰ to –825‰; Fig. 8) and gas hydrate-bound methane (Δ¹⁴C = –985‰; Pohlman et al., 2009) to identify DIC sources. Isotopic mass balance models have been used to determine the radiocarbon composition of particulate organic carbon added to riverine and marine sediments (Blair et al., 2003), dissolved organic carbon (DOC) added to nearshore and open ocean systems (Mortazavi and Chanton, 2004) and seep-derived DOC expelled from gas hydrate-bearing seeps (Pohlman et al., 2011). The ¹⁴C-content of the pore water DIC is an integrated signal from buried seawater DIC and DIC produced during early sediment diagenesis (including AOM, organoclastic SR and net methanogenesis), an approach that is complementary to rate measurements targeting specific processes. The Δ¹⁴C value of pore water DIC (Δ¹⁴C_{pw}) is de-
scribed by a two-source end member model, expressed in terms of the DIC concentration in each sample,

\[ C_{pw} \cdot \Delta^{14}C_{pw} = C_{sw} \cdot \Delta^{14}C_{sw} + C_{sed} \cdot \Delta^{14}C_{sed} \]  

\[ C_{pw} = C_{sw} + C_{sed} \]

where \( C_{pw} \) is the total DIC concentration in each pore water sample, and \( C_{sw} \) and \( C_{sed} \) are the DIC concentrations in each sample derived from the buried seawater component and the DIC contributed by sediment diagenesis, respectively. Similarly, \( \Delta^{14}C_{pw} \) is the measured \( \Delta^{14}C \) value of the pore water DIC derived from seawater DIC (\( \Delta^{14}C_{sw} \)) and DIC contributed by sediment diagenesis (\( \Delta^{14}C_{sed} \)). Using Eq. (9) to replace \( C_{red} \) in Eq. (8) produces a linear equation where the slope, \( m \), (Fig. 11) is equivalent to the \( \Delta^{14}C \) of the diagenetic DIC, \( \Delta^{14}C_{pw} \). See the Electronic Annex for the measured \( C_{pw} \) and \( \Delta^{14}C_{pw} \) values used in the model.

The model estimate for the \( \Delta^{14}C \) of the diagenetic DIC component (\( \Delta^{14}C_{sed} \)) is \(-1017 \pm 18\%_{o} \) (Fig. 11), which is consistent with a DIC contribution from a strictly fossil carbon (i.e., \( \Delta^{14}C = -1000\%_{o} \)) source. Potential fossil or near-fossil DIC sources include methane (\(-985\%_{o}, \) Pohlman et al., 2009) oxidized by AOM, as well as remineralization of deeply-buried fossil OM and DOC (Egeberg and Barth, 1998; Heuer et al., 2009). Because TOC in the SZ is non-fossil (\(-949\%_{o} \) to \(-470\%_{o} \) Fig. 8), a significant contribution from TOC oxidized by SR is not possible. The model includes 36 DIC samples from all seven cores (Fig. 5; Table 4) along the transect, so this conclusion is independent of sediment depth or methane flux.

To test the robustness of the isotope mass balance model, we performed the same analysis using \( \Delta^{14}C \)-DIC data from pore waters of shelf sediments in the southeastern Mediterranean Sea (Sivan et al., 2004) and the Santa Monica Basin in the California continental borderland (Bauer et al., 1995). The estimated \( \Delta^{14}C \) of diagenetic DIC added was \(-229 \pm 18\%_{o} \) and \(-222 \pm 30\%_{o} \), respectively, for the two studies (Fig. 11). In both cases, the inputs are consistent with and supported by additional evidence for at least a partial contribution from non-fossil OM decomposition by SR. Evidence that respiration of non-fossil OM added DIC into pore water at the non-seep sites investigated by Si-van et al. (2004) and Bauer et al. (1995), where AOM was not identified as an active process, bolsters the validity of the model results from this study and supports the conclusion that decomposition of sediment TOC by SR does not contribute significant quantities of DIC to pore waters at Bullseye vent.

### 5.5. Sediment organic matter bioavailability as a structuring factor for methane biogeochemistry and emissions

The geologic and geophysical setting of a seep is the primary structuring factor controlling the quantity of methane transported to the seafloor (e.g., Trehu et al., 2004). The fraction of that methane susceptible to AOM is determined by the quantity of sulfate penetrating the seafloor via molecular diffusion and fluid pumping by seep biota (Sahling et al., 2002; Torres et al., 2002; Niemann et al., 2006b), alternate electron acceptor availability (Beal et al., 2009), reoxidation of sulfides (Arvidson et al., 2004; Riedinger et al., 2010) and competition for sulfate by microbes that degrade oil and hydrocarbons (Joye et al., 2004; Orcutt et al., 2010). Our results suggest that sedimentary OM bioavailability is an additional factor regulating sulfate availability for AOM.

To evaluate if sedimentary OM-content is also related to AOM efficiency, we compared methane fluxes from the SMT to the sediment water interface (SWI) for Bullseye vent and a GoM methane seep with 3-times greater OM-content (Lapham et al., 2008). Both cores were located in diffusion-dominated regions of the seep. Even though deeper SMTs at the GoM seep (593 ± 261 cmbsf) have smaller incoming diffusive methane fluxes than the shallower Bullseye vent SMTs (397 ± 124 cmbsf), the GoM SMT to SWI methane flux (0.53 ± 0.22 µmol m\(^{-2}\) d\(^{-1}\)) was, on average, 27 times greater than the Bullseye SMT to SWI flux (0.02 ± 0.02 µmol m\(^{-2}\) d\(^{-1}\)) (Table 4). Thus, a greater fraction of methane fluxing into the OM-poor SMTs is consumed, suggesting a higher methane oxidation efficiency in OM-poor sediments within diffusive flux regimes.

Using the bathymetry and flux regime of Bullseye vent as a model, we define 3 regions where the effect of sedimentary OM-content on methane flux differs (Fig. 12). In Re-

<table>
<thead>
<tr>
<th>Site</th>
<th>Core</th>
<th>SMT depth</th>
<th>CH(_{4}) gradient (µM cm(^{-1}))</th>
<th>( r^2 )</th>
<th>Diffusive CH(_{4}) flux to SWI (µmol m(^{-2}) d(^{-1}))</th>
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</thead>
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<tr>
<td>Bullseye vent</td>
<td>C1</td>
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<td>0.003</td>
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<td></td>
<td>30</td>
<td>967</td>
<td>0.092</td>
<td>0.78</td>
<td>0.680</td>
</tr>
</tbody>
</table>

* Surface value not included.

† Lapham et al. (2008).

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**Table 4** Methane fluxes from the sulfate methane transition (SMT) to the sediment water interface (SWI).
Region A, a steeper pore water sulfate gradient creates a shallower SMT in the OM-rich setting, thereby providing sufficient sulfate to satisfy AOM and organoclastic SR. All methane is quantitatively consumed in both the OM-poor and OM-rich scenarios. In Region B, there is sufficient sulfate flux to balance AOM and SR in the OM-poor system, but not the OM-rich system. The SMT is absent in the OM-rich system and methane fluxes from the sediments to the overlying water column. In Region C, the methane flux overwhelms AOM and SR regardless of sedimentary OM-content. OM-content has the greatest influence on AOM capacity and methane emissions within Region B. The location and magnitude of methane emissions from Region B for a seep will depend on the net methane flux and the combination of factors that determine electron acceptor availability, including OM-content. Additional field investigations, laboratory studies and analytical models are necessary to quantify the role of OM-reactivity as a structuring factor for regulating methane emissions from seeps.

5.6. Implications for ocean methane emissions

Although oceanic methane emissions presently account for only 2% of the global atmospheric methane budget (Reeburgh, 2007), over millennial time scales ocean warming has the potential to overwhelm AOM and release vast quantities of methane presently stored as gas hydrate to the ocean and atmosphere (Dickens et al., 1995). Previous methane releases associated with gas hydrate dissociation and dramatic ocean chemistry changes (Zachos et al., 2005) are recorded in the geologic record and coincide with warming events (Hinrichs et al., 2003; Kennett et al., 2003).

With respect to contemporary climate change, gas hydrate within high-latitude continental margins is most vulnerable to dissociation (Maslin et al., 2010). Although it is not anticipated that methane liberated from gas hydrate will affect climate over the next several hundred years (Ruppel, 2011), models of warming along Arctic continental margins predict that hydrate destabilization and subsequent oxidation in the ocean will lead to ocean acidification and hypoxia, if present warming trends continue (Biastoch et al., 2011; Elliott et al., 2011). However, since AOM does not cause acidification or hypoxia, if AOM consumes more methane than recent studies assume (Biastoch et al., 2011; Elliott et al., 2011), the environmental impact of destabilized gas hydrate and gas released from sedimentary basins will be less than predicted.

High latitude margins frequently contain 2–3 km thick accumulations of Late Cenozoic glacigenic material that extend to the continental slope and rise (Dowdeswell, 1987; Elverhoi et al., 1995). In fact, the rate of sediment delivery...
by ice sheets exceeded that of the Amazon and Mississippi River systems by at least an order of magnitude during the late Cenozoic (Dowdeswell et al., 2010). Thus, OM-poor glacial-marine deposits most likely overlay at least some gas hydrate-bearing sediments within high-latitude continental margins. Our findings that methane seeps dominated by glacially-derived sediments may be more efficient AOM bioreactors than their OM-rich counterparts suggests that models and budgets quantifying the contribution, fate and impact of methane from seeps should consider seep sediment origins and OM reactivity.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2013.01.022.

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