Composition of shelf methane seeps on the Cascadia Continental Margin

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[1]   Methane reservoirs and seeps are an active component of the continental margin carbon budget and represent a poorly characterized pathway for reduced carbon cycling and methane input to the atmosphere. Active gas seeps from three shelf settings on the Cascadia Continental Margin off Oregon and Northern California contain nearly pure methane with a heavy carbon isotope composition (-29 to $-35‰$). An extensive study of the gas seep at Coquille Bank, Oregon, revealed a warm, buoyant pore fluid associated with the pockmark. As methane enters the water column above these seeps in a steady gas stream, a fraction escapes directly to the atmosphere while the balance dissolves into local seawater. Measured oxidation rates are too slow for significant local oxidation within the water column near the seep. Large mats of pink and white bacteria, including *Beggiatoa* spp. are found around the vent, demonstrating the activity of sulfide oxidizers in this ecosystem. **Citation:** Collier, R. W., and M. D. Lilley (2005), Composition of shelf methane seeps on the Cascadia Continental Margin, *Geophys. Res. Lett.*, *32*, L06609, doi:10.1029/2004GL022050.

1.   Introduction

[2]   *Pockmarks* are seafloor depressions that often record the recent activity of fluid seepage through the sediments. These crater-like features have been extensively documented on continental shelves throughout the world oceans [*Hovland and Judd*, 1988; *Hovland et al.*, 1993] and are often associated with the seepage of hydrocarbons – primarily gas – from sediment reservoirs. In spite of their common occurrence, most shallow active systems are difficult to study and remain poorly characterized. The gas released is primarily methane of both biogenic and thermogenic origin [*Schoell*, 1980] and the significance of this source to the marine and the atmospheric carbon budgets has not been fully documented [*Judd et al.*, 2002; *Milkov et al.*, 2003]. The potential ecological role for these systems as a primary source of carbon or by enhancing fisheries habitat/production on continental shelves remains unknown [*Hovland and Judd*, 1988; *Levy and Lee*, 1988; *Juhl and Taghon*, 1993; *Carey et al.*, 1994; *Drazen et al.*, 2003]. The complete characterization of these shelf sources has particular significance given their proximity to the sea surface, with potential direct transfer of this greenhouse gas to the atmosphere. Given their very close proximity to other gas sources deeper on the convergent margin, including gas hydrate reservoirs [*Suess et al.*, 1999; *Valentine et al.*, 2001], their geochemistry has broad significance to our ability to track methane sources and sinks on the Cascadia Convergent Margin off Oregon [*Kulm et al.*, 1986].

[3]   Between 1990–1992, we participated in a series of multidisciplinary dives, using the submersible *Delta*, to characterize active methane seeps on the shelf along the Cascadia Continental Margin off Oregon and Northern California (Figure 1). Most of our research focused on a single site near Cape Blanco, Oregon, on Coquille Bank. Other work included reconnaissance sampling of seeps off central Oregon at Heceta Bank [*Pearcy et al.*, 1989; *Embley et al.*, 2002] and northern California near the Eel River at the Little Salmon and Table Bluff seeps [*Orange et al.*, 2002]. During the dives, gas samples were collected by the submarine directly from bubble streams at the seafloor using a syringe sampler. Sediment and porewater samples were collected using a box core dropped from the sub into the center of the pockmark. Bacterial mat samples were collected onto filters using a submersible pumping system. Background box cores, CTD-transmissometry data, water column samples, and current velocity profiles were collected from the *R/V Wecoma* which supported portions of the dive program. Below we describe the geochemistry of these active gas seeps and associated fluids.

2.   Description of the Vents

[4]   The Coquille Bank seep is located at $43°02.0'$N, $124°40.2'$W, approximately 28 km southwest of Coos Bay, Oregon at a depth of 132 m (Figure 1). The pockmark is 4–6 m deep, 7–9 m wide, and 15–18 m long, with 45–50° walls on the North side. The walls of the crater are composed of indurated sediments and solid calcite crusts. The continuous escape of large bubbles (5–10 cm diameter) is accompanied by the resuspension of pockmark sediments well above the crater floor. The water column was notably turbid more than 60 meters above the vent as the bubble stream rises all the way to the sea surface (Figure 2). Other than the ebullition of gases, no other visible fluid flow could be seen at the vent.

[5]   Biological activity at the vent is high compared to the surrounding benthic environment [*Juhl and Taghon*, 1993] and extensive bacterial mats surround the pockmark. The most common mat was a thick, rugose, salmon colored mat found closest to the center of the vent. There was also a thinner, white mat that tended to form small circles on the pockmark rim. Phase-contrast light micrographs of the pinkish mat material revealed very large bacterial filaments

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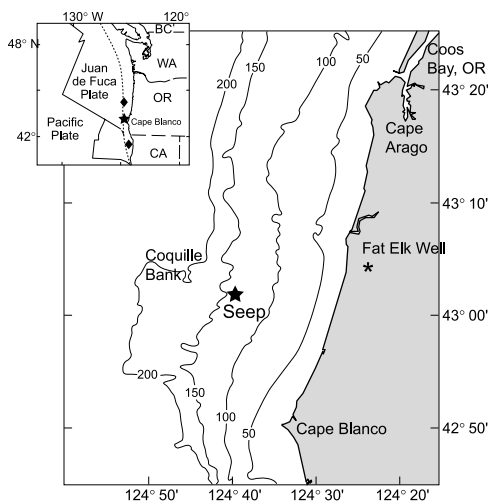[2]School of Oceanography, University of Washington, Seattle, Washington, USA.

Figure 1. Map of fluid vent sites sampled on the continental shelf off Oregon and northern California. The seep location near Coquille Bank is shown (star). The Heceta Bank and Table Bluff (Eel River) seeps (diamond) are also shown in the inset.

(50 μm diameter), very similar to the *Beggiatoa* mats seen at the Guaymas Basin hydrothermal vents [*Jannasch et al.*, 1989].

[6] Two other gas seeps on the Cascadia Margin shelf were sampled in September, 1991. Gas flow at the Table Bluff seep, near the Eel River, California (40°42.3′N, 124°23.0′W, 43 m bottom depth) penetrated a sandy bottom with limited evidence of bacterial mats although it was populated by a large number of small crabs. The Heceta Bank seep, located near the southern summit of the bank off Florence, Oregon (44°00.2′N, 124°52.2′W, 83 m bottom depth) was primarily characterized by small, intermittent bubble streams surrounded by white, filamentous bacterial mats. Numerous other seeps have been observed by ROV dives on Heceta Bank [*Embley et al.*, 2002].

## 3. Seep Geochemistry

3.1. Vent Gases

[7] Gas samples were collected from the gas flows at the base of the Coquille Bank pockmark. Other samples were collected from the slower seeps at the pockmark rim near the bacterial mats, however, we were unable to distinguish any significant differences in the hydrocarbons in these samples. The composition of the gas (Table 1) is dominated by methane (>95%) with a small percentage of nitrogen/argon/oxygen that could have been stripped by the gas bubbles from seawater. The ratio of methane to heavier hydrocarbons (C2 + C3) is high (>1000) suggesting that this "dry gas" may have been generated from a very high-temperature, "mature" hydrocarbon source [*Bernard et al.*, 1976]. The carbon and hydrogen isotopic compositions of the Coquille Bank samples are extremely heavy ($\delta^{13}C = -28.7‰$; $\delta D = -129‰$), consistent with a thermogenic origin [*Schoell*, 1980]. The seep gases from Heceta Bank and Table Bluff are also dominated

by methane with heavy carbon isotopic compositions (Table 1).

3.2. Vent Porewaters

[8] The porewater associated with the Coquille Bank pockmark was remarkable: the temperature of the porewater, 5 cm below the sediment surface, was 15°C compared with 7.5°C in the local bottom water. The total dissolved solids of the pore fluid was less than 60% of seawater and the ion ratios were distinctly non-marine. Vertical profiles of the pore fluid chemistry at the vent were concave approaching the sediment surface demonstrating the upward advection of this extremely buoyant fluid. Relative to seawater, the pore fluid is depleted in Cl^-(204 mM), Na^+(236 mM), K^+(2.2 mM), Mg^{2+}(11.4 mM), and SO_4^{2-}(6.9 mM) and enriched in Ca^{2+}(30.2 mM). Although the calcium concentration is three times higher than seawater, the pH and $\sum CO_2$ are relatively low and the pore fluid is undersaturated with respect to calcite ($\Omega \approx 0.1$). The core sediments at the center of the seep contain <1% calcium carbonate whereas massive calcite crusts and bacterial mats found around the edges of
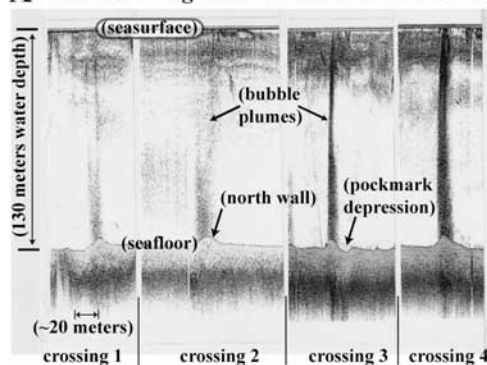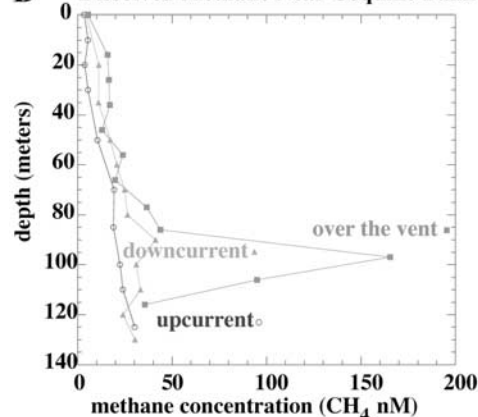

Figure 2. (a) Acoustic images (50 kHz) from four separate crossings of the Coquille Bank pockmark-seep during a 12-hour period. The first and third crossing clearly show both the pockmark depression and its pronounced north wall; the second and fourth crossing did not pass directly over the center of the depression. (b) Vertical profiles of methane concentrations collected 200 m upcurrent, directly over, and 200 m downcurrent of the seep. See color version of this figure in the HTML.

Table 1. Chemical Composition of Gas Phases on the Cascadia Shelf Seeps[a]

	Coquille Bank	Eel River–Table Bluff	Heceta Bank
methane (CH_4)	98.0%	98.1%	93.2%
ethane (C_2H_6)	900 ppm	40 ppm	30 ppm
propane (C_3H_8)	7–15 ppm		
(C1/C2 + C3)	1075	26000	32000
methane $\delta^{13}C$	−28.7‰	−35.5‰	−30.8‰
methane δD	−129‰	−176‰	−163‰

[a]Methane carbon and hydrogen isotopes were analyzed by the UW Stable Isotope Lab, (P. Quay) and at GEOMAR, Germany (E. Suess). Hydrogen sulfide was not detectable by odor and molecular hydrogen was below analytical detection (<2 ppm). The helium concentration at Coquille Bank was 50 ppm with $^3He/^4He$ (R/R$_A$) = 0.3 (i.e. crustal source); analyses performed by the Helium Isotope Lab, NOAA-PMEL, J. Lupton.

the pockmark are supported by significant anaerobic oxidation of methane coupled with sulfate reduction which contributes CO_2, alkalinity and sulfide to the system at the edges of the pockmark [Kulm et al., 1986; Hovland et al., 1987].

[9] Assuming that 20% of the pore fluid volume is derived from seawater, nearly all of the sulfate, magnesium and potassium can be accounted for by that source. The remaining pore fluid end-member (80%) appears to be a Na^+-Ca^{2+}-Cl^- "formation fluid" associated with the hydrocarbon reservoir. The crustal $^3He/^4He$ ratio preclude significant high-temperature basalt interaction controlling this fluid. The oxygen isotopes, $\delta^{18}O$, of the vent pore waters are +3.2 to +5.2‰ (SMOW), as compared to −0.35‰ for the local seawater and background pore waters. The δD of the vent porewater is −5.1‰ compared to −1.9‰ in the surrounding seawater. The heavy $\delta^{18}O$ is not compatible with an unaltered meteoric source for the formation fluid ($\delta^{18}O \approx -8$ to −13; $\delta D \approx -55$ to −95). Although decomposition of gas hydrates produces water with $\delta^{18}O$ = 2 to 4‰ heavier than the source seawater [Hesse and Harrison, 1981; Kvenvolden and Kastner, 1990], the δD values should be at least +20‰ heavier than seawater, indicating that this formation fluid is unlikely to be related to relict marine hydrate decomposition.

[10] We believe the most likely hypothesis is that the formation fluid results from extensive equilibration with deeper sedimentary deposits at elevated temperatures. Clayton et al. [1966] identified this process as the primary control on the isotopic composition of formation brines from a variety of environments. A shallow well, located directly onshore of the seeps ("Fat Elk Well", see Figure 1), produces a dry gas nearly identical in composition to the Coquille Bank seep ($\delta^{13}C$ = −28.4‰) and yields a fluid with remarkably similar chemical and isotopic composition. This is the first report of highly evolved formation fluids in the shelf sediments on the Cascadia Margin, although their specific origin and evolution remain enigmatic.

3.3. Methane Distributions in the Water Column

[11] Bubble plumes from these seeps ascend all the way to the sea surface (Figure 2a) while an unknown fraction of the gas dissolves within the water column. Studies of large hydrocarbon seeps in the Santa Barbara Channel [see Clark et al., 2000; Leifer and Patro, 2002] suggest that the methane dissolved into the water column is roughly equivalent to that transferred directly to the atmosphere by bubbles breaking at the sea surface. No clearly defined

dissolved methane plume could be mapped downstream of the Coquille Bank seeps given our limited sample set (Figure 2b). Current measurements near the vent (ADCP) showed highly variable and reversing tidal currents ranging over 30 cm/sec which rapidly disperse materials injected into this high-energy regime. Although the warm, low salinity pore fluids are very buoyant, no evidence of a fluid plume was observed visually or with the CTD sensors as commonly seen with other buoyant plumes [Hay, 1984; Middleton and Thomson, 1986]. A water sample collected by the sub less than 1 meter above the pockmark floor had a methane concentration over 500 nM, yet its salinity was indistinguishable from background seawater. The maximum concentration of dissolved methane in the water column was greater than 150 nM above the Coquille Bank seep (Figure 2). However, there are not enough methane profiles to make an estimate of the methane inventory or associated fluxes into this highly-dynamic water column or to the atmosphere.

[12] In order to compare in situ turnover rates to physical processes, microbial methane oxidation rates were measured in the water column, sediments, and in the mat material using ^{14}C-labeled methane spikes [de Angelis et al., 1993]. The specific oxidation rates were quite low, ranging from 10^{-3} to 10^{-5} day^{-1} or turnover times for methane from 1.5 to 90 years. In contrast, aerobic oxidation rates in surface sediments were two orders of magnitude faster with turnover times on the order of days. These data suggest that almost all the methane that does escape the sediment is most likely to be released directly to the atmosphere or transported away from the vent where atmospheric exchange with these shallow waters continues.

4. Significance and Conclusions

[13] New methane gas seeps have been identified and sampled from several seafloor locations on the Cascadia continental shelf and their chemical composition has been characterized. The genetic relationships between the gases and coexisting fluids with their depositional sources and regional geology is complex and beyond the scope of this work. This margin has a complex history of active tectonics and rapid sedimentation [Goldfinger et al., 1997] with accretionary compaction and dewatering, extensive faulting, and wide variety of depositional environments extending back into the Eocene. We believe these gas sources on the shelf and upper slope are common, quantitatively significant and must be considered in regional-to-global models of methane fluxes along with those documented further offshore on the accretionary structures of the convergent margin [Kulm and Suess, 1990; Orange et al., 2002; Judd et al., 2002]. In particular, these shallow sources release gas streams that ascend through the water column directly to the atmosphere [Leifer and Patro, 2002] and methane that dissolves into near-surface waters that regularly equilibrate with the atmosphere [e.g., Rehder et al., 2002]. These gases have a significant thermogenic source and are isotopically much heavier than the largely biogenic gases associated with methane hydrate deposits offshore [Suess et al., 1999; Heeschen et al., 2005]. A complete discussion of the sources and fate of methane on this margin must *explicitly* consider multiple end-members and mixing with these

heavier isotopic sources across the highly energetic eastern boundary California Current system, overlying the Cascadia margin [*Heeschen et al.*, 2005].

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