Methane sources, distributions, and fluxes from cold vent sites at Hydrate Ridge, Cascadia Margin

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[1] To constrain the fluxes of methane (CH4) in the water column above the accretionary wedge along the Cascadia continental margin, we measured methane and its stable carbon isotope signature (δ13C-CH4). The studies focused on Hydrate Ridge (HR), where venting occurs in the presence of gas-hydrate-bearing sediments. The vent CH4 has a light δ13C-CH4 biogenic signature (−63 to −66‰ PDB) and forms thin zones of elevated methane concentrations several tens of meters above the ocean floor in the overlying water column. These concentrations, ranging up to 4400 nmol L−1, vary by 3 orders of magnitude over periods of only a few hours. The poleward undercurrent of the California Current system rapidly dilutes the vent methane and distributes it widely within the gas hydrate stability zone (GHSZ). Above 480 m water depth, the methane budget is dominated by isotopically heavier CH4 from the shelf and upper slope, where mixtures of various local biogenic and thermogenic methane sources were detected (−56 to −28‰ PDB). The distribution of dissolved methane in the working area can be represented by mixtures of methane from the two primary source regions with an isotopically heavy background component (−25 to −6‰ PDB). Methane oxidation rates of 0.09 to 4.1% per day are small in comparison to the timescales of advection. This highly variable physical regime precludes a simple characterization and tracing of “downcurrent” plumes. However, methane inventories and current measurements suggest a methane flux of approximately 3 × 10⁶ mol h⁻¹ for the working area (1230 km²), and this is dominated by the shallower sources. We estimate that the combined vent sites on HR produce 0.6 × 10⁴ mol h⁻¹, and this is primarily released in the gas phase rather than dissolved within fluid seeps. There is no evidence that significant amounts of this methane are released to the atmosphere locally.


1. Introduction

[2] Atmospheric methane (CH4) is a greenhouse gas that absorbs infrared radiation 25 times more efficiently than CO2 [Lelieveld et al., 1993, 1998]. There has been a renewed effort to study the possible sources of CH4 entering the atmosphere because of the potential importance of CH4 in climate changes in the past [e.g., Dickens et al., 1995; Kennett et al., 2000, 2003; Hesselbo et al., 2000; Kennedy et al., 2001; Kasting and Steffert, 2002] and because there has been a continuous increase in its atmospheric concentration over the past 150 years [Etheridge et al., 1992; Lelieveld et al., 1998]. A substantial “unknown” in the global methane budget is the nature and fate of CH4 in the oceans and, in particular, along the continental margins, such as the Cascadia Margin. In these environments, methane clathrate hydrates can be significant reservoirs. The stability zone for these hydrates, which depends on conditions of temperature and pressure, usually begins at water depths below 300–500 m [Kvenvolden, 1993]. The estimates of the amount of methane stored in gas hydrates worldwide range between 1 × 10¹⁵ and 115 × 10¹⁵ m³ of methane at STP, constituting by far the largest reservoir of CH4 known [Kvenvolden, 1988, 1993, 1999; MacDonald, 1990; Gornitz and Fung, 1994; Milkov, 2004]. These reservoirs may have an important impact on the global carbon cycle [Kvenvolden, 2002; Dickens, 2003].
[3] Until recently, the ocean was thought to play a minor role in the present-day atmospheric CH$_4$ budget, accounting for just 2–4% (10–20 Tg CH$_4$ yr$^{-1}$) of the total methane released to the atmosphere [Cicerone and Oremland, 1988; Bates et al., 1996]. Since the discovery of new shelf vent sites and “cold vents” related to sedimentary gas hydrates, estimates of the CH$_4$ emission rate to the atmosphere from the seabed have been revised and range from 18–48 Tg CH$_4$ yr$^{-1}$, or 4–9% of the global budget [Hornafius et al., 1999; Judd, 2000; Judd et al., 2002; Kvenvolden et al., 2001]. An equivalent amount of seabed methane is thought to dissolve into seawater [Kvenvolden et al., 2001]. A goal of ongoing research at continental margins is to obtain a better estimate of the impact of cold vents on the oceanic and atmospheric methane budget. In this paper, we describe data obtained from hydrate-bearing sites along the Oregon continental margin, and use these data to more accurately quantify the fate and flux of methane released from the seafloor.

[4] At the Cascadia subduction zone, where the Juan de Fuca Plate is subducted obliquely under the continental North American Plate, a thick accretionary complex has developed [Kulm et al., 1986; DeMets et al., 1990; MacKay et al., 1992]. Our study focused on the characteristic morphological high within the secondary accretionary complex known as Hydrate Ridge (HR). As shown in Figure 1, Hydrate Ridge has two local topographic highs, the northern (NHR) and southern Hydrate Ridges (SHR). At NHR (depth = 590 m) the amplitude of tectonic folding is greatest, and it is characterized by extensive carbonate deposition at the surface [Tréhu et al., 1999; Johnson et al., 2000, 2003]. In contrast, SHR (depth = 790 m) has sediment layers that are tightly folded, and it is predominantly covered with more recent sediments. Two additional ridges of the secondary accretionary complex are South-East Knoll (SE-Knoll; depth = 620 m), which resembles NHR, and North-West Knoll (NW-Knoll; depth = 900 m), which is sediment covered, similar to SHR [Tréhu et al., 1999]. A strong, bottom-simulating reflector (BSR) under these ridges, at sub-bottom depths between 74 and 120 m, is evidence of extensive deposits of gas hydrates which are underlain by sediments containing free gas [Tréhu et al., 1999, 2004; Tréhu and Flueh, 2001]. According to MacKay et al. [1994], the gas occupies 1–5% of the sediment porosity beneath the BSR at NHR. At SHR, shallow layers of gas hydrates even outcrop on the seafloor [Suess et al., 1999, 2001].

[5] Suess et al. [1999] were the first to describe the importance of gas hydrates and free methane gas at Hydrate Ridge, where fault zones feed localized fluid and gas vents. The venting sites are surrounded by abundant chemosynthetic communities which are supported by sulfate reduction and anaerobic oxidation of methane [Boetius et al., 2000; Elvert et al., 2000; Sahling et al., 2002]. Thus much of the advecting methane is oxidized within the sediment and stored in either the chemosynthetic biomass or massive authigenic carbonates [Bohrmann et al., 1998; Greinert et al., 2001; Teichert et al., 2003]. In the water column above the vent sites of NHR, Suess et al. [1999] found CH$_4$ concentrations to be 2 to 3 orders of magnitude above background levels. The heterogeneity of the CH$_4$ concentrations was thought to result from the spatial distribution of very active vent sources and their temporal fluctuations. Initial estimates of the dissolved methane flux into the water column ranged from 20 to 375 mol m$^{-2}$ yr$^{-1}$ [Linke et al., 1994; Suess et al., 1999; Torres et al., 2002]. In contrast, very little is known about the fluxes of gaseous methane at these cold vent locations. Only the estimate of 22 × 10$^6$ mol yr$^{-1}$ is known for a single vent site at NHR, where methane accounts for 99% of the vented gas phase [Torres et al., 2002]. Modeling results [Luff and Wallmann, 2003] and water column measurements [Grant and Whiticar, 2002] demonstrate that the gas venting is an important process for transport of CH$_4$ into the water column at Hydrate Ridge. Heeschen et al. [2003] reported acoustic observations of methane gas plumes that consistently rose to just above the top of the gas hydrate stability zone (GHSZ; 510–490 m) at Hydrate Ridge and SE-Knoll.

[6] On the basis of these previous studies, the distribution of methane in the regional water column is mainly controlled by oxidation of methane derived from vent sources associated with gas hydrates [Valentine et al., 2001; Grant and Whiticar, 2002]. However, the fluxes from other methane sources along the continental margin have not been characterized, and the complex hydrographic environment has not been considered. For example, Hydrate Ridge is located within the California Current system, the dynamic eastern boundary current of the NE Pacific, characterized by strong coastal upwelling due to the prevailing southerly winds during summer and early fall. This current system is characterized by extreme hydrographic variability, offshore transport in the surface Ekman layer, and the formation of a powerful, meandering, southward-flowing coastal jet with core velocities of 50 to 80 cm s$^{-1}$ [Huyer, 1977, 1983; Huyer et al., 1979, 1991; Kosro and Huyer, 1986]. The poleward-flowing geostrophic undercurrent with a core depth of 100–350 m has an average core layer velocity of 0.18 m s$^{-1}$ and is found 20–25 km off the shelf break along the slope and can extend much deeper in the water column [Huyer et al., 1991; Kosro et al., 1991; Pierce et al., 2000; Kosro, 2002]. The undercurrent frequently turns offshore and forms anticyclonic eddies, especially when passing coastal promontories [Strub et al., 1991; Collins et al., 1996; Huyer et al., 1998; Garfield et al., 1999; Barth et al., 2000; Pierce et al., 2000].

[7] The carbon isotopic composition of methane, $\delta^{13}$C–CH$_4$, has proven to be a particularly powerful tool for identifying different methane sources and tracing the flow of carbon through different reservoirs and processes such as oxidation or mixing [e.g., Whiticar, 1999]. Methane produced deep within the accretionary wedge by microbial activity (fermentation) is highly depleted in $^{13}$C. This biogenic process results in isotopically light methane pools. The thermogenic production of CH$_4$ during thermal “maturation” of deeply buried sediments is not accompanied by significant isotopic fractionation and produces isotopically heavier methane that is closer in composition to its organic carbon source. According to Whiticar [1999], a diagnostic boundary between thermogenic and biogenic CH$_4$ is found at roughly $-50\%$ PDB (Peedee Belemnite Standard). Extremely light carbon isotopic ratios of $-71$ to $-62\%$
Figure 1. Sample locations and bathymetry of the TECFLUX study area. (a) Overview of the working area within the Cascadia Margin (inset) showing the locations of all CTD stations as well as the lines of the hydrographic sections shown in Figure 5. Enlarged views of (b) Northern Hydrate Ridge (NHR) and (c) Southern Hydrate Ridge (SHR) show the location of vent-focused and near-field sampling. For the location of Southern Temple, see Figure 10.
PDB are found in the gas hydrates at Hydrate Ridge and demonstrate its biogenic origin [Kastner et al., 1998; Suess et al., 1999]. On the other hand, there are natural gas vents found on the nearby shelf and slope off Oregon which have δ^{13}C-CH_{4} values as heavy as −28% PDB, demonstrating a thermogenic origin [Collier and Lilley, 1995, 2005]. Microbial oxidation of methane results in a kinetic isotope fractionation due to the preferential use of 13C over 12C [Whiticar, 1999]. After significant oxidation of methane, this process results in residual methane pools that become isotopically heavier than the source methane.

[8] To help constrain the behavior and flux of methane in the water column which is associated with the significant reservoirs of methane hydrates and venting along continental margins, we acquired an extensive data set of methane concentrations and associated stable carbon isotope ratios between 1998 and 2000 along the Oregon Margin. The interpretation of these distributions required the simultaneous characterization of the Eastern Boundary current system including hydrographic properties and current observations.

2. Methods

[5] As listed in Table 1, the TECFLUX project comprised seven cruises over the Cascadia Margin off Oregon between 1998 and 2000. All of which included water column sampling [Torres et al., 1998, 1999; Bohrmann et al., 1999; Linke et al., 2001]. During these cruises, samples for CH_{4} concentrations and carbon isotopic compositions were collected from 130 vertical or towed CTD casts (Figure 1). Data from the 1998 cruise were discussed by Kastner et al. [1999]. The complete data set from 1999 and 2000 is available in an auxiliary table.1

[10] Seabird CTDs (conductivity, temperature, and depth sensors) and rosette samplers were used for hydrographic transects. All CTDs had been calibrated within 6 months of use. The CTDs were outfitted with oxygen sensors (SBE13) and optical turbidity sensors, including a transmissometer (SeaTech, 25 cm) and/or a backscatter sensor (SeaTech OBS). Additional water samples were collected from other vehicles including the ZAPS (towed ZAPs (towed Zero Angel Photometer System [Klinkhammer and McManus, 2001]), DSRV ALVIN, ROV ROPOS, and benthic landers.

[11] An in situ methane sensor (METS, GKSS-Forschungszentrum, Germany) was used during all CTD and ZAPS deployments. Although calibration was not generally possible for these dynamic systems because of the METS sensor’s slow response time, it allowed qualitative observations and it was critical for positioning the sample collection and obtaining water samples from thin layers of CH_{4}-rich plumes [Klinkhammer et al., 1999]. Hull-mounted echosounding systems with frequencies between 12–18 kHz were used to directly detect and track gas bubble plumes in the water column [Heeschen et al., 2003].

[12] Two current meters (Alpha Omega, VACM 9605) were deployed on a mooring at 500 m and 600 m water depths. The mooring was located south of NHR (44°38.5′N, 125°06.4′W, bottom depth 673 m) and was deployed between April and October 1999.

[13] Oxygen concentrations were determined with the CTD oxygen sensor and confirmed by Winkler titration [Grasshoff et al., 1983]. Methane concentrations in water samples were determined at sea using a modified vacuum degassing method [Lammers and Suess, 1994; Rehder et al., 2001]. This entailed obtaining 400-mL samples of seawater from the rosette samplers using glass syringes and immediately transferring them into pre-evacuated 600-mL glass bottles. Head-space gas and water phases were allowed to equilibrate before the resulting gas phase was recompressed to atmospheric pressure, and the CH_{4} mole fraction of the total extracted gas was determined by gas chromatography using flame ionization detection (FID). Bottled mixtures of 10.0 ppm ±2% and 1002 ppm ±5% CH_{4} in synthetic air from Scotty Specialty Gases were used for standards. Replicate analyses of two series of samples from a single hydrocast with about 6 nmol L^{-1} (n = 9) and 0.16 nmol L^{-1} (n = 6) yielded a precision of 2% and 9%, respectively.

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The amount of dissolved CH$_4$ in each water sample was calculated as the product of the methane mole fraction in the extracted gas phase and the total amount of gas in the sample at STP. The total gas concentration of the sample was calculated by adding the measured dissolved oxygen concentration and the calculated nitrogen and argon concentrations. Nitrogen and argon concentrations were assumed to be at saturation relative to their atmospheric partial pressures, taking into account in situ temperatures and salinities [Weiss, 1970]. The degree of CH$_4$ saturation in the water relative to equilibrium with the atmosphere was determined with equations from Wiesenburg and Guinasso [1979] using an atmospheric CH$_4$ concentration of 1.79 ppm which was taken from the NOAA records (ftp://ftp.cmdl.noaa.gov/ccg/ch4/flask/month; cited September 2004). Because CH$_4$ has a solubility of about 2 mmol kg$^{-1}$ seawater at 4$^\circ$C and 1 atm [Duan et al., 1992], it can be expected that no degassing occurred during sample recovery.

The $\delta^{13}$C-CH$_4$ ratios in the gas extracted from the water samples were determined with a Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS), applying a method originally described by Merritt et al. [1995] and modified by Grant [2000] at the SEOS laboratory of the University of Victoria. A Finnigan MAT 252 mass spectrometer (Finnigan, Bremen, Germany) was used in combination with a preparative sample pre-concentration loop and a gas chromatograph linked in series with a microvolume combustion reactor (Cu/CuO/Pt at 910$^\circ$C). Following sample injection, the contaminants N$_2$ and O$_2$ were eluted from the gas samples in a cooled preparative column which contained a molecular sieve to retain CH$_4$. Water was removed using a selectively permeable Naphion tubing assembly. To increase sensitivity, the open split was modified to maximize the amount of sample directed into the mass spectrometer. Replicate air samples with amplitudes as low as 300 mV yielded a precision of 0.8\% PDB for samples measured in 1999 and 0.9\% PDB for samples measured in 2000.

3. Results and Discussion

To determine the behavior, significance, and associated flux of methane released from the cold vents of Hydrate Ridge and related features of the accretionary complex, we investigated the characteristics of the vent sources, the strong California Current, and the resulting distributions of methane and $\delta^{13}$C-CH$_4$ in the water column.

3.1. Methane Inputs and Distributions

3.1.1. Hydrate Ridge Vent Sites

Dissolved methane in close proximity to the vent sites of southern and northern Hydrate Ridge (SHR and NHR) reaches extremely high concentrations and is very heterogeneous in time and space (Figures 2a–2c). The highest CH$_4$ concentrations were usually confined to thin layers, several tens of meters in thickness, and elevated 80 ± 50 m above the seafloor. Within these layers, CH$_4$ concentrations reached 1400 nmol L$^{-1}$ at SHR and 4400 nmol L$^{-1}$ at NHR. Methane maxima over 200 nmol L$^{-1}$ were frequently accompanied by smaller separated peaks above and below (10–150 nmol L$^{-1}$). Between the peaks, concentrations often dropped to values less than 5 nmol L$^{-1}$ and were sometimes as low as the regional background values of 0.5–1.5 nmol L$^{-1}$. At both NHR and SHR, the samples taken nearest to the bottom were usually elevated in CH$_4$, but only occasionally contained these most extreme concentrations.

Methane concentrations in the water column near the vent sites also varied with time over 3 orders of magnitude (Figure 2c). Successive GPS-navigated CTD profiles from SHR and NHR, which are generally positioned to within a 50 m radius and taken over intervals of just a few hours, identify methane maxima that range between 10 nmol L$^{-1}$ and 1000 nmol L$^{-1}$. Samples from a single CTD station, collected within a 1-hour period (on the downcast and upcast), showed concentration changes as large as 1 order of magnitude (Figure 2b: SO143/97-19).

These highly variable and sharply-defined CH$_4$ maxima above the vent sites of SHR and NHR are likely caused by the transport and dissolution of methane bubbles from the seafloor as opposed to fluid-phase injection from the cold seeps. The highest concentrations of dissolved CH$_4$ detected by the METS sensor and rosette samples almost always occur when and where rising gas bubble plumes were detected by acoustic methods. Although mixed layers were frequently observed within 100 m above the HR vent sites (see section 3.3), the CH$_4$ peaks at these depths showed no correlation with density or other hydrographic structures which would be expected had the methane peaks been caused by the rise of methane-laden vent fluids. The cold vent fluids at Hydrate Ridge, with densities very similar to bottom water, spread outward along isopycnals, and are partly responsible for the elevated CH$_4$ concentrations seen in nearly all bottom samples. Damm and Budéus [2003] discuss a similar fate for dissolved methane from a cold seep in the Norwegian Sea, whereas patterns of trans-isopycnal methane distributions were found at the sites of natural gas vents such as at Coal Oil Point [Clark et al., 2000] and in the gas-hydrate-bearing Eel River Basin [Valentine et al., 2001].

Ongoing research on dissolution processes within rising gas-bubble plumes at various hydrocarbon vent sites suggests that the bubbles can induce an upwelling flow ($v_{up}$) by transferring momentum to the surrounding fluids [McDougall, 1978; Leifer et al., 2000; Leifer and Judd, 2002; Leifer and Patro, 2002]. As the bubbles rise in the water column, bubble size decreases (as long as the rate of dissolution overcomes the rate at which the bubble size increases owing to the hydrostatic pressure decrease). As bubble size decreases, $v_{up}$ decreases to zero and the remaining gas phase is “deposited” in the water column at that depth. This process was termed “bubble deposition” by Leifer and Judd [2002]. The depth of maximum deposition strongly depends on the release radii of the bubbles, the seabed depth, the vertical velocity, and the hydrostatic pressure. Further, it will be altered by the gas-hydrate skin which armors the rising bubbles through the GHSZ and decreases the dissolution rate [Rehder et al., 2002b]. Heeschen et al. [2003] observed that acoustic images of
bubble plumes at Hydrate Ridge vanished just above the GHSZ at water depths of 460 to 500 m. The depths of dissolved methane maxima above Hydrate Ridge, however, show that the maximum deposition depths are still within the GHSZ. The multiple peaks in methane concentration observed at Hydrate Ridge vent sites (Figure 2c) may relate to varying release radii or bubble plume input density. At NHR, there are at least three separate gas vents, further complicating the character of the vent plume.

The variability of the gas venting activity at NHR has been well documented with video [Torres et al., 2002; K. Nakamura, National Institute of Advanced Industrial Sciences and Technology, Japan, personal communication, 2002]. These observations demonstrate significant tidal components superimposed on gas venting activity at NHR. At SHR, where continuous video observations are lacking, our repeated hydrocasts suggest no tidal variations in the CH₄ concentrations (Figure 3). If all CH₄ maxima (>100 nmol L⁻¹) above NHR and SHR are compared to the tidal cycle, a correlation between low tide and highest CH₄ concentrations is found at NHR, but not at SHR. The contrasting behavior may relate to the different sub-bottom depths of the methane gas reservoirs, different sub-surface structures, or mechanisms triggering the gas venting. At NHR, deep faults reach below the relatively shallow BSR [MacKay et al., 1994; Westbrook et al., 1994]. Changes in hydrostatic pressure with the tides may directly affect the movement and release of this gas. At SHR, the connection to the deeper BSR is more complex. Shallower faults, combined with a system of

![Figure 2](image-url)

**Figure 2.** Examples of methane profiles in single CTD casts. Methane profiles for (a) NHR and (b) SHR. (c) Methane profiles for time series of samples at NHR and SHR. Note that different scales are used to display the methane concentrations in Figures 2a–2c, and that the depth scales differ as well.
lithologically-controlled permeability variations in the sediment, were recently described as possible fluid and gas pathways at SHR [Tréhu et al., 2004]. Gas hydrate dynamics or changes in gas pressure might control the gas release [Suess et al., 1999; Tryon et al., 1999].

3.1.2. Other Submarine Features of the Accretionary Complex

In addition to the data from HR, hydrographic studies were undertaken at four other distinct submarine features: SE-Knoll, NW-Knoll, the BSR-Outcrop to the north at 500 m depth [Tréhu et al., 1995], and a mound-like structure to the south, called “Southern Temple” (Figures 1 and 10). All of these features proved to be active methane sources (Figure 4). The CH₄ profiles near the summit of SE-Knoll resemble those of the Hydrate Ridge vent sites and suggest active methane gas venting. However, CH₄ maxima observed at SE-Knoll were 2 orders of magnitude lower than at HR. The profiles above NW-Knoll and the BSR outcrop had maximum CH₄ concentrations in the samples closest to the seafloor (11 nmol L⁻¹). These were probably caused by

Figure 3. Correlation between the tidal cycle (at Newport harbor) and the methane maxima of each CTD cast at NHR (N, dark shading) and SHR (S, light shading) below 480 m depth over several weeks during summer 1999. For the correlation between methane ebullition and the tidal cycle, CH₄ maxima exceeding 100 nmol L⁻¹ were taken into account. Low concentrations could either result from a shut down of the source or be a sampling artifact caused by changing current directions. The station numbers of the time series shown in Figure 2c are marked in the boxes above the lower diagram.

Figure 4. Methane profiles and the stable carbon isotopic signatures (‰ PDB) of deep methane maxima obtained from other submarine features.
Figure 5
venting of methane-laden fluids. At Southern Temple, elevated CH₄ concentrations (up to 12 nmol L⁻¹) were spread over 80 m of the water column above the mound, suggesting a weak bubble ebullition or strong fluid flow and enhanced vertical mixing, which is common in this area.

### 3.1.3. Regional Methane Distribution

[25] The cold-seep sources discussed above introduce methane into the complex California Current environment. The variable current regime coupled with the temporal variability of the venting prevents the formation of down-current CH₄ plumes. Instead, methane is more widely dispersed and its distribution is further altered by offshore transport from shelf and upper slope sources (Figure 5). In order to better constrain these methane inputs over larger spatial scales, a series of hydrographic sections was collected across the Cascadia Margin. These sections were located in an attempt to constrain the fluxes from the vents (Figures 5a–5d). In hydrographic sections obtained further north (NH-1) and south (NH-2) of HR (Figures 5e and 5f), CH₄ concentrations were already less than 8 nmol L⁻¹.

[26] In comparison with the deep water CH₄ enrichments at Hydrate Ridge, offshore methane maxima above 480 m depth were usually broader, reaching concentrations as high as 35 nmol L⁻¹ (Figures 5a—5d). Throughout the working area the water column was usually elevated in methane between 100 to 300 m depth. The measured concentrations of 5 to 22 nmol L⁻¹ CH₄ corresponded to 100–600% supersaturation with respect to the recent atmospheric mole fraction of CH₄ of 1.79 ppmV. The hydrographic sections on this continental margin clearly show strong sources of methane at the shelf edge seafloor (Figures 5e—5h). Also, in situ production of methane is common in the upper water column [Karl and Tilbrook, 1994]. Near-bottom samples taken from just off the shelf had maximum CH₄ concentrations of 55 nmol L⁻¹ (Figure 5h). There was a higher frequency of maxima above 480 m in sections collected in the year 2000 (SO-1,-3,-4,-5) compared to those collected in 1999 (SO-2, NH-1, NH-2, WA-1).

[27] In surface water the process of air-sea exchange causes smaller CH₄ supersaturations. They 34% in 1999 and 65% in 2000. These values are similar to continuously measured surface methane concentrations obtained in 1999 by Rehder et al. [2002a], who found only small supersaturations in the area of Hydrate Ridge, while toward the shelf edge, the saturation increased to 150% owing to coastal upwelling.

### 3.2. Methane Sources and Biogeochemical Processes

[27] Figure 6a illustrates the depth distribution of the stable carbon isotope ratios of methane, δ¹³C-CH₄, in water samples collected at Hydrate Ridge vent sites. It shows that the isotope signatures are clearly separated into two groups, a shallow group with relatively heavy δ¹³C-CH₄ signatures and a deep group with much lighter ratios. At both NHR and SHR, the shallow water samples have values between −12 and −40‰ PDB, whereas below 480 m water depth, the δ¹³C-CH₄ signatures ranged between −42 and −68‰ PDB. The delineation between the two groups is very sharp and occurs at the same depth for both NHR and SHR, despite the different bottom depths of the vents. The depth of change in δ¹³C-CH₄ is consistent with the upper limit of the GHSZ at 490–510 m, the upper limit of the weakening bubble plumes, and at the same time marks a discontinuity in the hydrographic regime, the details of which are discussed below. These results indicate that the methane budgets below and above 480 m are dominated by different methane sources.

[28] The origin of the two methane isotopic groups can be interpreted from the δ¹³C-CH₄ as a function of CH₄ concentrations for all samples analyzed in the working area (Figure 6b). This correlation shows two distinct peaks, one between −28 and −38‰ PDB and the other between −58 and −68‰ PDB. These peaks represent the isotopic end-members of the two main methane sources contributing to the inventory.

[29] The isotopically light end-member measured in water samples within the GHSZ above HR is very well defined, and according to the classification of Whiticar [1999] the methane is of biogenic origin. The highest CH₄ concentrations at HR have δ¹³C-CH₄ values that are identical to those measured in vent gas taken with the submersible Alvin. The average δ¹³C-CH₄ value of the gas was −66‰ PDB at SHR and −63‰ PDB at NHR. Differences in gas pathways, storage, or gas hydrate formation may lead to differences in the availability for microbial oxidation.

[30] At 400 m, very few elevated methane concentrations with light δ¹³C-CH₄ signatures suggested scarce transport of NHR vent gas above the GHSZ (Figure 6a). At this depth, isotopically heavier methane accounts for nearly the entire methane inventory. This end-member with intermediate concentrations has a wider range of isotopic ratios and relates to sources on the shelf and upper slope. It is observed in near-bottom water samples close to the shelf edge and in the numerous CH₄ peaks at depths of about 400 m and shallower. The δ¹³C-CH₄ signatures measured in waters above the upper continental slope (Figure 6b, triangles)

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**Figure 5.** Methane concentrations along regional transects shown in Figure 1. (a, b) SO-1 and SO-2, showing cross sections from NE-SW transects in the area of NHR; (c, d) SO-3 and SO-4, showing cross sections from NE-SW near SHR. (e, f, g) NH-1, NH-2, and SO-5, showing cross sections from the upper continental slope to the HR areas; (h) WA-1, showing a cross section of the upper slope only. Note that there is considerable variation in the latitudinal and longitudinal scales of the figures. The black dots indicate all samples taken, and station numbers are annotated in the top of each figure. The density distribution is shown by the annotated white (red) contours. See color version of this figure at back of this issue.
varied between -20 and -56‰ PDB, suggesting that this methane originates from a variety of sources. In section NH-1 (Figures 1 and 5a), the δ¹³C-CH₄ signature below the shelf edge (460 m water depth) is -28‰ PDB (15 nmol L⁻¹). According to the classification of Whiticar [1999], this signature indicates methane of thermogenic origin. In contrast, near-bottom water samples from 230 m depth in section WA-1 (Figures 1 and 5h) have a light δ¹³C-CH₄ signature of -56‰ PDB (55.2 nmol L⁻¹), probably resulting from seepage of biogenic methane produced in the sediments by microbial methanogenesis. Mixed intermediate ratios of -40‰ PDB are found in near-bottom water samples at depths of 400 to 600 m at the slope in SO-5 (Figures 1 and 5g).

[31] The majority of CH₄ concentration maxima sampled between 350 to 450 m depths throughout the working area have isotopic ratios between -26 to -34‰ PDB (Figure 6c). Samples obtained from CH₄ maxima above 350 m have similar isotope ratios (-25 to -35‰ PDB). These heavy ratios correspond to methane from known gas vents on the shelf with isotopic signatures of -28‰ PDB [Collier and Lilley, 2005]. The slightly lighter ratios are the result of a mixture with biogenic methane from slope seepage and/or from in situ methanogenesis in the particle-enriched layers that correlate with these shallow CH₄ maxima (see section 3.3.3). Samples with heavier isotopic signatures sometimes occur at very low CH₄ concentrations and represent residual methane left after extensive methane oxidation [Ward and Kilpatrick, 1993].

[32] The δ¹³C-CH₄ ratios of surface water samples collected along a west-to-east section across the shelf edge near Newport, Oregon (seafloor depths of 420–113 m), show the importance of coastal upwelling for the transport of methane from intermediate depths to the surface and thus to the atmosphere. The isotopic ratio of methane decreases toward the shelf from -46.7 to -42.4‰ PDB at the most inshore location (113 m water depth). As the isotopic composition gets progressively heavier toward shore, the methane supersaturation and the salinity increase while the water temperature decreases. Thus the enrichment in CH₄ on the shelf results from upwelling of isotopically heavier methane, possibly from the thermogenic sources. The offshore isotopic ratios, on the contrary, were in equilibrium with the atmospheric ratios [Holmes et al., 2000].

3.3. Hydrographic Controls on Methane Distributions
3.3.1. Water Masses off the Oregon Coast

[33] Through the preceding discussions of methane distributions and sources, we have clearly shown that the origin and spreading of water masses at the continental margin exerts a controlling influence on the fate of methane in this environment. Below we will review the basic distribution of water masses and the currents observed off central Oregon with a specific focus on the role of the California Undercurrent in the transport of methane from the various sources discussed above.

[34] As part of the TECFLUX field program, hydrographic surveys were carried out during the summers of 1999 and 2000. The main water masses off the Oregon margin can be recognized from the potential temperature-salinity diagram.
The warm Columbia River plume (S < 32.5) produces a shallow mixed layer in the upper 10–20 m of the water column which can be reinforced by seasonal warming. During periods of prevailing southerly winds, coastal upwelling of deeper water masses causes nearshore surface water temperatures to be colder and salinities to be higher. Below this seasonal pycnocline, a permanent halocline extends down to 120 m. The halocline is maintained by mixing of fresher, warm surface waters with Subarctic Pacific Water (SPW; \( \sigma = 25.8 \text{ kg m}^{-3} \)). The colder SPW is entrained by the shallow southward-flowing California Current jet at 48°N and transported along the coast.

(Figure 7a). The warm Columbia River plume (S < 32.5) produces a shallow mixed layer in the upper 10–20 m of the water column which can be reinforced by seasonal warming. During periods of prevailing southerly winds, coastal upwelling of deeper water masses causes nearshore surface water temperatures to be colder and salinities to be higher. Below this seasonal pycnocline, a permanent halocline extends down to 120 m. The halocline is maintained by mixing of fresher, warm surface waters with Subarctic Pacific Water (SPW; \( \sigma = 25.8 \text{ kg m}^{-3} \)). The colder SPW is entrained by the shallow southward-flowing California Current jet at 48°N and transported along the coast.

Below these shallower water masses, warm and saline water influenced by Equatorial Pacific Water (EPW; \( \sigma = 26.6 \text{ kg m}^{-3} \)) is transported northward by the California Undercurrent at a core depth of 200–300 m [Tchernia, 1980; Lynne and Simpson, 1987, and references therein]. The influence of the EPW decreases below the undercurrent to depths of approximately 480 m [Talley, 1993]. The gas hydrate-bearing vent sites are located within the NPIW where average bottom water potential temperatures were 4.65 ± 0.1°C at NHR, 4.1 ± 0.1°C at SHR, approx-
3.3. Current Regime at Hydrate Ridge

The current meter records of NHR from water depths of 500 m and 600 m yielded coherent but slightly different mean direction during a five month deployment (April–August 1999, Figure 8). At 600 m, there was a considerably stronger westward component in the currents than at 500 m. Currents at both depths showed rotation over ~30-day periods caused by mesoscale eddies. They also displayed strong oscillating tidal currents on diurnal timescales which result in complete reversals of flow. The tidal variations were also observed in bottom ADCP measurements at SHR at 790 m depth [Linke et al., 2001]. These energetic near-bottom currents enhance mixing, and isopycnal layers rapidly develop and propagate through the water column above HR (Figure 7c). Rough bottom topography is known to induce stronger vertical mixing with breaking internal waves [Ledwell et al., 2000] and enhanced eddy formation [Haidvogel et al., 1991]. At both 500 and 600 m depths, the northward currents changed to southerly currents in early September, possibly reflecting a dynamic response to the late-season relaxation of upwelling and the coastal jet. This reversal has been observed annually in shallower shipboard ADCP data collected between 1997–1999 by Kosro [2002].

The average current speed to transit the resultant vector between mid-June and August was 6 cm s$^{-1}$ at both depths, whereas during September the southerly current speeds increased to 10 cm s$^{-1}$ at 500 m and 13 cm s$^{-1}$ at 600 m. Averaging these current speeds for the 5-month deployment yields 0.315 km h$^{-1}$ (9 cm s$^{-1}$). This arithmetic average approximates the speed that water moves past HR, and can be used to estimate the residence time of water and thus the “clearing time” for methane introduced into the water column of the working area. A clearing time of 4 days

Figure 8. Progressive vector plots of current meter measurements at 500 m (shaded line) and 600 m (black line) depth starting 10 April 1999 (circle) and ending 1 October 1999 (squares). Interruptions in the plot, marked by double black lines, are due to short time recoveries. Average current speeds are given for the time period from 14 June to 1 August and 1 September to 1 October 1999. Reversal currents were observed in relation to the tidal cycle by the current meter measurements (enlargement).

Figure 9. Sketch of possible movement of the California Undercurrent (black arrows) at the approximate latitude of HR. Pockmark fields shown in the figure were first described by Embley et al. [2002], while the gas vent sites on the Heceta Bank were found by Collier and Lilley [1995] at depth of 90 m. Currents at HR were mostly to the north and northwest but also showed eddy formation (Figure 8). As discussed in the text, the undercurrent or mesoscale eddies produced within might possibly transport methane from the sources at Heceta Bank to the region of HR causing the observed variability in methane concentration and the isotopic character above 480 m.
(0.01 years) is calculated by dividing the length of the working area along the main SE-NW current axis by the current speed. Although the currents are highly variable, clearly, the water masses and local chemical inputs do not remain within this section of the margin environment for very long.

3.3.3. Offshore Transport of Methane and Nepheloid Layers With the California Undercurrent

As discussed above, the change in hydrographic properties, and the δ13C-CH4 composition, at around 480 m water depth represents a transition between water masses of different origin. Above this depth the water masses are transported with the California Undercurrent which flows northward hugging the continental slope, whereas the underlying NPIW is more pelagic in origin.

In July 2000 an ADCP section at 44°N (GLOBEC, http://top.coas.oregonstate.edu/~ctd/index.html; cited September 2004) detected the California Undercurrent at core depths of 150–400 m and with current speeds of 20 cm s⁻¹ along the slope of Heceta Bank. This bank is a coastal promontory to the south-southeast of HR that can deflect the undercurrent offshore as far as 100 km into the area of Hydrate Ridge as observed in 1998 by Kosro [2002] (Figure 9). Gas vents, large pockmark fields, and gassy sediments that expel methane are abundant along the shelf and slope of Heceta Bank (Figure 9). The deflected California Undercurrent transports this methane and benthic nepheloid layers offshore.

The origin of the shallower methane maxima from these slope areas is supported by the isotope ratios and by the correlation with a reduced light transmission and elevated temperatures (Figure 10). The last two are characteristics of detached benthic mixed layers originating from the upper slope. Transported offshore, these layers are called intermediate nepheloid layers (INLs) [e.g., Pak et al., 1980; Thorpe and White, 1988; Washburn et al., 1993; Moum et al., 2002]. In addition to outside methane sources, INLs often have increased CH4 concentrations and methane turn-
overs due to a higher in situ production and an elevated number of methane oxidizers [Ward and Kilpatrick, 1993]. These features explain the slight deviation toward lighter isotopic ratios in the offshore maxima compared to a source of $-28\%_{\text{PDB}}$ on one hand, and the heavy isotopic signatures in methane-depleted “older” INLs on the other hand (Figure 6c). The CH$_4$ content of the INL also varies owing to the different origins on the slope. The higher frequency of shallower CH$_4$ peaks in the year 2000 (SO-1, -3,-4,-5) compared to 1999 may be due to the frequent changes in the position of the California Undercurrent on the slope which were observed by Kosro [2002].

4. Synthesis

4.1. Controlling Features: Sources, Advection, Mixing, and Oxidation

[41] The study of the methane inputs, distributions, and isotopic compositions has identified two significant methane sources along the Oregon margin: the isotopically light CH$_4$ from vent sources along the accretionary complex and the isotopically heavier sources from the inshore slope. Within the water column, the fate of methane includes either dilution or microbial oxidation.

[42] The methane from below 480 m within the study site can be represented by mixtures of three end-members clearly distinguished by their $\delta^{13}$C-CH$_4$ compositions (Figure 11). The first end-member is the deep, isotopically light vent methane which is rapidly diluted. The second end-member represents a heavy ($-25$ to $-6\%_{\text{PDB}}$) “background” CH$_4$ component which is found offshore at low methane concentrations of 0.5 to 2 nmol L$^{-1}$. Most of the methane variations at these depths can be well represented by the mixtures of these two end-members, falling along the shaded mixing curves in Figure 11. Only samples in the 5–15 nmol L$^{-1}$ concentration range, which originate closer to the slope, lie above these binary mixtures and show an additional influence of the third isotopically heavier sources on the slope. There is enough scatter in the intermediate-to-low concentration range of the deep water $\delta^{13}$C-CH$_4$ ratios that one cannot graphically distinguish the impact of methane oxidation from binary mixing.

[43] The isotopically heavy background CH$_4$ likely is the unoxidized residual of methane introduced elsewhere along the continental margin which is advected into the vicinity of HR. This conclusion is supported by relatively short residence times of the water on the margin and methane oxidation rates of only 0.09 to 4.1% per day. These rates were determined in water samples above HR which were incubated with $^{14}$C (for methods, see de Angelis et al. [1993]). These oxidation rates equal a microbial oxidation turnover time of 0.07 to 3.2 years. At an advective “clearing time” of about 0.01 years, the methane oxidation can therefore only account for a maximum CH$_4$ decrease of 14% in the entire working area. Thus our data clearly suggest that dilution is primarily responsible for the observed decrease in CH$_4$ concentrations and that oxidation is only important on longer temporal and spatial scales. Models concerning methane oxidation at continental margins [e.g., Valentine et al., 2001; Grant and Whiticar, 2002] should therefore integrate the advection of isotopically heavy “background water.” This is especially true if look-
ing at small temporal and spatial scales. Possible additional methane sources should be discussed in any case.

4.2. Methane Inventory and Fluxes

Because of the large number of sources and the complexity of the hydrography along the Cascadia margin, it was not possible to simply calculate fluxes through constrained volumes, a method that has been successful for deep hydrothermal plumes [Kadko et al., 1990; Lavelle et al., 1998]. Instead, a first-order estimate was made by calculating the total excess methane inventories in subregions of the margin and assuming that these must be replenished over a defined clearing time estimated from measured currents. Calculation of the inventory allows us to compare the relative significance of primary sources across the margin, and the resulting flux estimates can be compared with direct estimates from the vent sites and fluxes from other marine environments.

We divided the study site into shallow/deep and inshore/offshore boxes that were well constrained by our samples (Figure 12). The north-south boundaries of the volume were defined to include the NH-1 and NH-2 sections (Figure 1) over a total depth range of 100–860 m. In order to separate the influence of upper slope sources from those related to gas hydrate-bearing sediments, the upper and lower boxes were divided at 480 m depth. The inshore slope/shelf sources were most effectively separated from the offshore accretionary complex sources including Hydrate Ridge, by a division at 125°W. In order to better reflect the fluxes from the known sources on HR (and supported by the larger number of profiles collected there), two nested sub-regions were defined around each summit. NHR and SHR sub-region inventories contained all CTD profiles between the sections SO-1 to SO-2 and SO-3 to SO-4, respectively (see Figures 1 and 12b). Inner, vent-focused boxes at NHR and SHR included all profiles within a small polygon that surrounded any profile with CH₄ concentrations greater than 100 nmol L⁻¹. These areas were approximately 200 m in diameter around SHR and 700 m in diameter around NHR which included at least three separate vent sources.

For each of these sub-regions, methane concentrations were integrated through the appropriate depth range within each CTD profile, and background concentrations were removed. The latter were estimated from the farthest offshore profiles collected over the Western Basin. These were 3.4 nmol L⁻¹ for samples shallower than 480 m and 0.6 nmol L⁻¹ for deeper samples. The resulting “excess” CH₄ inventories for each profile were gridded (Figure 12a), and these were integrated to arrive at an inventory for each sub-region. To the extent that this inventory represents “new methane” added within the control volumes and that currents continuously sweep through these volumes, we can make first-order estimates of the input flux of methane needed to support these inventories (Table 2). For the currents that “clear” the observed methane from the control volumes, we have chosen a mean speed of 9 cm s⁻¹ which was determined in the deep box at NHR (see section 3.3). This current speed is consistent with the mean of the maximum velocity at 325 m as determined from an extensive ADCP data set in summer 1995 [Pierce et al., 2000]. This data set includes cross-shore sections along the west American coast that reach from the shelf to a distance of 50 km offshore. For the depth-averaged layer from 125 to 325 m a mean of the maximum velocity was 0.18 ± 0.01 m s⁻¹. The applied clearing time might thus be slightly under-

![Figure 12. Distribution of methane sources in the study area showing (a) inventories and (b) calculated methane fluxes. For these estimates, seven boxes were considered: the total working area, one offshore and one inshore box, one NHR and SHR sub-region (gray box), and one NHR and SHR vent region (small rectangle within sub-regions). Each box consists of a shallow range of 100–480 m (upper panel in Figure 12a and shaded numbers in Figure 12b) and a deep range of 480–860 m (lower panel in Figure 12a and black numbers in Figure 12b). The deeper Eastern Basin (125°W) was set as the arbitrary boundary separating inshore waters from offshore waters. All methane inventories and methane flux estimates are also listed in Table 2.](image-url)
estimated for the shallower inshore box where the core of the California Undercurrent should be found. Further errors in this analysis result from the single inventory for each control volume in this variable system and from the rough assumption concerning methane that is transported into the control volumes through their boundaries. Therefore we assume the final estimates to represent the order of magnitude of the methane fluxes.

[47] The total methane flux over all depths between 100 and 860 m was approximately $4 \times 10^4$ mol h$^{-1}$, of which 40% came from sources within the GHSZ, i.e., at depths below 480 m. Because of the difference in box sizes, the area-normalized methane fluxes above and below the GHSZ are approximately the same ($0.5$ mmol m$^{-2}$ d$^{-1}$) (Table 2). Within the GHSZ, CH$_4$ fluxes ($0.5$ mmol m$^{-2}$ d$^{-1}$) are the same in the inshore area east of 125°W and in the offshore area where Hydrate Ridge and its gas vents are located. This suggests that strong methane venting is not restricted to Hydrate Ridge, but rather is a common occurrence along the accretionary wedge of the Cascadia Margin. In spite of the significance of shallower sources, the methane flux from the deeper gas hydrate-bearing sediments is a substantial fraction of the total budget from the margin.

[48] Within the shallower volume above the GHSZ, about 80% of the methane inventory is contained in the inshore area where the shelf/slope methane sources are located. Nevertheless, over SHR, shallow and deep methane fluxes were equivalent, although not from the same source. This emphasizes the significance of offshore transport by the California Current system to the shallower box. Many of the samples in the SHR sub-region inventories were collected in the year 2000 when transport by the California Current was stronger.

[49] The methane fluxes from the deep sub-regions of NHR and SHR each account for approximately $0.3 \times 10^8$ mol CH$_4$ h$^{-1}$. This is comparable to the CH$_4$ gas flux of $0.25 \times 10^8$ mol h$^{-1}$ estimated by Torres et al. [2002] for the strongest venting area at NHR. The order-of-magnitude difference in the area-normalized flux at the inner, vent-focused boxes at SHR and NHR is because the three vent sources included in the NHR vent box are spread over a wider area [Heeschen et al., 2003]. In contrast, all the profiles at SHR focus on the single vent site.

[50] The methane flux of 328 mmol m$^{-2}$ d$^{-1}$ from the SHR vent box primarily reflects methane gas ebullition and could be compared to flux estimates for methane transported via vent fluids into the bottom water at SHR of 100 mmol m$^{-2}$ d$^{-1}$ [Boetius et al., 2000; Torres et al., 2002]. However, this fluid flow is restricted to regions covered with bacterial mats, an area of roughly 100 m$^2$ [Tryon et al., 2002]. The area of the SHR vent box is $3 \times 10^4$ m$^2$ such that the total methane flux estimate is about 2 orders of magnitude larger than the fluid flow. This difference further emphasizes the importance of the gas phase fluxes into the water column compared to the transport of CH$_4$ via fluid flow.

[51] The methane fluxes estimated for the various sub-regions of the Cascadia Margin and HR vent sources can be compared with fluxes from other marine methane sources. Specifically, the estimates for the deep HR sub-regions ($0.3 \times 10^8$ mol h$^{-1}$, Table 2) can be compared to fluxes found at some other well-characterized gas seeps. For example, a flux of $0.4 \times 10^4$ mol h$^{-1}$ has been estimated for the Tommeliten field in the northern North Sea (120 bubble plumes, 70 m water depth, area of 6.5 km$^2$ [Hovland et al., 1993]). The methane fluxes of 15 $\times 10^4$ mol CH$_4$ h$^{-1}$ enter the water column at the Coal Point Oil seeps on the California shelf, which are the strongest natural gas seeps known [Clark et al., 2000]. Marine hydrothermal systems also release methane to the deep ocean, and a flux of $1.6 \times 10^4$ mol h$^{-1}$ has been estimated for the main Endeavour Ridge vent system [Rosenberg et al., 1988; Kadko et al., 1990]. The total deep, hydrate-bearing section of the Cascadia Margin produces 1.5 $\times 10^4$ mol CH$_4$ h$^{-1}$, and the full marine section flux is approximately $4 \times 10^4$ mol h$^{-1}$. This flux already accounts

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**Table 2. Methane Excess Inventories and Methane Fluxes of the Hydrate Ridge Area**

<table>
<thead>
<tr>
<th>Region</th>
<th>Area, km$^2$</th>
<th>Excess CH$_4$ Inventory, mol</th>
<th>Clearing Time, hours</th>
<th>Net CH$_4$ Flux, mol h$^{-1}$</th>
<th>Area-Normalized CH$_4$ Flux, mmol m$^{-2}$ d$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>100–480 m Depth</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1231</td>
<td>$2.4 \times 10^6$</td>
<td>95</td>
<td>$2.5 \times 10^4$</td>
<td>0.5</td>
</tr>
<tr>
<td>West of 125</td>
<td>472</td>
<td>$0.4 \times 10^6$</td>
<td>70</td>
<td>$0.5 \times 10^4$</td>
<td>0.3</td>
</tr>
<tr>
<td>East of 125</td>
<td>758</td>
<td>$2.0 \times 10^6$</td>
<td>88</td>
<td>$2.2 \times 10^4$</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>480–860 m Depth</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>734</td>
<td>$1.0 \times 10^6$</td>
<td>74</td>
<td>$1.4 \times 10^4$</td>
<td>0.5</td>
</tr>
<tr>
<td>West of 125</td>
<td>472</td>
<td>$0.7 \times 10^6$</td>
<td>70</td>
<td>$1.0 \times 10^4$</td>
<td>0.5</td>
</tr>
<tr>
<td>East of 125</td>
<td>261</td>
<td>$0.3 \times 10^6$</td>
<td>56</td>
<td>$0.5 \times 10^4$</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>100–480 m Depth</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NHR subregion</td>
<td>47</td>
<td>$1.3 \times 10^4$</td>
<td>22</td>
<td>$0.6 \times 10^3$</td>
<td>0.3</td>
</tr>
<tr>
<td>SHR subregion</td>
<td>37</td>
<td>$5.8 \times 10^4$</td>
<td>22</td>
<td>$2.6 \times 10^3$</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>480–860 m Depth</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NHR subregion</td>
<td>47</td>
<td>$8.3 \times 10^4$</td>
<td>22</td>
<td>$3.8 \times 10^3$</td>
<td>1.9</td>
</tr>
<tr>
<td>SHR subregion</td>
<td>37</td>
<td>$5.7 \times 10^4$</td>
<td>22</td>
<td>$2.6 \times 10^3$</td>
<td>1.7</td>
</tr>
<tr>
<td>NHR vent box</td>
<td>0.376</td>
<td>1042</td>
<td>2</td>
<td>532</td>
<td>34</td>
</tr>
<tr>
<td>SHR vent box</td>
<td>0.029</td>
<td>218</td>
<td>0.5</td>
<td>400</td>
<td>328</td>
</tr>
</tbody>
</table>

*Changes in clearing times result from different box geometries.*
for about 0.01–0.7% of the present estimates for global natural methane emissions from marginal seabeds to the hydrosphere and atmosphere [Howland et al., 1993; Judd, 2000; Judd et al., 2002; Kvenvolden et al., 2001]. Thus our results support recent statements about the importance of the continental margins for the methane cycle [e.g., Judd et al., 2002].

5. Conclusions

[52] The multiyear survey of the methane distributions in the water column at Hydrate Ridge revealed a complex system which is controlled by numerous sources. In the gas hydrate stability zone, the main fluxes reflect methane gas phase input. The timing of this methane gas eubullition is different between Southern and Northern Hydrate Ridge. The isotope ratio of water column methane is close to the hydrate stability zone, the main fluxes reflect methane gas transport of isotopically heavier methane from various sources. The resulting methane inventory is determined by the offshore transport of isotopically heavier methane from various sources on the upper slope and shelf by the energetic California Current system. The isotopic ratios at these depths vary between −56 to −28% PDB with a peak at about −30% PDB.

[53] The California Current system, with frequent mesoscale eddies and current variability over a range of time-scales (tidal to interannual), results in the rapid mixing of methane away from these sources. The resulting methane found along the margin can be understood in terms of the mixing of three end-members, which can be distinguished by their δ13C-CH4 signatures: (1) a deep, isotopically light source at HR; (2) a shallow thermogenic source near −30% PDB; and (3) a very heavy, low-methane “background” component ranging up to −6% PDB. The heavy isotope ratios for the background methane and the relatively large scatter in the isotopic values among the mixing curves at low concentrations are evidence for isotope fractionation driven by methane oxidation. However, the “clearing time” of the margin section, estimated from current observations, is much less than the time needed to oxidize the methane to background levels. We did not observe the direct ascent of methane gas to the surface.

[54] Calculations showed that the methane flux originating on the upper continental slope and from shelf sources is twice as high (2 × 104 mol m⁻² h⁻¹) as the flux from the hydrate-related sources below 480 m. However, due to the smaller size of the deep water region, methane flux per area (0.5 mmol m⁻² d⁻¹) is about the same in the water column above and below the hydrate stability zone boundary. In conclusion, the methane flux from accretionary wedges must be considered when oceanic methane budgets are assessed.

[55] Acknowledgments. We greatly appreciate the support at sea by the masters and crews of R/V Ron Brown, R/V New Horizon, R/V Atlantis, R/V Sonne, and R/V Wecoma. We thank Julie Arrington, Barbara Bock, Magnus Ek, Nick Grant, Ulrich Kunz, Hinrich Schaefer, and Andrea Voorhees for their indispensable help at sea. Special thanks go to Michael Whiticar, Paul Eby, Hinrich Schaefer, and Nick Grant for their support at SEOS. For helpful comments on the manuscript we thank Robin Keir, Marta Torres, Sarah Hoffman, and Wolfgang Hukriede. Financial support for this work was granted by the National Science Foundation (OCE-9731157; OCE-9811471 and OCE-973123) and the German Federal Ministry of Education and Research (BMBF, Fkz 03G0143A and 03G014AKA). This is publication GEOTECH-40 of the program GEOTECHNOLOGIEN of the BMBF and the Deutsche Forschungsgemeinschaft (DFG).

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Figure 5
Figure 5. Methane concentrations along regional transects shown in Figure 1. (a, b) SO-1 and SO-2, showing cross sections from NE-SW transects in the area of NHR; (c, d) SO-3 and SO-4, showing cross sections from NE-SW near SHR. (e, f, g) NH-1, NH-2, and SO-5, showing cross sections from the upper continental slope to the HR areas; (h) WA-1, showing a cross section of the upper slope only. Note that there is considerable variation in the latitudinal and longitudinal scales of the figures. The black dots indicate all samples taken, and station numbers are annotated in the top of each figure. The density distribution is shown by the annotated white (red) contours.