Is methane venting at the seafloor recorded by δ^{13}C of benthic foraminifera shells?

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[1] The isotopic composition of the dissolved inorganic carbon (DIC) collected at sites of active methane discharge on Hydrate Ridge, Oregon, reveals anaerobic methane oxidation mediated by bacteria, with δ^{13}C$_{DIC}$ reaching values as low as −48‰ in the upper 4 cm of the sediment. In spite of the high sulfide levels in the discharging fluids, living specimens of the benthic foraminifera *Uvigerina peregrina* are abundant in the vents, probably owing to the rich bacterial food source. Although pore water δ^{13}C$_{DIC}$ is extremely low (−6 to −48‰), the δ^{13}C values of living (Rose Bengal stained) foraminifera shells collected from active methane seeps are not significantly lower than those observed in nonventing pelagic sediments, and are within the range expected from local organic matter decomposition (0 to −4‰). The apparent δ^{13}C disequilibrium between biogenic calcite and DIC suggests that at seep localities, foraminifera calcify mostly during periods when there is little methane discharge or during intermittent episodes of seawater flow into the sediments. The isotopic composition and Mg/Ca ratios of fossil (unstained) foraminifera recovered at carbonate-rich sites on the northern Hydrate Ridge reveals overprinting of the biogenic record by inorganic calcite with high Mg/Ca and anomalously low δ^{13}C values. Thus overprinting of the original isotopic composition of foraminifera by overgrowths or recrystallization at or below the sediment surface, rather than primary calcification in contact with ^{13}C depleted DIC, can explain extreme ^{13}C depletion observed in fossil foraminifera recovered from sites of active methane discharge. *INDEX TERMS:* 1615 Global Change: Biogeochemical processes (4805); 4804 Oceanography: Biological and Chemical: Benthic processes/benthos; 1040 Geochemistry: Isotopic composition/chemistry; 4267 Oceanography: General: Paleoceanography; *KEYWORDS:* methane hydrates, gas seeps, foraminifera, carbon isotopes

1. Introduction

[2] Modern release of methane from gas hydrate-bearing sediments has been reported in the Gulf of Mexico, Sea of Okhotsk, Eel River Basin, and the Oregon margin [e.g., *MacDonald et al.*, 1994; *Zonenshayn et al.*, 1987; *Field and Kvenvolden*, 1987; *Kennicutt et al.*, 1989; *Suess et al.*, 1999, 2001]. Natural gas seeps not related to gas hydrate formation may also contribute methane to bottom seawater [e.g., *Hovland et al.*, 1993]. Although release of methane from these sources to the ocean and atmosphere is relatively small at present [*Kvenvolden et al.*, 2001], it has been argued that seafloor methane fluxes have varied significantly in the past [e.g., *Dickens et al.*, 1995; *Kennett et al.*, 2000].

[3] The locations of currently active methane discharge constitute key environments in which to assess the influence of methane flux on the geochemistry and faunal characteristics of benthic foraminiferal assemblages. Because the δ^{13}C of foraminifera has been proposed as a paleoproxy for the location and degree of methane venting [e.g., *Rathburn et al.*, 2000], it is important to understand the population and isotopic response of living benthic communities to methane release.

[4] The documented foraminiferal assemblages in surface sediments associated with modern methane discharge sites do not appear to be endemic to cold seeps; rather, they are representative of the background meiofauna [e.g., *Rathburn et al.*, 2000; *Sen Gupta et al.*, 1997]. These observations contrast with observed faunal changes in the geologic record of Santa Barbara Basin, which have been interpreted as evidence for episodes of high methane concentration in the bottom waters of this basin during the late Quaternary [*Cannariato et al.*, 1999]. Even more uncertain is the isotopic response of the δ^{13}C of foraminifera associated with episodic release of ^{13}C-depleted methane at the seafloor. *Rathburn et al.* [2000] postulate that the isotopic composition of living specimens collected at the Eel River basin reflect local discharge and oxidation of methane. However, there are no δ^{13}C measurements of the dissolved inorganic carbon (DIC) in the pore water at these sites. Thus we cannot evaluate whether the isotopic composition of the foraminifera collected from seeps at Eel River basin indeed reflects equilibrium with a DIC pool that had been modified

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by methane oxidation. *Stott et al.* [2002] argued that in the Santa Barbara Basin the $\delta^{13}C_{DIC}$ in the upper 2 cm of the sediment is controlled exclusively by local oxidation of organic carbon, even though there is evidence for methane oxidation near the sediment water interface at these sites. The authors suggest that apparent δ^{13}C excursions in late Pleistocene sediments in this basin may represent changes in carbon rain and oxidation rather than release of methane to the water column through the destabilization of methane hydrates [*Kennett et al.*, 2000].

[5] Here we report on isotopic and geochemical data from near-surface sediments at Hydrate Ridge, a site of known methane discharge [*Suess et al.*, 1999, 2001], and document rates of anaerobic methane oxidation and depletion of the $\delta^{13}C_{DIC}$. We recovered abundant living specimens of *U. peregrina* from the highly reducing seep sites and found significant disequilibrium between δ^{13}C of biogenic calcite and $\delta^{13}C_{DIC}$. We infer that foraminifera calcify episodically during periods of low methane discharge and thus do not record the full isotopic depletion of pore waters. In contrast to the living shells, fossil foraminifera record large δ^{13}C depletions that must be linked in some way to a methane source. Isotopic and Mg/Ca measurements of fossil foraminifera shells from Hydrate Ridge reveal significant overprinting of the primary biogenic isotopic signal at sites of inorganic carbonate precipitation. Such secondary calcification, which occurs at the sediment surface or within the sediment column, may account for substantial δ^{13}C depletion observed in fossil foraminifera in venting regions.

2. Geologic Setting

[6] Hydrate Ridge is a 25 km long and 15 km wide ridge in the Cascadia margin accretionary complex, with northern and southern summits at water depths of 600 and 785 m, respectively (Figure 1). The ridge is capped by methane hydrate, as indicated by a strong, widespread bottom-simulating reflector (BSR) [*MacKay et al.*, 1994; *Trehu et al.*, 1999] and by the recovery of large quantities of methane hydrate [*Suess et al.*, 1999, 2001]. The northern summit represents a more mature stage in the evolution of the ridge as evidenced by extensive carbonate pavement, chemoherm development, and upward deflections of the BSR at a thrust fault. In contrast, the southern Hydrate Ridge region is less evolved, exhibiting only limited and localized accumulation of inorganic carbonate and minor departures in BSR depth from that predicted by the seawater/gas hydrate phase boundary and observed in seismic data [*Trehu et al.*, 1999, 2002].

[7] *Torres et al.* [2002] identified three distinct active fluid regimes at Hydrate Ridge. In the first province, methane gas ebullition occurs through localized channels in which gas velocities reach 1 cm s^{-1}. Underwater observations (ROPOS and *Alvin*) indicate that such gas bubbling is episodic, possibly with a tidal periodicity [*Torres et al.*, 2002]. In the second province, extensive bacterial mats drape sediments capped with methane hydrate crusts. Here fluid typically flows out of the sediments at rates ranging from 10 to 250 cm yr^{-1}. Sites colonized by

vesicomyid clams represent the third province. At these sites, *Tryon et al.* [2002] document an intermittent net flow of seawater into the sediments, at rates that are typically less than 10 cm yr^{-1}.

3. Methods

[8] The extensive carbonate crusts at the northern summit of Hydrate Ridge precluded coring of sediments in the vicinity of methane gas discharge (Figure 1). Here a sediment sample was collected (station R455) using the ROPOS grab. Bacterial mat sites (stations 5AD and 37AD) and clam-colonized areas (station 8AD) on Hydrate Ridge south were sampled by *Alvin* push cores. Background (i.e., nonventing) stations were sampled with a multicore at a mud volcano on the flank of the ridge (proximal mud at 13MC) and at a ponded basin north of Hydrate Ridge (distal mud at 22MC). In addition, we use data of *Suess and Whiticar* [1989] from stations 2 and 27, which are located on the first accretionary ridge, and from stations 4 and 26, which are west of the deformation front. As a control site we used data from core W8709A-13PC, recovered from northeast Pacific hemipelagic sediments on Gorda Ridge, well away from any methane vents. Station locations are in Table 1. All stations except W8709A-13P (which is off the map) are illustrated in Figure 1.

[9] Pore waters were extracted from the cores by sectioning sediment slices and centrifuging (7000 to 10,000 rpm) at in situ temperatures (4°C) under a nitrogen atmosphere within 2 hours of core retrieval. Pore water samples were filtered (0.45 μm filter), and the fluids were subsampled through a three-way stopcock into containers appropriate for the various analytes. The H$_2$S and total DIC content of the fluids were measured within 24 hours of recovery using spectrophotometric and coulometric techniques, respectively [*Torres et al.*, 1999]. We analyzed the isotopic composition of the dissolved inorganic carbon in subsamples preserved with HgCl$_2$ following the procedures described by *Ortiz et al.* [2000]. Analytical precision of δ^{13}C in these analyses is ±0.04‰ (1 standard deviation) based on replicate analyses of an internal laboratory standard. Dissolved calcium and magnesium in the pore fluids were analyzed by atomic emission spectrometry (AES), and the chloride and sulfate concentrations were measured by ion chromatography at Oregon State University. Analytical precision of these measurements is 2% of measured values based on replicate measurements of standard seawater. Sediment samples collected for the determination of methane oxidation rates were incubated on board after addition of ^{14}CH$_4$. Subsequently, ^{14}CO$_2$ and ^{14}C-cell carbon production were measured using liquid scintillation techniques at Humboldt State University.

[10] At each cored site an adjacent core (within 1 m) was collected for analyses of the abundance and isotopic composition of foraminifera. These cores were also extruded at sea and sliced at 0.5 and 1.0 cm intervals. Samples were stained with Rose Bengal in buffered formalin [*McCorkle et al.*, 1990]. After sieving at 125 μm, living (stained, protoplasm-full) and dead (unstained) shells of foraminifera were identified under microscopy, cleaned ultrasonically, dried,
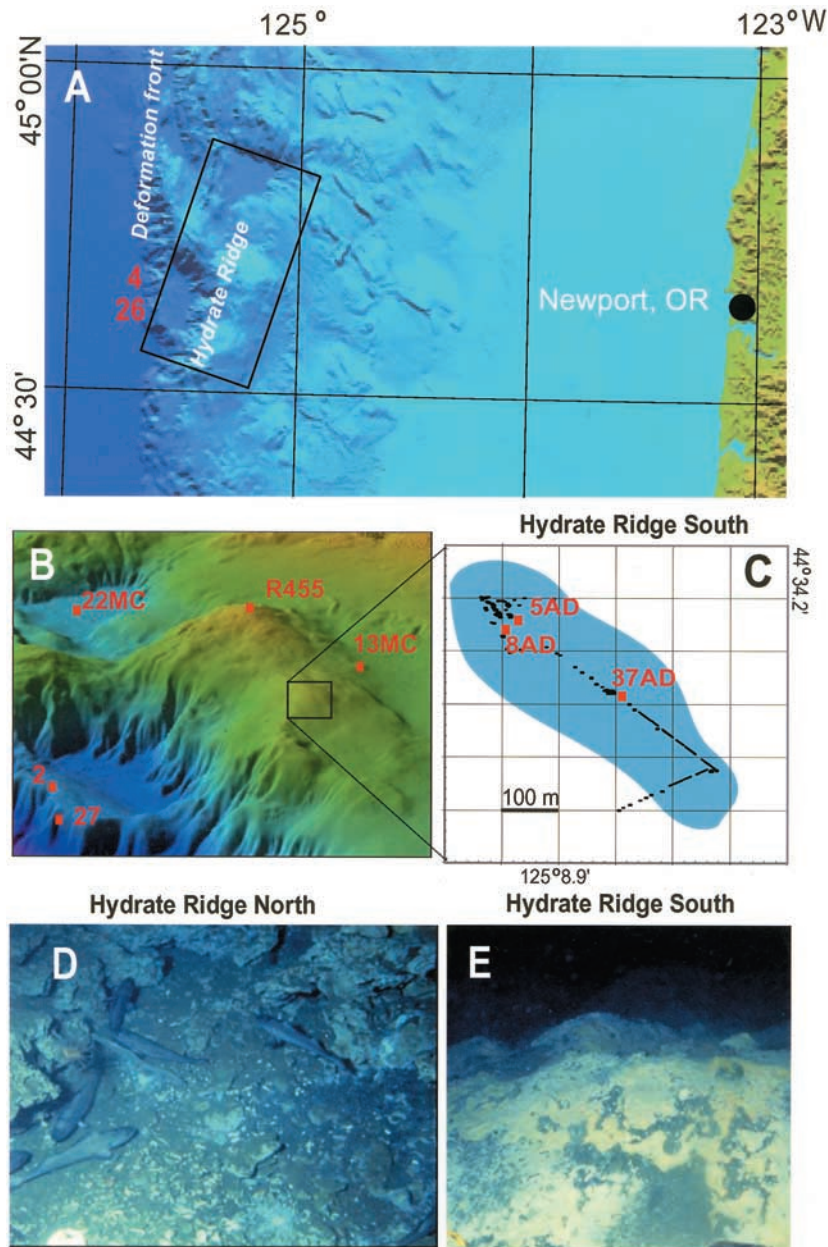
Figure 1. (a) Location of Hydrate Ridge on the Cascadia accretionary margin. Stations 4 and 26 denote cores W8306-26C and A8408-4 recovered west of the deformation front [from *Suess and Whiticar*, 1989]. Inset box shows the location of Figure 1b. (b) Detailed bathymetry of Hydrate Ridge (oblique view) illustrating the location of samples R-455, 13MC, and 22MC, which correspond to TFX98-8-R455, AT9906-13MC, and AT9906-22MC, respectively, and are listed in Table 1. Inset box shows location of Figure 1c. (c) Location of push core samples collected during *Alvin* dives on Hydrate Ridge South: 5AD and 37AD are cores A99-5AD3421 and A99-37AD3430, respectively, collected on bacterial mat sites; 8 AD is core A99-8AD3422 collected on a clam site. (d) Photograph illustrating the carbonate carapace that covers the northern summit of Hydrate Ridge, near R455. (e) Photograph of southern Hydrate Ridge, characterized by undulating topography of soft sediments covered by extensive bacterial mat fields (near sites 5AD and 37AD).

and analyzed for $\delta^{13}C$ and $\delta^{13}O$ in the calcite using a Finnigan/MAT 251 mass spectrometer at Oregon State University, with a precision of ±0.03‰ and 0.07‰, respectively. To determine the Mg/Ca ratio in subsamples of

foraminifera, hand-picked shells were sonicated and rinsed multiple times in double-deionized water. They were subsequently subjected to sequential cleaning steps in a "flowthrough" column. The clean shells were dissolved in weak

Table 1. Site Locations and Cores Used in This Study[a]

Site description	Core	Site	Latitude	Longitude	Depth, m
Bacterial mats					
	A99-5AD3421-1	HRS	44°34.234′N	125°08.900′W	780
	A99-5AD3421-5		44°34.234′N	125°08.900′W	
	A99-37AD3430-10	HRS	44°34.198′N	125°08.820′W	780
Clam field	A99-8AD3422-6	HRS	44°34.223′N	125°08.905′W	780
	TFX98-8-R455-3	HRN	44°40.203′N	125°05.867′W	590
Background sediments					
	AT9906-13MC-8	proximal mud	44°35.200′N	125°07.000′W	912
	AT9906-22MC5	distal mud	44°50.399′N	125°08.400′W	1826
Abyssal plain					
	W8306-26C	west of DF	44°39.00′N	125°20.50′W	2795
	A8408-4		44°40.00′N	125°21.60′W	2860
Control					
	W8709A-13PC	NE Pacific	42°07.0′N	125°45.0′W	2712

[a]Cores designated A99- are *Alvin* push cores; those designated AT9906 are multicores, and TFX indicates a video-steered surface sediment grab sample. HRS and HRN are Hydrate Ridge south and Hydrate Ridge north, respectively. Sites on the abyssal plain, west of the deformation front (DF) are from *Suess and Whiticar* [1989].

acid and analyzed in a VG Axiom high-resolution ICP-MS, as described by *Haley and Klinkhammer* [2002].

4. Results and Discussion
4.1. Fluid Flow Regime and Pore Water Data

[11] Hydrogen sulfide levels in the pore fluids decreased sequentially from the sites containing bacterial mats, to those of clam colonies (Figure 2). H_2S was below the detection limit at the background stations. *Sahling et al.* [2002] described the macrofaunal community structure on these active seeps and concluded that the sulfide flux controls the distribution of chemoautothrophic fauna on Hydrate Ridge. Bacterial mats dominate sites where the H_2S flux is >60 mmol m^{-2} day^{-1}, whereas clam communities colonize sites in which the H_2S flux ranges from 0.13 to 18 mmol m^{-2} day^{-1}. Nonventing sites with no detectable H_2S have no chemoautotrophic fauna [*Sahling et al.*, 2002]. Similarly, methane fluxes out of mat-covered sites (10 to 100 mmol m^{-2} day^{-1}) are orders of magnitude higher than those measured at clam sites (0 to 1 mmol m^{-2} day^{-1}) [*Torres et al.*, 2002]. The pore fluid profiles vary significantly over very small spatial scales (Figure 2). These data, as well as those from benthic chambers [*Torres et al.*, 2002; *Tryon et al.*, 1999], reflect a highly localized network of fluid pathways and episodic advection with variable flow rates and directions [*Tryon et al.*, 2002; *Torres et al.*, 2002].

[12] Elevated DIC values (relative to ambient seawater) in cores recovered from sites of active fluid discharge correspond to decreased dissolved sulfate because sulfate is consumed by bacterial oxidation of organic carbon and methane. The DIC source can be inferred from its isotopic composition by using a three-component mixing model of seawater, organic carbon, and methane, each with different δ^{13}C values [*Suess and Whiticar*, 1989]. On Hydrate Ridge, δ^{13}C$_{DIC}$ of pore water samples collected at bacterial mat sites reaches −40‰ in the upper 4 cm. In core 8AD, from a clam colony, the δ^{13}C$_{DIC}$ reaches −48‰ at 12 cm below seafloor. Clearly, such low δ^{13}C values measured in these stations affected by fluid venting are more negative than the minimum values of −22‰ for particulate organic carbon in this area [*Hedges and Mann*, 1979; *Hedges and Van Geen*, 1982]. Thus the δ^{13}C$_{DIC}$ data from Hydrate Ridge undoubtedly reflect oxidation of methane within the near-surface sediments, consistent with the very large rates of ambient methane oxidation rates measured in the upper 2 cm of the sediment (Figures 2 and 3). Background stations have relatively little ^{13}C depletion relative to bottom water (<0.05‰), as expected from pore fluids in near surface sediments where there is no significant methane oxidation [*McCorkle et al.*, 1997]. The ambient methane oxidation rate at these background sites (<1 nmol cm^{-3} day^{-1} at station 22MC) is orders of magnitude smaller than those measured at bacterial mat sites, which on Hydrate Ridge reach 700 nmol cm^{-3} day^{-1} (Figure 2).

4.2. Foraminiferal Response
4.2.1. Vent Populations and Food Sources

[13] The foraminifera species assemblages present at active seep sites on Hydrate Ridge are similar to those observed at background stations, with *Uvigerina peregrina* representing 50 to 90% of the living and dead shells. Elsewhere, the population distribution of foraminifera taxa at active seeps in Eel River basin and Gulf of Mexico is similar to that of nearby nonseep areas [*Rathburn et al.*, 2000; *Sen Gupta et al.*, 2001]. In Monterey Bay sediments, one species (*Spiroplectammina biformis*) was restricted to the seep environment [*Bernhard et al.*, 2001], but *S. biformis* is also found in many nonseep areas, and thus its presence cannot be considered as unique to seeps [*Bernhard et al.*, 2001].

[14] On Hydrate Ridge the standing stock of living benthic foraminifera increases at sites with higher methane concentrations, including extreme sites hosting vesicomyid clams or bacterial mats (Figure 2). At these sites the density of stained specimens varied from 1.1 to 4.2 shells cm^{-3}, whereas 0.6 to 1.6 shells cm^{-3} were present in background stations. This population increase near the seeps is surprising because the H_2S present at vent sites should be poisonous to foraminifera. For example, on the California margin, *U. peregrina* is one of the dominant benthic foraminiferal species in suboxic ([O_2] = 0.3 to 1.5 mL/L) environments; however, most of the benthic foraminifera are known to die during extended (>weeks) episodes of bottom
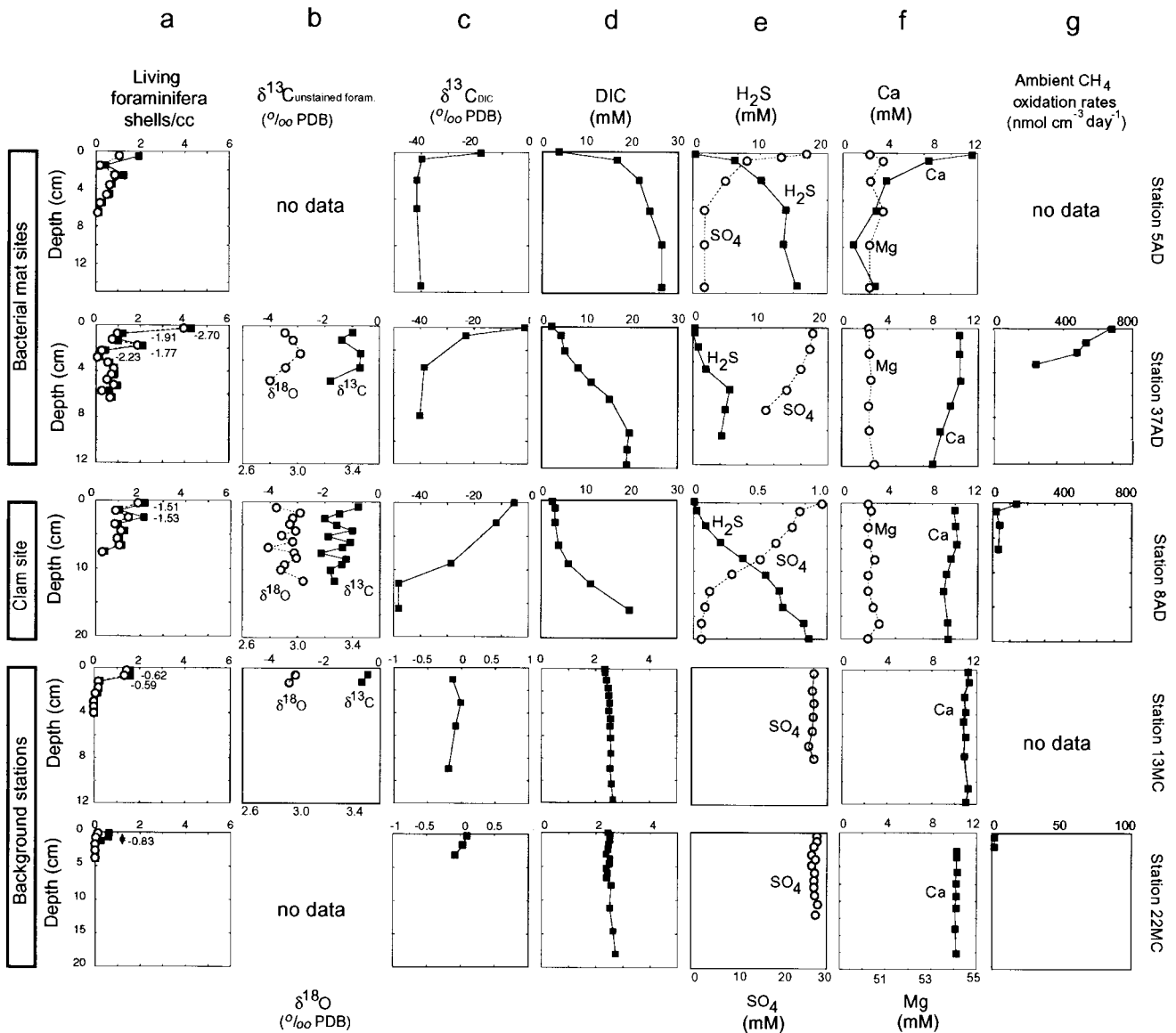
Figure 2. (a) downcore distributions of living cell abundance (*Uvigerina peregrina*, open circles; total cell count, closed squares) in cores from Hydrate Ridge. The δ^{13}C of calcite from living (stained) *U. peregrina* specimens is given next to the shell abundance in the left panels. (b) δ^{13}C and δ^{18}O of *U. peregrina* in unstained (fossil) shells. (c) δ^{13}C of DIC. (d–f) Concentration of dissolved species in the pore fluids. (g) Methane oxidation rates. Data illustrates variations in cores collected at bacterial mat sites (cores A99-5AD3421 and A99-37AD3430), clam colonies (core A99-8AD3422), and background sites (AT9906-13MC and AT9906-22MC). Note scale differences. Specific methane oxidation rates (equal to the fraction of available methane removed per unit time) are highest at clam sites; however, ambient methane oxidation rates (specific oxidation rates times methane content) are highest at bacterial mat sites owing to the higher methane concentration at these sites. The living benthic foraminifera in cores from seep sites do not show the extreme δ^{13}C depletion expected from the δ^{13}C values measured in the DIC. The location of the sites is shown in Figure 1.

water anoxia [*Bernhard and Reimers*, 1991; *Kouwenhoven et al.*, 1999]. Nevertheless, at other localities of methane discharge, populations of benthic foraminifera also increase near the active fluid discharge sites (e.g., Eel River seeps; *Rathbun et al.* [2000]). Consistent with these observations, we suggest that foraminifera are attracted to rich bacterial food sources at methane seeps. They clearly tolerate the

highly reducing seep environments, and this implies a biological strategy to utilize the abundant bacterial food while avoiding poisonous H$_2$S.

[15] Dense aggregates of a structured bacterial-archaea consortium have been identified in cores from active seeps on Hydrate Ridge, which apparently mediate the anaerobic oxidation of methane [*Boetius et al.*, 2000]. These organ-
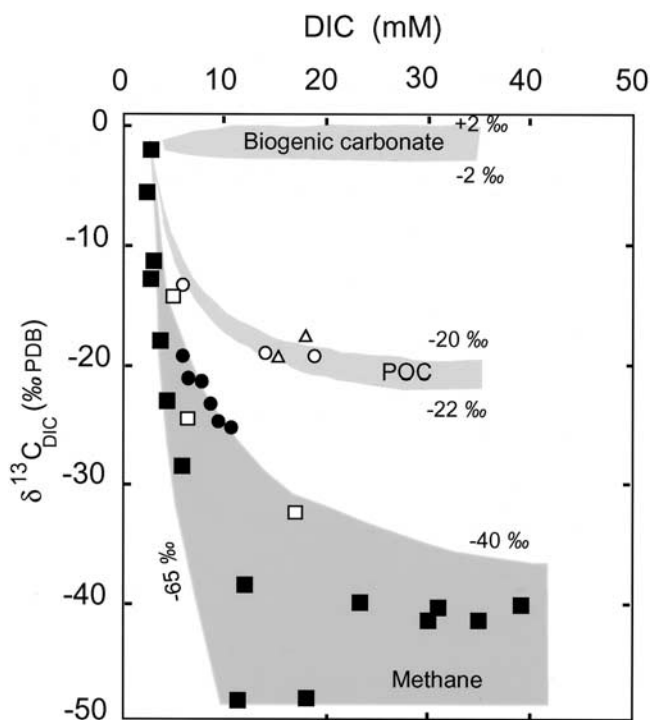
Figure 3. Total dissolved inorganic carbon (DIC) versus $\delta^{13}C_{DIC}$ of pore fluids in samples from Hydrate Ridge (closed squares). Data from *Suess and Whiticar* [1989] collected on the abyssal plain (open triangles, station 04; open circles, station 26) and on methane seeps located on the First Ridge of this accretionary prism (open squares, station 2; closed circles, station 27) are included for comparison. The gray fields depict a mixing model of three possible sources for the total DIC pool: dissolution of biogenic calcium carbonate (δ^{13}C = −2 to +2‰), decomposition of sedimentary organic carbon (POC, δ^{13}C = −20 to −22‰); and anaerobic oxidation of methane (δ^{13}C < −40‰). This latter source generates extremely low δ^{13}C in DIC, depending on the isotopic composition of the methane source. In samples from the abyssal plain (open triangles and circles) the bulk of the DIC is generated by organic carbon oxidation. In samples from Hydrate Ridge, methane oxidation is the principal mechanism generating the observed DIC concentrations.

isms constitute a rich food source for benthic foraminifera. Although no analyses of foraminiferal protoplasm were conducted on Hydrate Ridge samples, *Bernhard and Reimers* [1991] observed remains of the bacterium *Beggiatoa* in vacuoles within the protoplasm of the benthic foraminifera *Chilostomella ovoidea* collected in the Santa Barbara Basin. These observations support our speculation that the enhanced bacterial biomass associated with seeps on Hydrate Ridge may indeed play a role in supporting the population of *Uvigerina* at these sites.

4.2.2. Isotopic Response

[16] The calcite tests of living *U. peregrina* specimens at the seep sites have lower δ^{13}C (−2.7‰) than those at nonseep sites (−0.83‰). However, no δ^{13}C values were

found in living foraminifera as low as would be predicted by equilibrium with the pore fluids, in which $\delta^{13}C_{DIC}$ ranges from −6 to −48‰ (Figure 2). Although it remains uncertain where and when benthic foraminifera secrete $CaCO_3$, data collected from a variety of nonseep regions document calcification consistent with the pore water environmental microhabitats. For example, *McCorkle et al.* [1990] showed that the δ^{13}C values of infaunal taxa are consistently lower than those of epifaunal taxa and that the differences between foraminiferal carbonate often correlate with variations in the chemistry of sediment pore waters.

[17] Taxon-specific "vital" effects also seem to influence test composition; however, the δ^{13}C deviations predicted from pore water compositions are generally less than 3‰ and have been explained by specific life and calcification patterns. For example, *Mackensen et al.* [2000] suggested that the observed δ^{13}C values in the epibenthic *Lobatula lobatula* off northeast Greenland, which are 0.4‰ higher than the δ^{13}C of ambient bottom water indicates that this species calcifies before the ice-free season, when bottom water δ^{13}C is higher than at the time of sampling.

[18] In pelagic and hemipelagic settings, various species of the genus *Uvigerina* are known to occupy a near-interface infaunal habitat [*Corliss and Emerson*, 1990], where they record the δ^{13}C of the pore water in the top few millimeters of the sediment [*McCorkle et al.*, 1990]. The deep infaunal species *Globulimina affinis* from a variety of sites in the Pacific and Atlantic Oceans also records the pore water depletion of δ^{13}C [*McCorkle et al.*, 1990]. These, as well as recent data from the Santa Barbara basin [*Berelson and Stott*, 2003], strongly suggest calcification close to equilibrium with the ambient pore water. Variations in this pattern might reflect the organisms life cycles and mobility within the sediments.

[19] *Uvigerina* shells collected at methane seeps on Hydrate Ridge have much smaller variations in δ^{13}C of calcite than the measured $\delta^{13}C_{DIC}$ in the pore fluids (Figure 4). The magnitude of the disequilibrium is puzzling but could be explained if foraminifera calcify intermittently when venting is weak or absent or during episodes of downward fluid flow. The methane discharge on Hydrate Ridge is indeed highly episodic [*Torres et al.*, 2002]; thus it is possible that during periods of low discharge, bottom water relatively rich in oxygen and in ^{13}C could penetrate into the uppermost sediment layers. The magnitude of the disequilibria observed in samples from Hydrate Ridge suggests that foraminifera either stop calcifying when the flow of ^{13}C-depleted anoxic fluids is high (perhaps due to the presence of poisonous H_2S and lack of oxygen) or migrate to locations (such as the sediment-water interface, or nearby microhabitats) that contain more oxygen and less H_2S. Within these refugia the DIC would be less depleted in δ^{13}C. The high bacterial population fueled by methane oxidation, coupled with episodic irrigation of the otherwise extremely reducing sediments, seems to provide a favorable habitat for *Uvigerina* populations in spite of the occurrence of short periods of extreme anoxia driven by intermittent discharge of H_2S bearing fluids.

[20] This idea of intermittent calcification would also explain how benthic foraminifera survive episodes of very
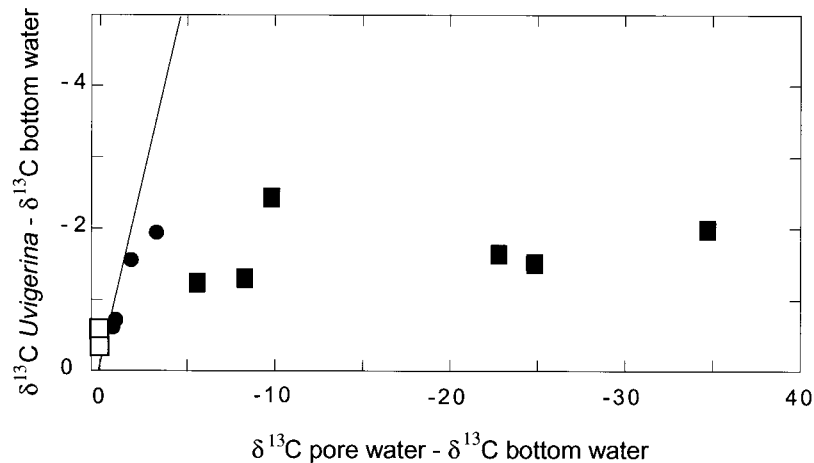
Figure 4. Relationship between the carbon isotopic composition of living (stained) *Uvigerina spp.* and that of the DIC in pore waters, reported as the difference from bottom water δ^{13}C$_{DIC}$ values. Solid circles [*McCorkle et al.*, 1990] represent specimens recovered from continental margin environments in the Atlantic and Pacific oceans. Open squares (this study) are for samples collected at nonseep sites; solid squares are for samples collected at sites of active methane venting. Divergence from the 1:1 line shows that foraminifera do not reflect the extent of the ^{13}C depletion in the pore waters and suggest that calcification occurs when venting is weak or bottom seawater irrigates the sediments.

low oxygen level. Living foraminifera recovered from sediments of the central California continental slope indicate that individuals may survive in anoxic sediments for short periods of time [*Bernhard*, 1992]. During episodes of low oxygen, foraminifera decrease their metabolic activities [*Karl*, 1980] and such temporary dormancy would also likely stop calcification until favorable conditions return. This life strategy is somewhat analogous to that proposed under more typical food-limited situations, in which benthic foraminifera wait in dormancy until an appropriate food supply, such as episodic rain of organic debris following a surface ocean bloom, becomes available [*Altenbach*, 1992; *Nees and Struck*, 1999]. This similarity, based on the ability to wait for favorable conditions, may explain the observations that species assemblages observed in seeps are essentially identical to those in neighboring nonseep environments and that there is a significant isotopic disequilibrium between the δ^{13}C of biogenic calcite and DIC at the methane discharge sites.

4.3. Overprinting of the Primary Biogenic Signal

[21] We have found limited ^{13}C depletion in shells of living benthic foraminifera around methane vents and have inferred that foraminifera are dormant and do not calcify during short intervals when conditions are hostile (i.e., anoxic intervals). However, larger isotopic depletion of fossil foraminifera shells is observed in the sediment record [e.g., *Wefer et al.*, 1994; *Rathburn et al.*, 2000]. How can this occur? One possibility is addition or replacement of calcite after the death of the foraminifera. To test this hypothesis, we extracted, cleaned, and analyzed dead (unstained) benthic and planktic foraminiferal shells and "pellets" composed of fine-grained authigenic carbonate from mud recovered within the area of active carbonate formation (see Figure 1) at the northern summit of Hydrate Ridge

(station R455). Values of δ^{13}C in the fossil shells of *U. peregrina* collected from this area are significantly lower (δ^{13}C < -6‰) than the isotopic composition measured in living and dead *Uvigerina* specimens (δ^{13}C from -0.6 to -2.7‰) recovered from the southern summit of the Ridge, where carbonate formation is minimal.

[22] Anomalously low δ^{13}C values were also measured in two planktic species, *Neogloboquadrina pachyderma* (sinistral) and *Globigerina bulloides*, from station R455 (Table 2). These planktic foraminifera grow in near-surface waters and calcify their shells near equilibrium with the seawater DIC, which in this area has a δ^{13}C of 0.5 ± 0.3‰ [*Ortiz et al.*, 1997]. For example, sinistral *N. pachyderma* collected in plankton tows at 42°N and 125.5°W have an average δ^{13}C value of -0.04 ± 0.03‰ [*Ortiz et al.*, 1996]. Thus the low δ^{13}C values measured in the shells of planktic species recovered from sediments in seep areas of intensive inorganic carbonate deposition (-7.2 to -9.8‰) must reflect postdepositional contamination, which was not removed by vigorous ultrasonic cleaning. An amorphous fine-grained carbonate sample collected at the same site as the foraminifera has δ^{13}C of -51‰, further establishing local formation of authigenic carbonates driven by methane oxidation.

[23] The calcite overgrowths or recrystallization responsible for the extremely low δ^{13}C values in both benthic and planktic foraminifera shells were not apparent by microscopic examination of the samples, nor were they removed by vigorous ultrasonic cleaning. A similar pattern of carbonate overgrowth was postulated to explain the isotopic data in foraminifera from active seeps in the Gulf of Mexico [*Sen Gupta et al.*, 2001]. Both planktic and benthic foraminifera at this site show δ^{13}C depletions that correlate with the amount of inorganic carbonate present in the sediments [*Aharon et al.*, 2001]. Furthermore, the δ^{13}C values of fossil foraminifera from cold seeps in the Eel River basin are

Table 2. Isotopic Composition and Mg/Ca Ratios of Foraminifera From Hydrate Ridge (Upper 2 cm) and Control Stations in the Northeast Pacific

ID	Sample Location	δ^{18}O, ‰ PDB	δ^{13}C, ‰ PDB	Mg/Ca, mmol/mol
	C. Wuellerstorfi (Epibenthic)			
1	northeast Pacific (live) core at 35°28′N, 122°21′W	2.4 to 2.6[a]	−0.20 to −0.01[a]	1.1 to 2.1 (estimated)[b]
2	Hydrate Ridge North (dead) grab R 455	2.28	−1.26	3 to 7 (n = 2)
	U. Peregrina (Endobenthic)			
3	northeast Pacific (live) core at 35°28′N, 122°21′W	2.6 to 3.3[a]	−1.2 to −0.5[a]	0.5 to 2.0 (estimated)[c]
4	background 1 (live) core 22 MC	3.25	−0.83	no data
5	background 2 (live) core 13 MC	3.05 to 3.06	−0.62 to −0.59	no data
6	Hydrate Ridge South (live) 37AD	2.87 to 2.97	−2.70 to −1.77	no data
7	Hydrate Ridge South (dead) 37AD	2.85 to 3.02	−2.03 to −0.79	8.94 ± 0.36
8	Hydrate Ridge North (dead)	3.39	−7.08	21 to 34 (n = 2)
	Sinistral N. Pachyderma (Planktic)			
9	northeast Pacific (live) plankton tow 42°N, 125.6°W	−0.33 ± 0.43[d]	−0.04 ± 0.03[d]	0.88 ± 0.5 (estimated)[c]
10	Hydrate Ridge South (dead) core 37AD-1	0.90	−1.52	0.66 (n = 1)
11	Hydrate Ridge South (dead) core 37AD-2	1.02	−4.87	no data
12	Hydrate Ridge North (dead) Grab R 455	1.39 ± 0.06	−7.18 ± 0.05	33 to 42 (n = 3)
	G. Bulloides (Planktic)			
13	northeast Pacific (live) planktow. 42°N, 125.6°W	0.0 ± 0.3[f]	0.0 ± 0.5[f]	1.7 ± 1[g]
14	Northeast Pacific (dead) core W8709A-13PC (316 cm, glacial age)	2.97[f]	−0.27[f]	1.5 ± 0.2[h]
15	Hydrate Ridge North (dead) grab R 455	1.75	−9.84	33 to 73 (n = 2)
	Inorganic Carbonate, <63 μ*m*			
16	Hydrate Ridge North (dead) grab R 455	4.40	−51.0	150 to 250[i,j]

[a]*McCorkle* [1997].
[b]Estimate assumes calcification at 3.5 to 4.7°C and Mg/Ca for *C. wuellerstorfi* [*Lear et al.*, 2000].
[c]Estimate assumes calcification at 4°C and Mg/Ca for *U. peregrina* [*Lear et al.*, 2000].
[d]*Ortiz et al.* [1996].
[e]Estimate assumes calcification at 14.5 ± 0.6, and Mg/Ca for *N. pachyderma* [*Nürnberg et al.*, 1996].
[f]*Ortiz et al.* [1997].
[g]Estimate assumes calcification at 11 ± 1, and Mg/Ca for *G. bulloides* [*Mashiotta et al.*, 1999].
[h]Measured Mg/Ca value (this study) implies calcification at 10 ± 1.5°C [*Mashiotta et al.*, 1999] in agreement with faunal transfer function temperature estimate [*Ortiz et al.*, 1997].
[i]This study.
[j]*Greinert* [1999].

consistently lower than the isotopic composition of stained specimens [*Rathburn et al.*, 2000]. Because the fossil samples were recovered deeper in the sediments than the living shells, the authors conclude that the differences in δ^{13}C might reflect stronger seep activity in the past. Another explanation might be that the fossil samples contain an overprinting of the primary isotopic signal by inorganic carbonate.

[24] Mass balance estimates based on our foraminifer δ^{13}C data indicate that a 3–20% contamination by inorganic overgrowths or recrystallization would explain the observed δ^{13}C shift. The largest degree of contamination seems to occur in samples recovered from the carbonate-rich vent area on the northern summit of the ridge. These estimates were based on end-member δ^{13}C values of 0.5‰ for biogenic carbonates in equilibrium with ambient waters and −51‰ for inorganic calcite dominated by methane-derived carbon.

[25] The oxygen isotopic distribution of the planktic species also reveals a pattern of biogenic calcite overprinting by inorganic carbonate (Figure 5). The δ^{18}O measured in a Holocene *G. bulloides* sample from surface sediments at station R455 (δ^{18}O = 1.75‰) is significantly higher than its modern living counterpart (δ^{18}O = 0.0‰) [*Ortiz et al.*, 1997]. The δ^{18}O values of inorganic carbonates recovered from Hydrate Ridge range from 3.68 to 4.86‰ [*Bohrmann et al.*, 1998]. Assuming inorganic carbonate precipitation with δ^{18}O of 4.4‰ (Table 2), the δ^{18}O in *G. bulloides* from station R455 (sample 15 in Figure 5) is consistent with our estimate of ∼22% inorganic carbonate contamination inferred from its δ^{13}C value.

[26] Other effects might also influence δ^{18}O of the shells. For example, if the fossil shells are of pre-Holocene age, changes in bottom temperature and ice volume would increase their δ^{18}O value, as shown by δ^{18}O of the
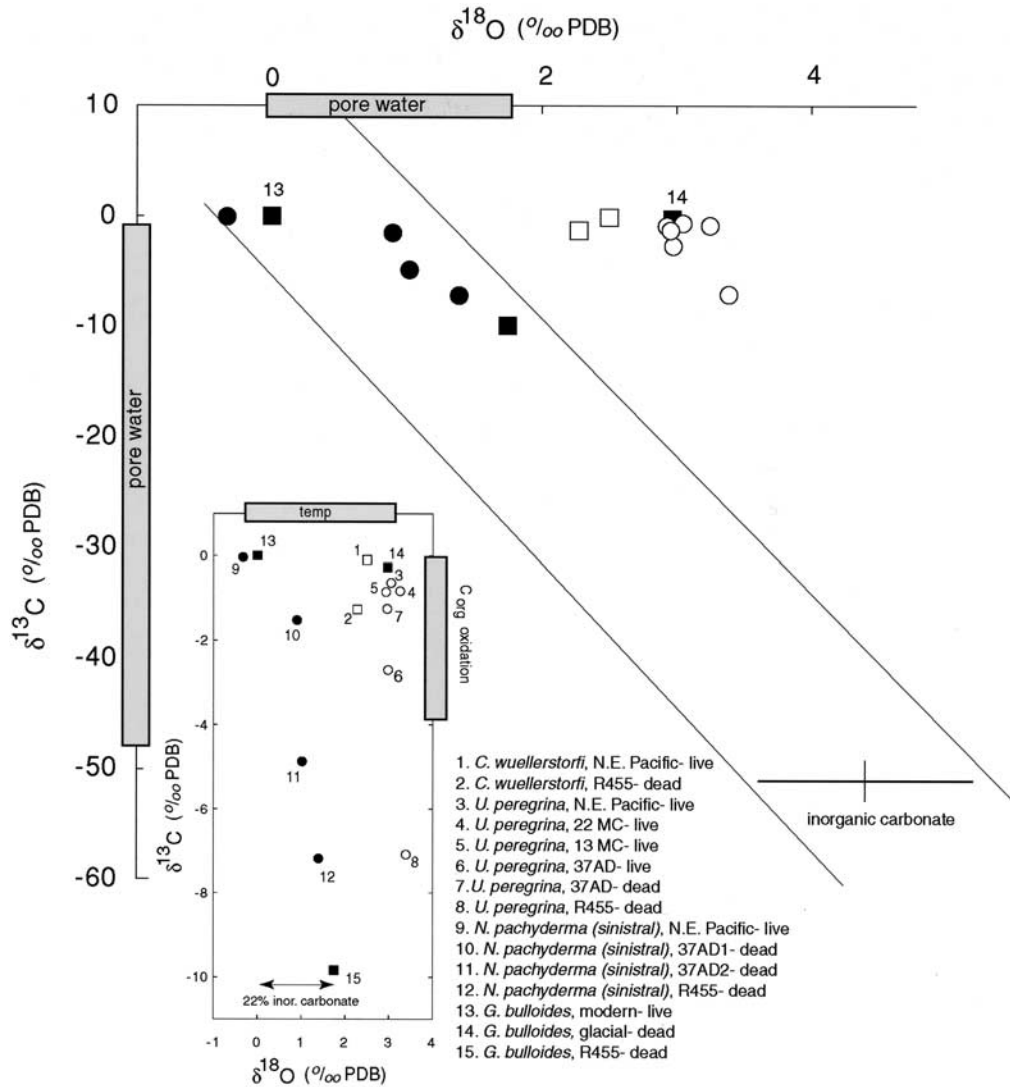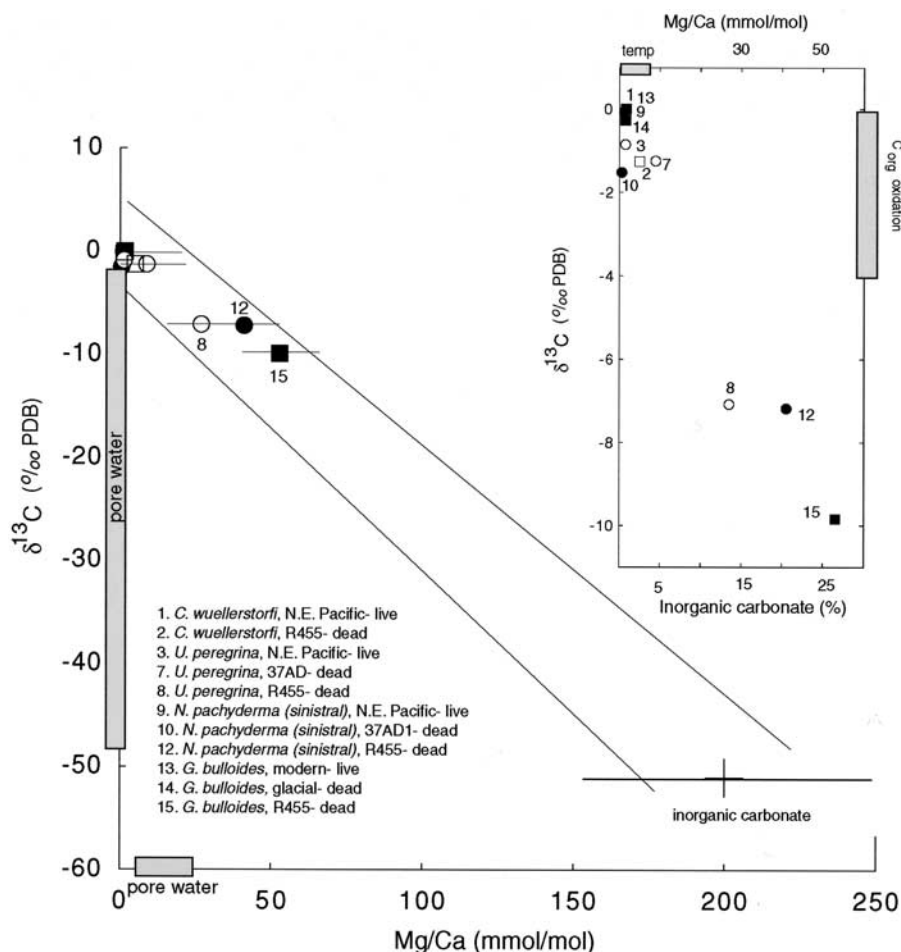
Figure 5. Relationship between $\delta^{13}C$ and $\delta^{18}O$ of planktic (solid symbols) and benthic (open symbols) foraminifera from Hydrate Ridge and northeast Pacific samples, and inorganic carbonate at Hydrate Ridge [from *Bohrmann et al.*, 1998]. Bars in the x and y axis show the range of $\delta^{18}O$ in near surface pore water the $\delta^{18}O$ of the water (E. Suess, personal communication, 2001) and of the $\delta^{13}C_{DIC}$ (this study) on Hydrate Ridge. The range of $\delta^{18}O$ changes in planktic foraminifera between modern and glacial conditions is illustrated by the isotopic composition of *G. bulloides* in samples 13 and 14. Inset shows a close-up view of the isotopic composition of foraminiferal samples. Expected range in the $\delta^{18}O$ of planktic foraminifera due to temperature changes are shown by the bar on the x axis. The range of expected $\delta^{13}C$ of *Uvigerina spp.* [*McCorkle et al.*, 1997] resulting from organic carbon oxidation is indicated by the bar on the y axis of the insert. Mass balance estimates based on $\delta^{18}O$ changes observed in *G. bulloides* from station R455 (sample 15) suggest that ~22% of the biogenic calcite in this sample has been replaced or supplemented by inorganic carbonate. Numbers for each sample correspond to designations given in Table 2.

G. bulloides recovered from an interval of core W8709A-13PC (316 cm) that corresponds to the Last Glacial Maximum [*Ortiz et al.*, 1997]. Samples 13 and 14 in Figure 5 illustrate that typical $\delta^{18}O$ fluctuations in the planktic foraminifera related to temperature and ice volume variations are of a similar $\delta^{18}O$ range as variations that may arise from inorganic contamination, but these samples lack the substantial $\delta^{13}C$ depletion that is associated with methane venting.

Also, methane hydrate dissociation is known to modify the $\delta^{18}O$ of the pore water [e.g., *Maekawa and Imai*, 2000] and thus might affect the $\delta^{18}O$ recorded in benthic foraminiferal shells. Indeed, the $\delta^{18}O$ measured in pore fluids at these sites reflect destabilization of gas hydrates and migration of deep-seated fluids (E. Suess, personal communication, 2002).

[27] To further establish whether the anomalously low $\delta^{13}C$ values measured in fossil tests reflect addition of

Figure 6. Relationship between δ^{13}C and Mg/Ca in planktic (solid symbols) and benthic (open symbols) foraminifera, including the δ^{13}C [*Bohrmann et al.*, 1998] and Mg/Ca (this study) of inorganic carbonate from Hydrate Ridge. Bars in the x and y axis denote Mg/Ca and $\delta^{13}C_{DIC}$ variations in near-surface pore fluids on Hydrate Ridge. Inset shows a close-up view of the δ^{13}C and Mg/Ca ratios of foraminiferal samples. Expected range of Mg/Ca ratios owing to temperature are shown by the bar on the upper x axis of this inset. The range of δ^{13}C of *Uvigerina spp.* [*McCorkle et al.*, 1997] expected from organic carbon oxidation is indicated by the bar on the y axis of the inset. The Mg/Ca measured *G. bulloides* from station R455 (sample 15) suggests that 28% of the biogenic calcite in this sample has been replaced by inorganic carbonate. Numbers for each sample correspond to designations given in Table 2.

isotopically light inorganic calcite after the death of the foraminifera, we analyzed the Mg/Ca ratios in foraminifera shells. Since the partition coefficient for Mg in foraminiferal (and other biogenic) calcite is orders of magnitude lower than values for inorganically precipitated calcite [*Nürnberg et al.*, 1996; *Greinert*, 1999], we postulate that the Mg/Ca ratio in the calcite shells could serve as an additional tracer of contamination with inorganic carbonate at or below the sediment surface. To test for possible analytical artifacts [e.g., *Boyle*, 1981; *Nürnberg et al.*, 1996], we conducted an experiment using *G. bulloides* shells from core W8709A-13PC (316 cm depth, Table 2). The foraminiferal shells were sonicated and rinsed multiple times in double-ionized water. They were subsequently subjected to sequential cleaning steps using hydroxylamine for removal of Mn-rich oxide coatings and diethylenetriamine pentaacetic acid for

removal of barite phases in a "flow-through" column [*Haley and Klinkhammer*, 2002]. The Mg/Ca ratio of 1.5 ± 0.2 mmol/mol obtained for this sample corresponds to a temperature of calcification of 10 ± 1.5°C using the calibration for *G. bulloides* from *Mashiotta et al.* [1999]. This temperature estimate based on Mg/Ca is in excellent agreement with the published sea surface temperature estimates based on the distribution of foraminiferal and radiolarian assemblages in the same sample [*Ortiz et al.*, 1997].

[28] In samples from Hydrate Ridge, dead foraminiferal shells with anomalously low δ^{13}C values also had anomalously high Mg/Ca ratios (Figure 6). The predicted changes in Mg/Ca caused by inorganic carbonate overgrowths are at least an order of magnitude larger than changes in Mg/Ca that might arise from reasonable variations in ocean water temperatures, which cover a range of 0.3 to 8 mmol/mol
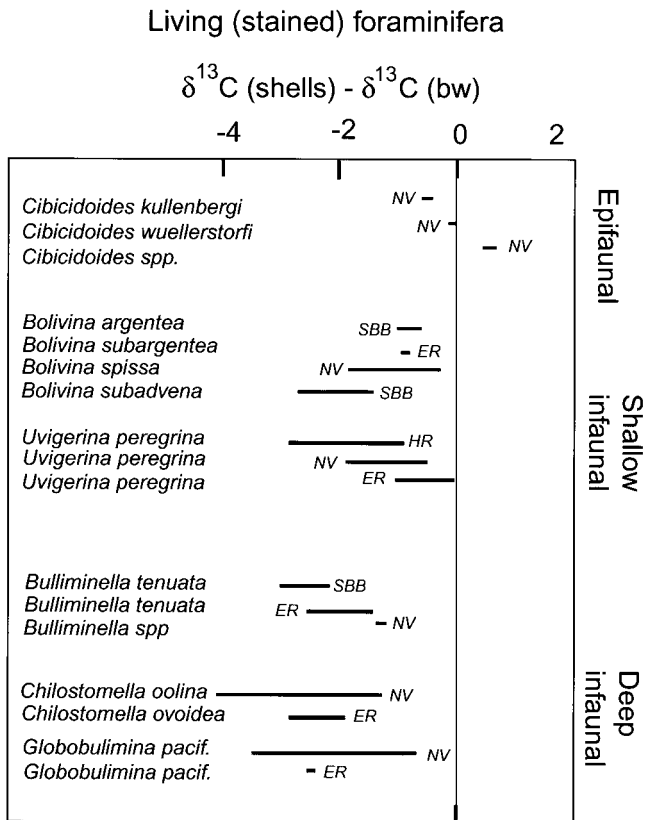
Figure 7. Average δ^{13}C offsets of shells from that of DIC in bottom water (δ^{13}C$_{bw}$) in living (stained) shells from epifaunal, shallow infaunal, and deep infaunal species of benthic foraminifera. Nonventing sites (indicated by NV) are samples collected from continental margin sediments [*McCorkle et al.*, 1997]; these isotopic variations are thought to reflect the rate of organic carbon oxidation in hemipelagic sediments. Samples from the Santa Barbara Basin (indicated by SBB) also reflect changes in δ^{13}C owing to organic carbon oxidation [*Stott et al.*, 2002]. Specimens collected from sites of active seepage on the Eel River basin are indicated by ER. [*Rathburn et al.*, 2000]. Samples from Hydrate Ridge (this study) are indicated by HR. The range of isotopic values in living shells from sites of active seepage cannot be distinguished from the variations recorded in shells, owing to changes in organic matter oxidation.

[*Nürnberg et al.*, 1996; *Mashiotta et al.*, 1999; *Lear et al.*, 2000]. Thus the Mg/Ca ratio can be used as an indicator of inorganic overprinting of the biogenic record for both planktic and benthic species. On the basis of a biogenic ratio for Mg/Ca of 1.5 mmol/mol and inorganic carbonate with a Mg/Ca ratio of ~200 mmol/mol [*Greinert*, 1999], we can estimate a degree of contamination in all our samples, as shown in the inset of Figure 6. Our estimate based on the Mg/Ca ratio measured in the *G. bulloides* sample from station R455 indicates a ~30% contamination of this sample with inorganic carbonate, which agrees with estimates of contamination based on its isotopic composition.

[29] Although the δ^{13}C signal of inorganic carbonate overprinting reflects precipitation of ^{13}C depleted DIC from oxidation of methane, the overgrowth and recrystallization processes may occur at various depths in the sediment column. Anomalously low δ^{13}C values in foraminifera thus do not necessarily reflect near-surface methane release. Rather, the presence of a low δ^{13}C signal can only ascertain oxidation of methane and inorganic carbonate mineralization at some undefined depth within the sediments and out of stratigraphic order. This implies that the timing of isotopic fluctuations driven by methane oxidation cannot be reconstructed unambiguously from the postburial signal.

4.4. Paleoceanographic Implications

[30] Our data show that the full isotopic depletion associated with the discharging fluids is not captured by living foraminifera near methane vent sites, and thus the isotopic signal of benthic foraminifera cannot be used to quantify fluid venting in these settings. It may be possible to use the depletion in ^{13}C of benthic foraminifera at seep sites as a qualitative tracer of fluid seepage, based on our finding that living shells of *U. peregrina* collected at seeps sites on Hydrate Ridge have a lower δ^{13}C value (−2.7‰) than shells collected at nonventing regions (−0.8‰).

[31] However, in addition to methane oxidation, diagenetic decomposition of organic matter also decreases the δ^{13}C in the DIC pool [e.g., *McCorkle et al.*, 1997], and the magnitude of these ^{13}C depletions is similar to (and thus not readily distinguishable from) the isotopic excursions recorded by *U. peregrina* from Hydrate Ridge and Eel River basin samples (Figure 7). This effect is not limited to *Uvigerina* but is apparent in living specimens of several foraminifera species recovered from the Eel River basin seeps [*Rathburn et al.*, 2000].

[32] The data from modern seep environments compiled in Figure 7 demonstrate that it is not possible to distinguish the effect of methane oxidation on benthic foraminifera from that resulting from local organic carbon degradation based solely on the δ^{13}C of the shell. In order to reconstruct past episodes of methane discharge, the actual locality of expected methane release should not be targeted for sampling since these sites would have experienced major changes in pore water chemistry, which may hinder biogenic calcification and enhance contamination with inorganic carbonate. Our finding that Mg/Ca ratios are elevated in foraminiferal samples with significant postdepositional overprints suggest a strategy to distinguish samples with substantial overprints from those that record primary isotopic signals of once-living shells.

[33] We have shown that benthic foraminifera will not record input of episodic methane venting at the sites where fluid discharge significantly changes the O$_2$ and H$_2$S concentration of the surrounding fluids. However, it is conceivable that methane could be added to a water mass in one location, oxidized, and the isotopic signal recorded elsewhere by foraminifera if the methane input is large enough to change the δ^{13}C of the DIC of the entire reservoir. For example, methane venting during the Paleocene/Eocene thermal maximum [*Dickens et al.*, 1995, 1997] remains possible as an explanation for the observed global δ^{13}C

shifts that are synchronous with widespread changes in CaCO$_3$ dissolution and extinction of benthic faunal in neritic to abyssal environments [e.g., *Kaiho et al.*, 1996; *Thomas*, 1998]. However, if the methane release does not significantly alter the bottom water isotopic signature away from the methane discharge sites, such smaller-scale events cannot be reliably reconstructed from the isotopic record preserved in benthic foraminifera.

4.5. Conclusions

[34] The isotopic composition of the DIC collected at sites of active methane discharge on Hydrate Ridge reveals anaerobic methane oxidation, with δ^{13}C reaching values as low as −48‰ in the upper 5 cm of the sediment. The isotopic composition of living foraminifera recovered from these sites, however, does not record the full isotopic shift of the DIC, even though the abundance of living benthic foraminifera near methane vents is higher than that at nonventing sites. The isotopic signal measured in living benthic foraminifera specimens from active methane seeps is not significantly different from the range of isotopic variability expected to result from organic matter decomposition in pore water.

[35] We infer that benthic foraminifera do not calcify within the highly reducing settings associated with active discharge of highly reducing fluids. Rather, they colonize these environments, perhaps attracted by the rich bacterial food supply, but secrete biogenic carbonate only during episodes of little or no discharge (or when seawater flows into the sediments) or they temporarily migrate to nearby sites that are less hostile. Thus these organisms do not quantitatively record the isotopic signal associated with methane seepage.

[36] Sites of localized methane discharge are often associated with inorganic precipitation of carbonate. At these locations, inorganic overprinting appears to be a likely mechanism to alter the isotopic record of biogenic calcite in fossil shells. At sites of intense inorganic carbonate buildup on Hydrate Ridge, up to 30% of the foraminifera shells of both benthic and planktic species have been replaced or supplemented by inorganic carbonate, leading to lower values of the ™$_{13}$C of dead specimens relative to their living counterparts. A combination of δ^{13}C, δ^{18}O, and Mg/Ca ratios may prove useful in evaluating whether δ^{13}C excursions observed in geologic records reflect an overprinting of the original record with inorganic carbonate at or below the sediment surface. This approach would be particularly important at sites where significant carbonate precipitation is known to occur as a result of massive methane venting on the seafloor. In summary, it appears that the primary cause of anomalous δ^{13}C depletion in foraminiferal shells at sites of methane seepage is overprinting of the biogenic record by inorganic carbonate overgrowths or recrystallization. These overprints might be related to oxidation of a methane source but could occur out of stratigraphic order. Nevertheless, it remains possible that large-scale regional or global events, such as global δ^{13}C depletion observed in the Late Paleocene thermal maximum, could be reliably recorded in foraminifera δ^{13}C because the effects δ^{13}C of depletion in this case extended beyond the zone of hostile vent-proximal environments.

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