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Reconstructing the history of fluid flow at cold seep sites from Ba/Ca ratios in vesicomyid clam shells

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Abstract

Hydrogen sulfide discharge at cold seep sites is recorded as enrichment in the barium to calcium (Ba/Ca) ratio in shells of vesicomyid clams collected live from cold seeps in Monterey Canyon and the Cascadia margin. A direct relationship between increased Ba fluxes from cold seeps and Ba incorporation into shells was established for the Cascadia margin site. For the Monterey canyon site, a 2-yr episode of high fluid flow centered on 1992 was inferred from coherent changes in the Ba/Ca profiles of three *Calyptogena kilmeri* shells. Comparison with precipitation and δ^{18}O data indicates that this high-flow period may have been driven by an increase in rainfall after the 1988–1990 California drought. High-resolution records preserved in clam shells are shown to be useful in elucidating characteristics, history, and possible mechanisms driving fluid discharge at continental margin seeps, thus establishing their potential use as paleotracers of fluid seepage events.

An extensive set of geophysical and geochemical measurements is currently available to document the flow and expulsion of fluids at transform and convergent margins. It is now recognized that such fluid discharge has far-reaching implications that include hydrocarbon prospecting, benthic ecosystem structure and function, and groundwater research (Moore 1999). At present, we are unable to incorporate geochemical data from cold seeps to models quantifying their effects on marine geochemical budgets because we lack a clear understanding of the spatial and temporal variability of these systems and of the mechanisms responsible for the advective transport. However, vent macrofauna may afford such an opportunity by recording in their shells the immediate environment in which they grow and thereby allowing us to reconstruct the variability in fluid discharge rates.

Vesicomyid clams live in association with sites of sulfide seepage along continental margins. Carbon and oxygen isotope records of calcareous macrofossils have long been used to obtain information on the biology of living and fossil specimens and on the physical environment in which they lived (Dettmann and Lohmann 1993). Advances in ion–microprobe and laser ablation (LA) techniques (e.g., Swart 1990; Perkins et al. 1991) have been used recently to reconstruct paleoenvironmental conditions from carbonate shells on annual to decadal time scales. For example, Stecher et al. (1996) have shown that the Ba/Ca composition recorded in mollusks recovered from the Delaware estuary reflect changes in the dissolved barium content of the estuarine waters. Analyses of Sr/Ca ratios in shells of *Calyptogena magnifica* from the East Pacific Rise have been used to reconstruct a 21-yr history of volcanic activity at the site (Hart and Blusztajn 1998).

Prior research has shown that migration of fluids through sediments and crust transports large volumes of geochemically altered fluids, which on venting at the seafloor, affect the bottom water chemistry (e.g., Han and Suess 1989; Martin et al. 1991). The most commonly used tracer of fluid venting is methane, and its concentration has been used to evaluate fluid discharge rates (Linke et al. 1994). Other elements, however, are also mobilized during fluid migration through the sediments. A large barium flux associated with cold fluid discharge was first documented in the Peru margin seeps (Torres et al. 1996). Even though barium sulfate is highly stable in oxic marine sediments, removal of sulfate in anoxic sediments usually enhances the dissolved barium

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concentration of the pore fluids. Barium remobilization in sulfidic sediments, coupled with advecting fluids, results in a high flux of barium to the bottom water. At the Peru margin seeps, Torres et al. (1996) measured a barium flux of 630 μmol m^{-2} d^{-1}.

We postulate that the barium release observed at cold seep localities will be recorded in the Ba/Ca ratios of clam shells through incorporation into the calcium carbonate lattice. We present data to illustrate the use of high resolution Ba/Ca data from vesicomyid clam shells as a recorder of changes in fluid discharge over periods of several years. Our results show that the clam shell record does indeed reflect the chemical variability observed at these sites, and that this record can be used to reconstruct fluid flow episodes at Monterey Canyon seeps, which we believe may be linked to an increase in precipitation in the surrounding land.

Study sites

We selected two locations of active fluid seepage with strong emissions of hydrogen sulfide: the first ridge of the Cascadia accretionary complex and the Monterey Canyon system.

Cold seeps were discovered at the Cascadia margin in 1989 at 2,000 m of water depth. Multichannel seismic data collected across the central Oregon accretionary prism have been used to show how the structural style and stratigraphy of the prism control the pattern of fluid flow observed at the seafloor (Kulm et al. 1986; McKay et al. 1992). In an east–west transect along 44°38.66′N, fluid discharge is associated with the frontal thrust and the backthrust, as well as along erosional exposures of sandy strata, as documented by a series of *Alvin* dives to that area (Kulm et al. 1986; Moore et al. 1990). The geochemical data available for the Cascadia margin (Carson et al. 1990; Linke et al. 1994; Kastner et al. 1995) allowed us to select two locations where different rates of fluid discharge result in significant changes in barium fluxes. Comparison of the Ba/Ca ratios from clam shells collected live at these different sites showed that the barium released with the discharging fluids was indeed recorded by the vesicomyid clams.

Fluid venting off Central California was first reported on the axial valley of the Monterey Fan system at 3,000 m water depth (Embley et al. 1990). More recently, chemosynthetic communities associated with fluid seepage at water depths ranging from 600 to 3,000 m have been documented at several additional locations in the Monterey Canyon (Barry et al. 1996). At these sites individual seeps vary in size (5 cm to >5 m in diameter) and configuration but usually include a central barren zone characterized by high levels of dissolved sulfide and by the absence of vesicomyid clams (Barry et al. 1997). Surrounding the barren zone, patches of bacterial mats can be observed on and around vesicomyid clam colonies. The concentration of dissolved reduced species exhibits strong horizontal gradients, with sulfide levels being highest at the central barren zone. The distribution of *C. pacifica* and *C. kilmeri* populations is aligned closely with the sulfide concentrations, suggesting specific capabilities of sulfide tolerance for the different vesicomyid species (Barry et al. 1997). Recent reports of benthic fauna associated with cold seeps on the Aleutian and Cascadia margins have also identified a close correlation of species distribution with variable sulfide concentrations in pore fluids (Wallman et al. 1997; Sahling et al. in press). These data provide an important biogeochemical background to interpret the Ba/Ca record preserved by the shells of these vesicomyid clams. Furthermore, studies on the growth rates of these individuals (Barry and Kochevar 1998) allow us to place the observed changes in the clam shell record into a time frame.

Methods

Fluid samples were collected over seeps on the Cascadia margin with the vent sampler (VESP), as described by Carson et al. (1990) and Linke et al. (1994). Basically, the instrument permits collection of sequentially timed water samples within a chamber placed directly over active vent sites. Changes in the concentration of dissolved components in these samples permit the estimation of their flux rates.

Methane was measured on board on samples recovered with the VESP by flame-ionization gas chromatography (Schmitt et al. 1991). The H_2S content of the fluids was obtained immediately after recovery using standard spectrophotometric techniques. Barium analyses were conducted on filtered and acidified samples using isotope dilution inductively coupled mass spectroscopy (ICPMS) following the procedure of Klinkhammer and Chan (1990).

Clam specimens were collected live from the sites of fluid seepage. Cross sections (10 mm thick) of the bivalve shells were cut from the umbo to the ventral posterior margin along the axis of maximum growth (Fig. 1A) using a water-cooled band saw equipped with a diamond-impregnated copper blade. To clearly the identify the shell structure, the shell cross section was polished with silicon carbide sandpaper. Carbonate samples from bivalve shells from site 2046 were obtained using a microdrill and the Ba/Ca ratio in the dissolved carbonate was measured by isotope dilution (ID)-ICPMS (Klinkhammer and Chan 1990). All the other shell samples were analyzed by laser ablation ICPMS using a modification of the procedures described by Perkins et al. (1991), Feng (1994), and Stecher et al. (1996). The polished samples were sectioned into pieces smaller than 20 mm long to fit into the ablation chamber and washed with deionized water. Bivalve shells were analyzed exclusively at low magnification, with samples collected by ablating the shell along the axis of maximum growth at 350-μm intervals. Parallel transects were obtained for the outer (nonprismatic) layer and middle (prismatic) layer of the shell (Fig. 1). For this study, we used data exclusively from the middle layer of the shell to avoid the effects of alteration of the outer shell record (Thorn et al. 1995; Stecher et al. 1996).

The system employed for this study was a Fisons VG PlasmaQuad PQ^{2+} inductively coupled plasma mass spectrometer coupled with a 500-mJ Spectron Laser Systems Nd : YAG laser operating at 1,064 nm. Samples are housed within a quartz ablation cell, and Ar is employed as a carrier gas. Instrumental stability, tuning, and mass calibration were checked initially using a solution nebulization setup. After

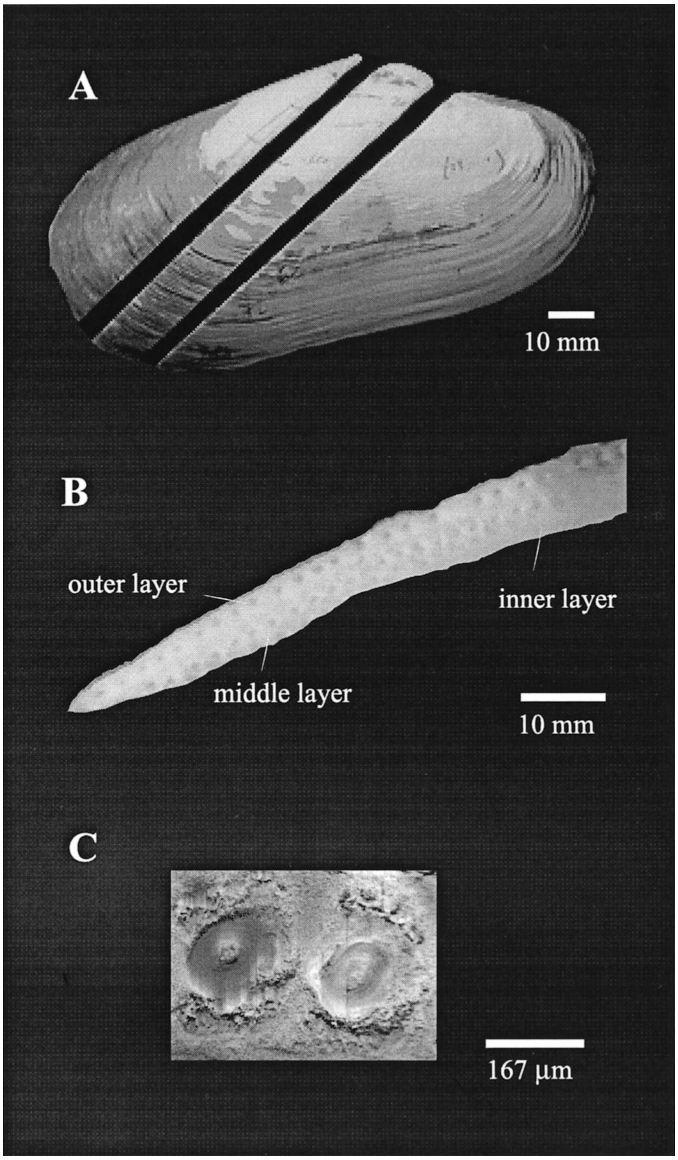

Fig. 1. (A) Photograph of clam shell (*C. kilmeri*) illustrating the section along the axis of maximum growth sampled for geochemical analyses. (B) Cross section of a shell (*C. pacifica*) after LA-ICPMS analyses of outer and middle layers. Ablation craters show the sampling spacing at 350-μm intervals. (C) scanning electron microscopy of ablation holes.

Table 1. Parameters used during LA-ICPMS analyses of clam shell samples.

ICP-MS operating conditions	
Instrument	VG Elemental PlasmaQuad PQ 2+
Forward power	1,500 W
Reflected power	<5 W
Ar flow rates (L min^{-1})	
coolant	13
nebulizer	1.1
auxiliary	0.7
Laser operating conditions	
Laser type	Nd : YAG, Spectron Laser Systems
Wavelength	1064 nm
Laser mode	Q-switched
Laser energy	540 V
Repetition rate	4 Hz
Shots per site	6

switching the sample-introduction system to the laser module, tuning was performed on NIST standard reference material (SRM) 612. All analyses were performed in pulse-counting mode, which offers highest sensitivity and a wide dynamic range. Operating conditions are presented in Table 1. Replicate analyses were performed on SRM 612 in both high and low magnification modes to determine instrumental stability before each run. The mean standard deviation of the instrument response was better than 7% in low magnification and 10% in high magnification. Argon blanks were acquired by firing the laser with the shutter closed at the beginning and end of each run, which consisted of up to 50 sample acquisitions along a transect. These blank values are interpolated over the course of the run and later subtracted from data acquired on standards and samples.

To quantify the laser yield, we normalized the variation of the signal intensity using ^{43}Ca (natural abundance = 0.135) as an internal standard. Feng (1994) successfully conducted quantitative analyses of bulk calcite and dolomite powders using the NIST 612 silicate glass as a nonmatrix matched calibration standard and ^{43}Ca as the internal standard. However, we observed variations in the mass response of the quadrupole and detectors when analytical runs were longer than 2 h. Because the mass response might vary within the mass range, the use of an internal standard does not completely compensate for these changes; thus, the mass response curve was monitored by replicate analyses of a pressed pellet standard every 10 sample spots. We selected a *Calyptogena* shell from a hydrothermal site near Galapagos as our reference material because its large size allowed for the collection of sufficient carbonate powder for a pressed pellet, as well as for chemical analyses using solution chemistry. The shell was milled with a 0.5-mm dental burr, and the powder was homogenized in an agate mortar. Pellets were made by mixing 100 μl of 1% polyvinyl alcohol solution with 1 g of carbonate and applying 3 tons pressure for 1 min using a hydraulic press. Pellets were affixed adjacent to the sample inside the quartz ablation cell. Data acquisition on the pellets was interspaced with sample acquisition to allow for verification of the mass response curve during the analysis run. Repeated (n = 22) analyses of the reference pellet within a 10-h run yielded a relative standard deviation of 12% for ^{43}Ca and 7% for ^{138}Ba (Hubbard 1999).

To evaluate the analytical accuracy of this approach, we obtained samples by milling sequential increments of clam shells under a flow-through clean hood. Material was scraped from areas that were previously analyzed by laser, weighed, and dissolved in quartz-distilled 0.45 N HNO_3. The dissolved material was then analyzed by ICPMS. The difference between Ba/Ca acquired by LA-ICPMS with those obtained by solution chemistry was less than 15%.

Similarly, samples from the middle layer of the shells

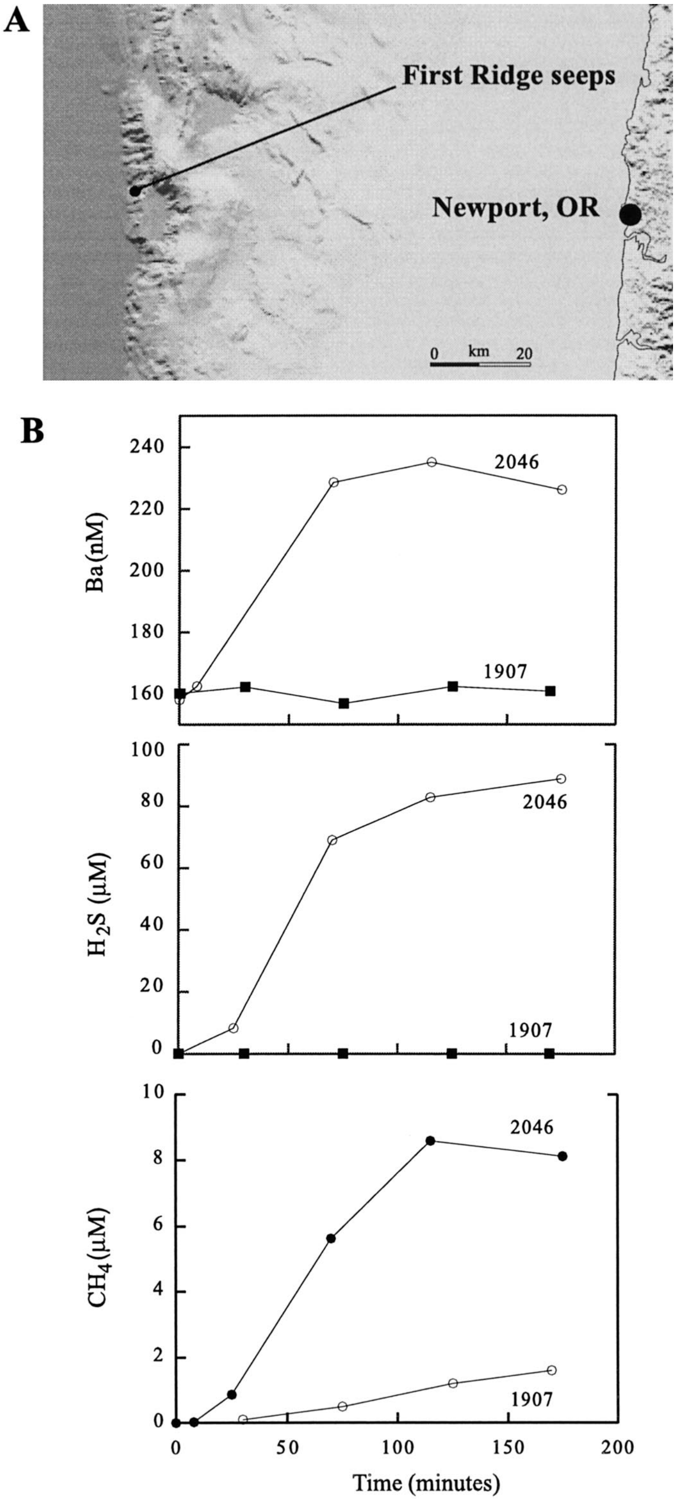

Fig. 2. (A) Location of *Alvin* dive sites 1907 and 2046 on the first accretionary ridge of the Cascadia margin. (B) Fluids collected over sites of active fluid discharge with VESP all show evidence of methane discharge. The samples from site 2046 show enrichment in their dissolved sulfide and barium levels during the time of deployment, whereas the sulfide and barium concentrations in samples from site 1907 are not significantly different from bottom water values.

Table 2. Description of bivalve shell samples used in this study.

Locality	Sample ID	*Calyptogena* species	Date collected	Shell length (mm)
Clam Field, Monterey	B-30	*C. kilmeri*	5 Apr 93	71
	T-63	*C. pacifica*	21 Jan 94	
	2110-12	*C. pacifica*	21 Sep 93	50
	97286	*C. kilmeri*	13 Oct 97	108
	96305	*C. kilmeri*	1 Nov 96	103
First Ridge, Cascadia	1907	Unidentified	Aug 87	49
	2046	Unidentified	Jun 88	84

were obtained with a dental microdrill for oxygen isotopic analyses of the carbonate powders ($\sim$500 μg) by mass spectrometry (Ortiz et al. 1996).

Results and discussion

Clams record chemical heterogeneity of seep zones—Methane release curves for vent sites 1907 and 2046 on the Cascadia margin are shown in Fig. 2. The higher methane fluxes measured during the 2046 deployment represent a rate of fluid discharge that is approximately eight times higher than flow measured at site 1907 (Linke et al. 1994). The flux of H_2S from the sediment measured at site 2046 was 3.7 mmol m^{-2} d^{-1}, whereas there were no detectable levels of hydrogen sulfide at site 1907. Consistent with these observations, we found a significant barium flux out of the sediments at site 2046 and no barium increase over bottom water levels in the fluids collected from the sulfide-free seep at site 1907 (Fig. 2B). Biogenic carbonate from bivalves collected live at Cascadia sites (Table 2) showed Ba/Ca ratios in agreement with the flux data (Fig. 3). The shells collected in the high-flux, high-sulfide, high-barium seeps (site 2046) had higher Ba/Ca ratios (4 to 13 μmol/mol) than did those from sites where the discharging fluids contained no sulfide (site 1907; Ba/Ca ratios < 5 μmol/mol).

Specimens from the Monterey site were collected live along a transect following the horizontal sulfide gradient (Fig 4., Table 2). High-resolution records of Ba/Ca along the axis of maximum growth (Fig. 1A) were constructed using LA-ICPMS. Significantly higher Ba/Ca levels were obtained in the *C. kilmeri* shell (2 to 80 μmol/mol) than in the *C. pacifica* samples ($<$2 μmol/mol; Fig. 5). This is consistent with the observation that *C. kilmeri* (B-30) dominates the vesicomyid assemblage at seeps with high sulfide levels where the concentration of dissolved barium is expected to be the highest, as shown for the Cascadia margin sites. *C. pacifica* shells (T-63 and 2110-12), which have the lowest Ba/Ca ratios in its shells, are from the dominant species at seeps with low sulfide levels; thus, the carbonate shells from these bivalves provide a record that reflects the history of the geochemical environment during their growth.

Clam shells as paleotracers of fluid flow—Recent data from a variety of cold seep regions show that these systems are highly dynamic with large changes in rates of fluid discharge over time (e.g., Orange et al. 1997; Tryon et al.

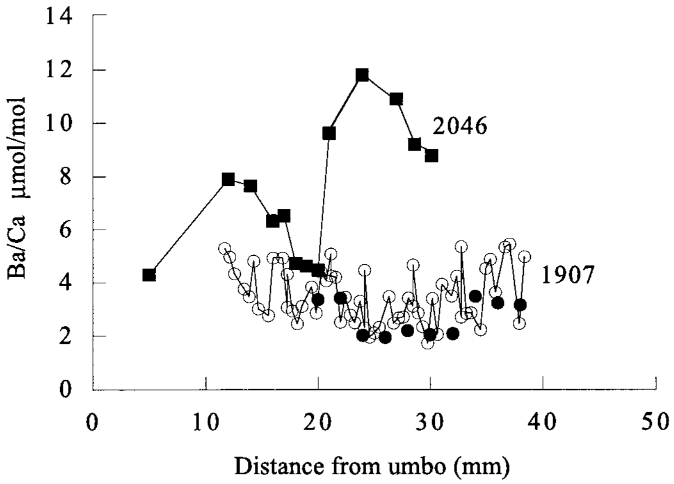

Fig. 3. Ba/Ca profiles versus distance from the shell umbo along the axis of maximum growth for samples collected on First Ridge, Cascadia. Data for sample 2046 (squares) were generated by ID-ICPMS on dissolved carbonate samples. Data for 1907 were obtained by LA-ICPMS; open and closed circles denote data collected on parallel tracks during two different analytical runs and are shown to illustrate the reproducibility of the analyses. The higher Ba/Ca ratios measured on the 2046 sample are in agreement with barium flux data collected at this site (Fig. 2B).

1999). To date, we have information on changes in the nature of fluid seepage over time scales of days to weeks, but we lack a tracer for fluid discharge that can span several years.

Ba/Ca profiles of *C. kilmeri*, being the more tolerant species for high-sulfide and high-barium environments (Fig. 5), suggest changes in the dissolved barium concentration during the life of the clam. Although the stable carbon ratios of shell carbonate of vesicomyids are consistent with a seawater source of carbonate, variations in Ba/Ca ratios are almost certainly due to changes in porewater composition in the upper sediments driven by the advecting fluids.

To assign an approximate age to the events recorded by the carbonate shells, we used the *C. kilmeri* growth rates determined from tag–recapture experiments at ''Clam Field'' (Barry and Kochevar 1998). Several (50 to 100) individuals were collected with a remotely operated vehicle, labeled, and measured to the nearest 0.1 mm. The clams were returned immediately to the site of collection, recovered after 8 to 18 months, and remeasured. The growth interval data for each species was used to fit von Bertalanffy growth curves. Results of this analysis (shown in Fig. 6) document a period of enhanced barium concentration in the fluids that spans 1 to 2 yr, centered on 1992.

The source of fluid flow at the Clam Field site is unclear; however, Barry et al. (1996) suggest that fluid seepage at this location may derive from fresh water percolating into the Monterey Formation in the Santa Cruz Mountains. The Monterey Formation is a highly fractured, hydrocarbon-bearing shale that underlies the Purisima formation in Monterey Bay and outcrops on the walls of the Monterey Canyon between 875 and 920 m deep (Greene 1977). Ground water flowing through this organic-rich unit will accumulate sulfides and methane, leading to the high sulfide and methane

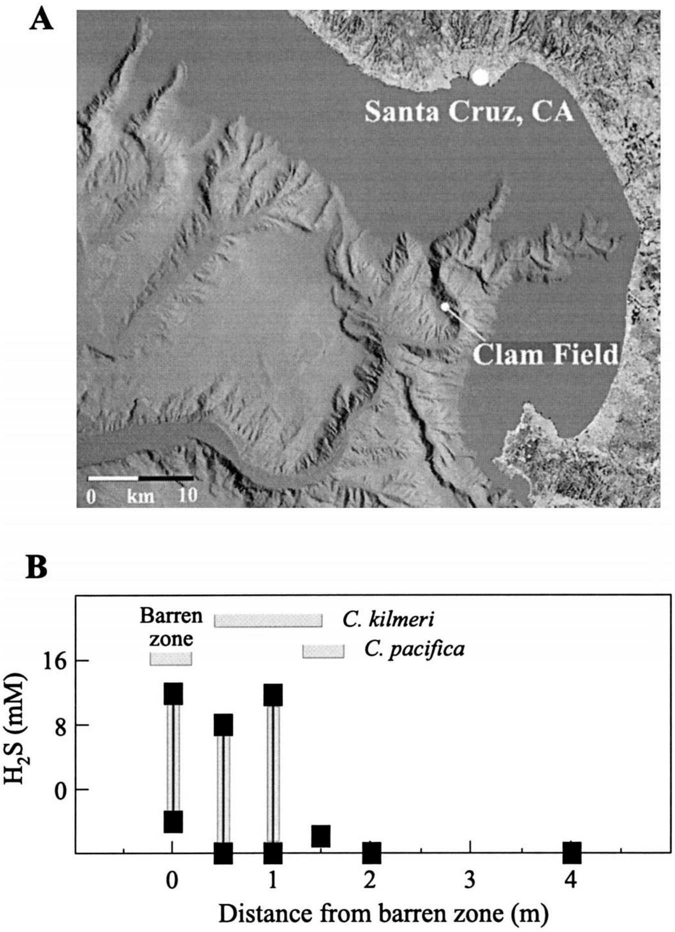

Fig. 4. (A) Location of the seep sites in the Monterey Canyon. (B) Zoning of vesicomyid clam populations at sites of cold seepage follow the dissolved sulfide levels in the upper 10 cm of the sediment: *C. kilmeri* colonize zones of higher sulfide content than *C. pacifica.* The variations in chemistry and associated fauna within a 4-m transect illustrated here have also been mapped at other localities of fluid seepage in Monterey Bay (Barry et al. 1997).

levels that characterize the Clam Field seeps (Barry et al. 1996). Therefore, the increase in barium discharge recorded for the 1991–1992 period most likely reflects a hydrological response of the system to an increase in rainfall following the drought experienced in California from 1988 to 1990, as shown in Fig. 7 (California Department of Water Resources data, http://cdec.water.ca.gov/).

To substantiate this hypothesis further, we obtained oxygen isotopic data for the *C. kilmeri* shell 96305, which showed the largest Ba/Ca signal (Fig. 5). Although much coarser in resolution than the Ba/Ca records obtained by laser ablation, δ^{18}O values were lowest during the episode of enhanced barium incorporation into the shell (Fig. 8). This suggests an increase in meteoric water contribution to the overall fluid discharge at the Monterey Canyon seeps during the periods of enhanced barium release, consistent with our proposed mechanism of precipitation-driven fluid discharge.

To directly correlate the extent of the barium signal recorded in the *C. kilmeri* shells to the barium composition of the discharging fluid, we need data on the barium partition-

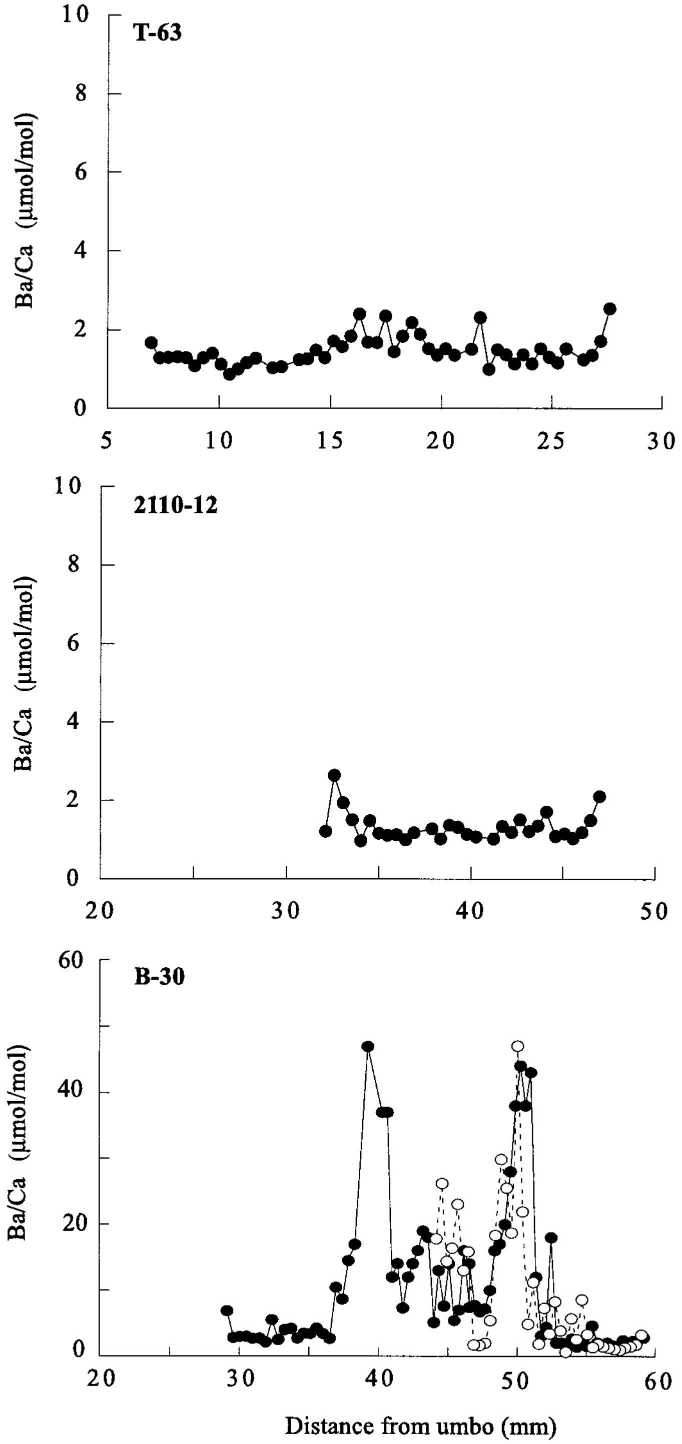

Fig. 5. Ba/Ca profiles versus distance from shell umbo along the axis of maximum growth for two specimens of *C. pacifica* (T-63 and 2110-12) and one specimen of *C. kilmeri* (B-30). All bivalves were collected live from Clam Field in Monterey Bay (*see Table 2* for sample description). Data were generated by LA-ICPMS. The parallel tracks for *C. kilmeri* sample B-30 represent data collected during two different analytical runs and are shown to illustrate the reproducibility of the analyses.

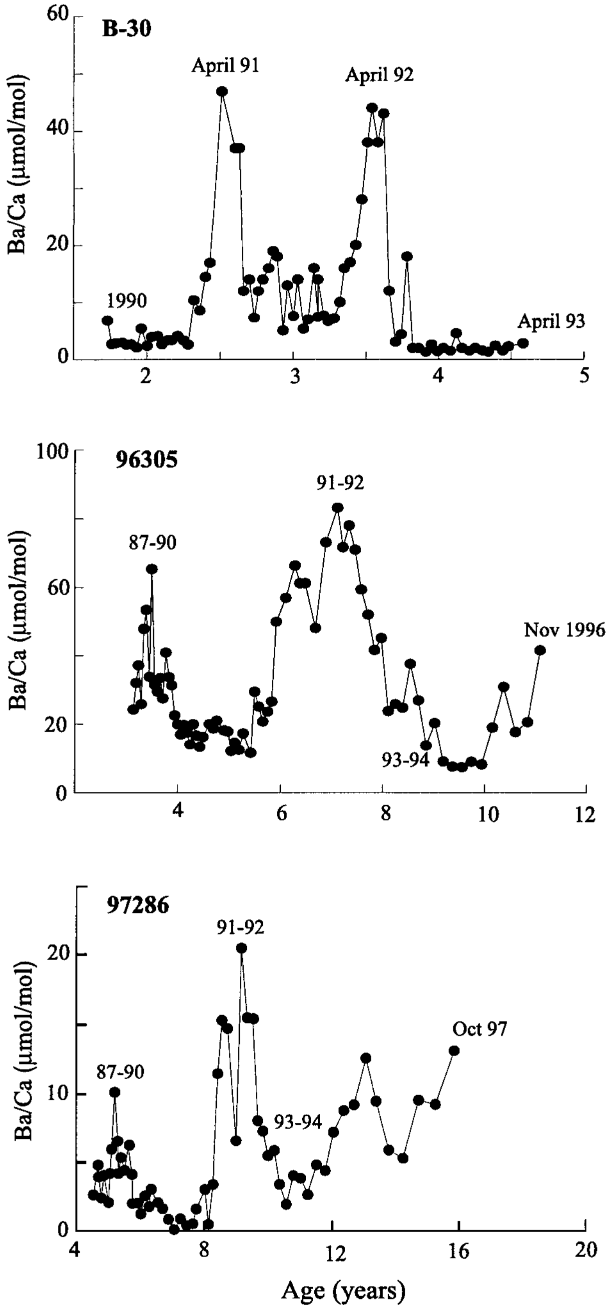

Fig. 6. Profiles of Ba/Ca versus estimated ages in three samples of *C. kilmeri* species collected live from Clam Field (*see Table 2* for sample description). Note that the three samples record an episode of enhanced Ba/Ca centered around 1992, which lasted for approximately 1 to 2 yr.

ing coefficient for *C. kilmeri*. The Ba/Ca ratio of shells is related to the dissolved Ba/Ca ratio of pore fluids in the upper 10–30 cm of sediment (which supports clam growth) by the function

$$K_D = (Ba/Ca)_{carbonate}/(Ba/Ca)_{water} \qquad (1)$$

where K_D is the partitioning coefficient. Although the Sr/Ca ratios of various bivalves are known in the context of paleotemperature studies (Lutz 1981; Hart and Blusztajn 1998),

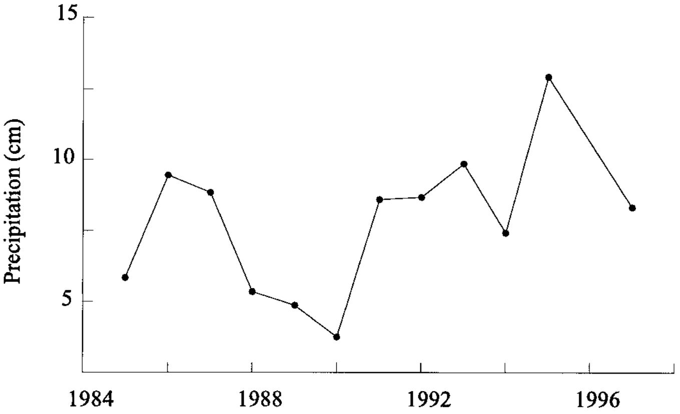

Fig. 7. Yearly average precipitation data from 1985 to 1998 at the Big Sur Park Station (BGS, elevation 80 m) of the National Park Service.

there is no equivalent database for the incorporation of barium. As a first approximation, we can use an estimate for K_D of 0.16, based on the empirical model of Onuma and coworkers for trace element partition in molluscan shells (Onuma et al. 1979) derived solely from ionic radius considerations. Using this value, a Ba/Ca ratio in the shell of 80 μmol/mol would represent a barium concentration in the fluids of 5 μM. Alternatively, if we use the empirical relationship between barium concentration in bottom water and the Ba/Ca ratio of benthic foraminifera (Lea 1993) as an indicator of barium incorporation in biogenic carbonates, an 80 μmol/mol Ba/Ca ratio would correspond to a dissolved barium concentration of 3 μM. This value, although high, is consistent with the barium concentrations measured in pore fluids associated with seeps on the second accretionary ridge of the Cascadia margin at a depth of only 10 cm (Torres unpubl. data). Similarly, values as high as 25 μM are known to occur in the advecting pore fluids of the Peru margin (Torres et al. 1996). Barium levels in VESP samples from the Cascadia margin indicate flux rates of 20 to 70 μmol cm^2 yr^{-1} (Fig. 2B), which are comparable with barium flux rates measured at cold seeps in the Peru Margin. These extremely high values of dissolved barium at cold seep sites are in agreement with the observation of barite deposits in such environments (Torres et al. 1996) and might represent a currently unrecognized source of barium for oceanic bottom waters.

Conclusions and significance—Chemical profiles of clam shell samples recovered from areas of active fluid venting provide information on the spatial and temporal variability at cold seeps. Records preserved on these shells are consistent with studies that document the tremendous chemical heterogeneity (Barry et al. 1997; Wallman et al. 1997) and highly dynamic nature (Tryon et al. 1999) of fluid flow at cold seep sites. Results presented here are evidence that Ba/Ca ratios in carbonate shells can be used as a proxy of fluid discharge over periods of several years. Changes in the composition of the discharge fluids documented in these records provide a link between fluid discharge and climate, suggesting that fluid flow may be driven, at least in part, by rainfall patterns on the California coast.

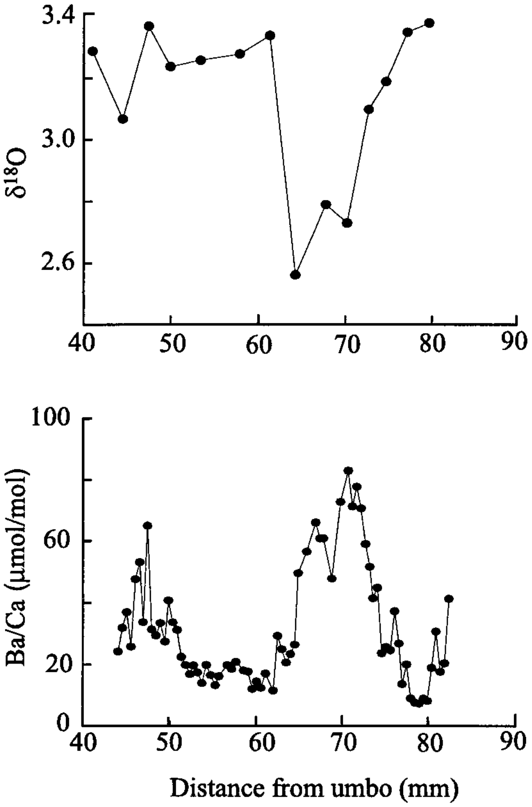

Fig. 8. Comparison of the δ^{18}O and Ba/Ca data for *C. kilmeri* sample 96305. The isotopic data show a decrease in δ^{18}O values corresponding with the increase in Ba/Ca ratios recorded at 65–75 mm from the shell umbo. This section corresponds to the 1991–1992 period (Fig. 6) of increased rainfall, which followed 2 yr of low precipitation (Fig. 7).

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