

# Methanogenic calcite, $^{13}\text{C}$ -depleted bivalve shells, and gas hydrate from a mud volcano offshore southern California

James R. Hein\*

William R. Normark

Brandie R. McIntyre

Thomas D. Lorenson

Charles L. Powell II

U.S. Geological Survey, 345 Middlefield Road, Menlo Park, California 94025, USA

## ABSTRACT

Methane and hydrogen sulfide vent from a cold seep above a shallowly buried methane hydrate in a mud volcano located 24 km offshore southern California in 800 m of water. Bivalves, authigenic calcite, and methane hydrate were recovered in a 2.1 m piston core. Aragonite shells of two bivalve species are unusually depleted in  $^{13}\text{C}$  (to  $-19\text{‰}$   $\delta^{13}\text{C}$ ), the most  $^{13}\text{C}$ -depleted shells of marine macrofauna yet discovered. Carbon isotopes for both living and dead specimens indicate that they used, in part, carbon derived from anaerobically oxidized methane to construct their shells. The  $\delta^{13}\text{C}$  values are highly variable, but most are within the range  $-12\text{‰}$  to  $-19\text{‰}$ . This variability may be diagnostic for identifying cold-seep-hydrate systems in the geologic record. Authigenic calcite is abundant in the cores down to  $\sim 1.5$  m subbottom, the top of the methane hydrate. The calcite is depleted in  $^{13}\text{C}$  ( $\delta^{13}\text{C} = -46\text{‰}$  to  $-58\text{‰}$ ), indicating that carbon produced by anaerobically oxidized methane is the main source of the calcite. Methane sources include a geologic hydrocarbon reservoir from Miocene source rocks, and biogenic and thermogenic degradation of organic matter in basin sediments. Oxygen isotopes indicate that most calcite formed out of isotopic equilibrium with ambient bottom water, under the influence of gas hydrate dissociation and strong methane flux. High metal content in the mud volcano sediment indicates leaching of basement rocks by fluid circulating along an underlying fault, which also allows for a high flux of fossil methane.

**Keywords:**  $^{13}\text{C}$ -depleted bivalve shells, cold seep, methane hydrate, mud volcano, California margin basin.

## INTRODUCTION

Gas and fluid fluxes along continental margins are related to tectonic-sedimentary processes and physicochemical conditions that produce cold seeps, warm springs, and methane hydrates (e.g., Obzhirov et al., 2004). Hydrates are being extensively studied because of their potential contributions to mass wasting, energy resources, abrupt global climate change, and global carbon mass balance. Cold seeps are especially important because of their association with large gas and fluid fluxes, unique biological communities, and formation of authigenic minerals (e.g., Boetius and Suess, 2004). Cold seeps and methane hydrates may be directly associated when hydrate occurs at or near the seafloor, as is the case described here.

Biological communities associated with cold seeps generally display high density and low diversity, usually with only one or two macrofauna taxa, the most common being mollusks and tube worms (Levin et al., 2000). Bacteria and archaea are also integral in the biogeochemistry of these systems. Both the mineral deposits formed at cold seeps and the

biological communities with their multifarious interactions are not as yet fully understood.

Here we describe a cold seep fed by fluids and gases from both a near-surface gas hydrate within a mud volcano and deep-seated fluids released along a fault (Fig. 1). The cold seep supports dense populations (covering the entire surface area) of *Lucinoma* and *Vesicomya* bivalves, and this is the first reported occurrence of unaltered bivalve shells strongly depleted in  $^{13}\text{C}$  (to  $-19\text{‰}$   $\delta^{13}\text{C}$ ).

## RESULTS AND DISCUSSION

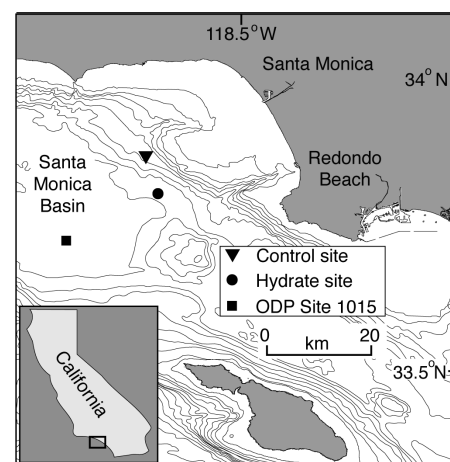
### Geology of the Mud Volcano

The Santa Monica Basin mud volcano (Normark and Piper, 1998, their Fig. 11) is above the San Pedro Basin fault along the northeast margin of the basin. The mud volcano is  $\sim 300$  m in diameter at the base and has 30 m of relief. The mud volcano ascended through well-bedded sediment on the lower slope of the basin (Fig. 1), which is anoxic below sill depth. The uppermost turbidite and lower-slope sediment upwarped on the flanks of the mud volcano by diapiric movement were correlated with latest Quaternary deposits drilled at Ocean Drilling Program (ODP) Site 1015 (Normark and McGann, 2004). No internal structure is resolved under the mud volcano summit on

either high-resolution deep-tow boomer or single-channel air-gun seismic-reflection profiles (see Fisher et al., 2003, their Figs. 16c–16e), likely a result of sediment deformation and high gas content. The reservoir horizon for the gas in the hydrate may be as shallow as 200 m below the regional seafloor based on reflection amplitude anomalies seen in most profiles across southern Santa Monica Basin (see discussion, maps, and seismic profiles in Normark and Piper, 1998).

### Cores, Samples, and Analyses

During cruise A1-03-SC in July 2003 (MV *Auriga*), a 2.1 m piston core (P1) taken at 800 m depth unexpectedly recovered methane hydrate at the summit of a mud volcano (Fig. 1). Six additional cores (4–240 cm) taken within a 15 m radius of core P1 contained bivalve shells or shell fragments and authigenic calcite, but not hydrate. All cores smelled strongly of hydrogen sulfide. Violent degassing of the hydrate recovered between 162 and 212 cm in core P1 resulted in extrusion of that section of core. Both open and sediment-filled vertical channels occur in three cores, likely gas and/or fluid escape pathways. Core P1 consists of whole and fragmented shells and authigenic calcite clasts as long as 7 cm in olive green-brown silty mud.



**Figure 1.** Bathymetry of California borderland and location of seep-hydrate site at 800 m water depth on northern slope of Santa Monica Basin and control site at 550 m depth; 100 m contour interval. ODP—Ocean Drilling Program.

\*E-mail: [jhein@usgs.gov](mailto:jhein@usgs.gov).

TABLE 1. MINERALOGY AND ISOTOPIC COMPOSITION OF CARBONATE ROCKS AND BIVALVE SHELLS RECOVERED FROM GAS HYDRATE SEEP SITE

Sample no.	Depth in core (cm)	Description	Dominant carbonate	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)	T (°C)*
<b>Gravity Core 1</b>							
G1-D-47-49	47-49	<i>Lucinoma</i> shell fragment	Aragonite	—	0.1	2.3	8.6
G1-C-39-43	129-133	Rock w/shell fragments	Aragonite	—	-48	2.9	5.7
G1-C-48-50	137.5-140	Whole <i>Lucinoma</i>	Aragonite	—	-12.9	3.4	3.6
G1-C-48-50	137.5-140	Whole <i>Lucinoma</i> -acetic acid	Aragonite	—	-12.4	3.3	4.0
<b>Piston Core 1</b>							
P1-D-0-2	0-2	Whole <i>Lucinoma</i> shell (live)	Aragonite	—	-18.9	2.5	7.8
P1-D-6-8A	6-8	<i>Vesicomya</i> shell fragment-H <sub>2</sub> O <sub>2</sub>	Aragonite	—	-18.7	2.0	9.9
P1-D-13-16	13-16	<i>Lucinoma</i> shell	Aragonite	—	-12.4	2.3	8.6
P1-D-13-16A	13-16	<i>Lucinoma</i> shell-H <sub>2</sub> O <sub>2</sub>	Aragonite	—	-12.5	2.3	8.6
P1-C-0-10	62-72	<i>Vesicomya</i> shell fragment	Aragonite	0.709177	-16.8	2.7	6.9
P1-C-10-12A	72-74	<i>Vesicomya</i> shell fragment-H <sub>2</sub> O <sub>2</sub>	Aragonite	—	-17.1	2.3	8.6
P1-C-40-43	102-105	Clam coquina	Aragonite	—	-45.9	3.2	4.4
P1-B-7-14	119-126	<i>Vesicomya</i> shell fragment	Aragonite	—	-12.9	1.7	11.1
P1-B-36-39	148-151	Rock fragment	Low-Mg calcite	—	-54.3	3.9	0.9
P1-A-35-38	197-200	<i>Lucinoma</i> shell fragment	Aragonite	—	-0.8	2.7	6.9
<b>Piston Core 4</b>							
P4-D†	0-66	Rock fragment	Low-Mg calcite	0.709177	-58.2	3.7	1.5
P4-C-1-6.5	67-72.5	Rock fragment	Low-Mg calcite	0.709185	-55.1	3.9	0.9
P4-C-38-39	104-105	<i>Lucinoma</i> shell fragment	Aragonite	—	-7.6	2.2	9.0
P4-B-33.5-36	149.5-152	Rock fragment	Low-Mg calcite	—	-58.4	3.9	0.9

Note: Precision of Sr isotopes was  $\pm 0.000008$ ; for  $\delta^{13}\text{C}$  was 0.2‰;  $\delta^{18}\text{O}$  was 0.1‰; dash means not analyzed; PDB—Peedee belemnite.

\*Calculated using dissolved inorganic carbon (DIC)  $\delta^{18}\text{O}$  of  $-0.29$ ‰ (Grossman, 1984); temperature (T) equation for calcite from Anderson and Arthur (1983) and for aragonite from Grossman and Ku (1986).

†Position unknown within 0-66 cm interval because mud was removed for analyses.

Living *Lucinoma aequizonatum* (Stearns) and *Vesicomya elongata* (Dall) were recovered from the top of core P1, as were shells (often fragmented) from the rest of the cores. The living bivalve specimens were washed and refrigerated onboard ship. *Vesicomya* is a filter feeder commonly found at cold seeps and in sulfide-rich habitats (e.g., Barry et al., 1997). All *Vesicomya* species investigated rely on chemoautotrophic endosymbiotic bacteria for nutrition, and eastern Pacific species live at the sediment surface or are partly buried (Coan et al., 2000). *Lucinoma aequizonatum* (Stearns) is a filter feeder living below the sediment-water interface and is found in sulfide-rich habitats (e.g., Cary et al., 1989). Both species support sulfide-oxidizing symbiotic bacteria (e.g., Brooks et al., 1987).

Gas was collected from the headspace of 10 sediment-sample containers. Methane was the dominant gas, with minor amounts of CO<sub>2</sub> and HS<sup>-</sup> (8.2%, 0.18%, and 0.002%, respectively). Trace amounts of heavier hydrocarbon gases were also detected. Five CH<sub>4</sub> and CO<sub>2</sub> gas samples from three cores (P1, P2, G2) were analyzed for carbon isotopes. Sediment gas chemistry indicates a structure I hydrate (Sloan, 1998), although it was not analyzed directly.

A 5.4 m piston core was collected from a nearby site (Fig. 1) at 550 m depth, which has comparable bottom-water temperature and O<sub>2</sub> content as found at the P1 site; this core was used as a control to compare sediment chemistry.

Standard methods were used for chemical (55 elements by X-ray fluorescence, inductively coupled plasma-mass spectrometry [ICP-MS], ICP, and cold-vapor atomic absorption), isotopic (O, C, Sr), mineralogic (X-ray diffraction [XRD]), and gas analyses. Only unaltered shells as determined by XRD, trace element analysis, and microscopic inspection were analyzed for isotopes. To confirm that contamination was not an issue, two bivalve valves were cut in half, and half of one specimen was etched with acetic acid and half of the other with hydrogen peroxide; the counterpart of each was analyzed untreated. Additional shells were treated with hydrogen peroxide without an untreated counterpart. Treatment with 30% hydrogen peroxide (for 24 h to remove organic matter) and 25% acetic acid (for 15 min to remove potentially unseen authigenic calcite) changed the carbon isotopic compositions only within analytical error (Table 1).

### Carbonate Mineralogy

XRD shows that the authigenic carbonate is predominantly low-Mg calcite (Table 1), which is rare at near-surface seep sites, where high-Mg calcite and aragonite are typically more common (e.g., Bohrmann et al., 1998). The shells of both bivalve species are aragonite.

### Bivalve Shell Chemical Composition

The chemical compositions of unaltered *Lucinoma* and *Vesicomya* shells are similar ex-

cept for As and Ba contents. Arsenic is nearly 6 times higher in *Lucinoma* (2.9 ppm) than in *Vesicomya* (0.5 ppm) shells, and Ba is 2.6 times higher in *Lucinoma* (420 ppm) than in *Vesicomya* (159 ppm). Sr (3590-4150 ppm) and Mg (300-400 ppm) concentrations are similar to those found in other aragonite marine bivalve shells. Mn (<5 ppm) and Fe (200 ppm) contents are low, attesting to the pristine nature of the shells (Roesijadi and Crecelius, 1984). Ni (mean 8.9 ppm), Mo (5.5 ppm), Cu (1.9 ppm), and Ce (1.8 ppm) are enriched compared to nonvent bivalves (Roesijadi and Crecelius, 1984).

### Carbonate and Gas Isotopes

Carbon isotopes ( $-46$ ‰ to  $-58$ ‰  $\delta^{13}\text{C}_{\text{PDB}}$  [PDB—Peedee belemnite]; Table 1) of the authigenic calcite clearly indicate that oxidized methane was the main carbon source. These negative values combined with the occurrence of traces of heavier hydrocarbon gases indicate that both biogenic and thermogenic methane production are likely at this site.

Shells of living and dead *Lucinoma* and *Vesicomya* display a wide range of  $\delta^{13}\text{C}$  values ( $+0.1$ ‰ to  $-19$ ‰  $\delta^{13}\text{C}$ ), although 8 of 11 values are between  $-12$ ‰ and  $-19$ ‰. These shell  $\delta^{13}\text{C}$  values are much lower than those reported previously for unaltered shells of marine macrofauna, the lowest being  $\sim -8$ ‰ (e.g., Paull et al., 1989). The  $\delta^{13}\text{C}$  values obtained here indicate two carbon sources for most of the shells, oxidized methane and seawater bicarbonate.

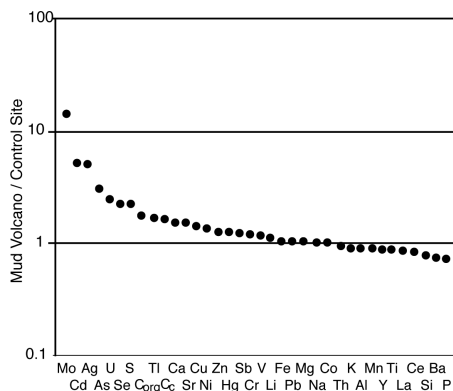
The bivalve shells and authigenic calcite have  $\delta^{18}\text{O}_{\text{PDB}}$  values that range from 1.7‰ to 3.4‰ and 3.7‰ to 3.9‰, respectively (Table 1). This range of values is mostly heavier than would be predicted based on the bottom-water temperature (5.1 °C; Table 1; Emery, 1960) and indicates that temperature-induced fractionation alone cannot account for the degree of disequilibrium. The  $^{18}\text{O}$ -rich samples may reflect formation close to a dissociating hydrate, which produces heavy seawater O<sub>2</sub> (Maekawa, 2004). The shell  $\delta^{18}\text{O}_{\text{PDB}}$  variability likely reflects vital effects (Tanaka et al., 1986), hydrate dissociation accompanied by a strong methane flux (Kastner et al., 1998), and variable flux of deep-seated fluids.

Representative shell and methanogenic calcite samples have the same  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio as seawater, within analytical error (Table 1). This indicates that Sr in both the authigenic calcite and aragonite shells was derived from seawater.

Five gas samples show a range of  $\delta^{13}\text{C}$  values from  $-30.3$ ‰ to  $-58.5$ ‰ (mean  $-39.8$ ‰) for CO<sub>2</sub> and  $-73.1$ ‰ to  $-81.1$ ‰ (mean  $-75.8$ ‰) for CH<sub>4</sub>.

### Diagenesis and $^{13}\text{C}$ Depletion in Bivalve Shells

Sample pretreatments were designed to evaluate the possibility that diagenesis caused

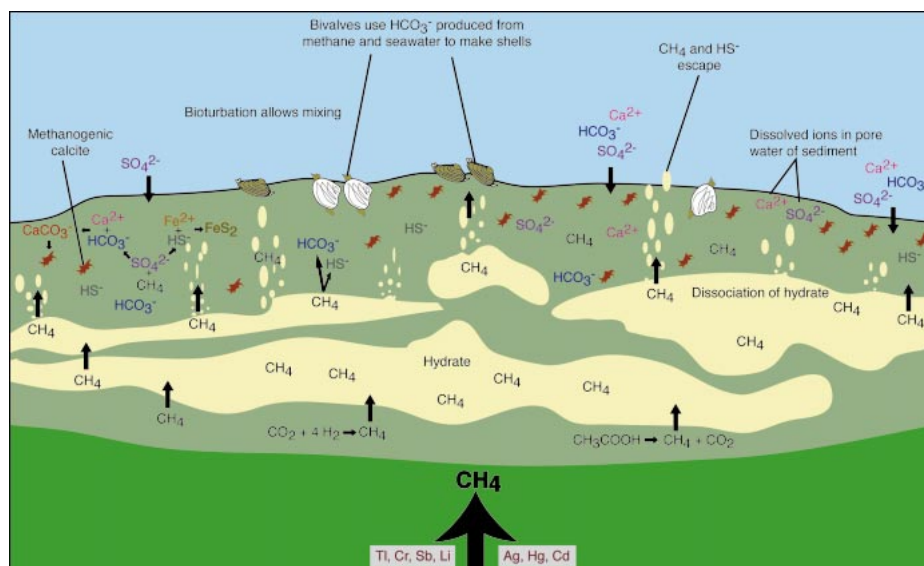


**Figure 2.** Select elements in mud volcano sediment compared to sediment at control site (see Fig. 1). Elements above ratio line equal to 1 are enriched in mud volcano sediment, and those below line are enriched in control site sediment.

$^{13}\text{C}$  depletion in the shells. Those results indicate that diagenesis was not the cause, a conclusion supported by other evidence. The authigenic carbonate is calcite and the shells are aragonite. XRD shows no detectable calcite in the shells, which means that calcite, if present, is  $<0.5\%$ . Such a small amount of authigenic calcite (with a  $\delta^{13}\text{C}$  of  $-58\%$ , our most  $^{13}\text{C}$ -depleted value) in the shells cannot explain their  $\delta^{13}\text{C}$  values based on mass balances. Diagenesis should affect infauna bivalves more than epifauna bivalves; this is not found here. Diagenesis should affect the deeply buried shells more than the near-surface ones; this is also not found here. Chemistry of the bivalve shells suggests that they are unaltered. The collective evidence strongly indicates that diagenesis did not cause the unusual  $\delta^{13}\text{C}$  values of the shells.

### Sediment Composition

Compared to the control site (Fig. 1), sediment from the mud volcano has nearly 15 times more Mo and 5.2–2.2 times more Cd, Ag, As, U, Se, and S (Fig. 2). The mud volcano also has 60%–80% more organic C (mean 2.6%), carbonate C (mean 1.5%), Ti, Ca, and Sr, and 20%–40% more Cu, Ni, Zn, Hg, Sb, Cr, and V than the control site. Mo, U, Cr, and V are redox-sensitive elements concentrated in anoxic environments, which characterize both sites, thus suggesting that metal supply is the main difference. Ag, Hg, Cd, Ti, Li, Cr, As, and Sb were in part leached from basement rocks by deeply circulating fluids, as occurred at a nonhydrate site farther to the south along the San Clemente fault (Hein et al., 2006). Similar Si/Al ratios in control and mud volcano sediments further indicate that Ag is from a deep source and not the result of an augmented biosilica component. These differences cannot be explained by minor differences in sediment mineralogy, major-element composition, sedimentation rates, or



**Figure 3.** Conceptual model for Santa Monica Basin seep-hydrate site and formation of  $^{13}\text{C}$ -depleted calcite and bivalve shells. Methane is derived from geologic reservoir and transported along fault zone with metals (large arrow bottom center) and from microbial and thermal degradation of organic matter in basin sediment below the hydrate. Archaea oxidizes organic matter to produce  $\text{CH}_4$  and  $\text{CO}_2$ .  $\text{CH}_4$  is partly trapped during hydrate formation, but some escapes to vent at seafloor. Authigenic calcite forms in upper  $\sim 1.5$ – $3.0$  m of sediment from carbon derived from anaerobically oxidized methane with  $\delta^{13}\text{C}$  of  $\sim -75\%$  and seawater  $\text{HCO}_3^-$  with  $\delta^{13}\text{C}$  of  $\sim 0\%$ . Bivalve shells reflect larger proportion of seawater dissolved inorganic carbon, with as much as 25% coming from anaerobically oxidized methane. Diagram is not to scale; hydrate upper surface likely varies from  $\sim 1.5$  to 3 m subbottom; lateral distance is tens of meters; vertical distance below hydrate is greatly condensed.

sediment ages. The only viable explanation for the strong metal enrichments is a deep-seated source that also likely provided hydrocarbons to the site.

### CONCEPTUAL MODEL

The Santa Monica Basin cold-seep-hydrate site is characterized by many biogeochemical processes described for other hydrate sites (e.g., Boetius and Suess, 2004). However, the Santa Monica Basin site has unique geological and tectonic characteristics and contains the first documented occurrence of strongly  $^{13}\text{C}$ -depleted macrofauna shells.

The mud volcano receives basement-derived metals by fluid transport along an underlying fault. Petroleum and gases also migrate along this fault zone, because their generation from organic-rich Miocene source rocks is characteristic of basins along the southern California margin (Isaacs and Garrison, 1983). This fossil source of methane augments methane produced by microbial and thermal degradation of organic matter in basin and continental-margin sediments, thereby increasing the total gas flux (Fig. 3). The ascending methane becomes trapped in part during formation of hydrate, the top of which is near 1.5–3.0 m subbottom. Some methane escapes to higher levels by dissociation of the hydrate and by way of breaches in the hydrate layer caused by laterally discontinuous formation and postformational fracturing (Fig. 3). The  $\delta^{13}\text{C}$  values of the authigenic calcite

and the requirement for bicarbonate indicate that carbon is derived from anaerobically oxidized methane coupled with bacterial sulfate reduction ( $\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$ ). The  $\text{HCO}_3^-$  produced by this reaction combines with  $\text{Ca}^{2+}$  to precipitate calcite. As long as sulfate from seawater is supplied to the upper sediment layers, the anaerobically oxidized methane-sulfate reduction will continue to operate. Some methane escapes to the water column unoxidized, as does some  $\text{CO}_2$  and  $\text{HS}^-$ . The methane flux at the sediment-water interface must be very high to support the dense chemosynthetic community. The high methane flux implies that fluid flow rates in the sediment are high (Luff and Wallmann, 2003) and reflects the supply of methane from several sources.

Authigenic calcite  $\delta^{13}\text{C}$  values reflect a mixed carbon source from oxidized methane, with a mean  $\delta^{13}\text{C}$  of  $-75\%$ , and seawater bicarbonate (dissolved inorganic carbon, DIC), with  $\delta^{13}\text{C}$  of  $\sim 0\%$ . These two end members yield maximum contributions of carbon from oxidized methane of 61%–78% for the calcite, assuming no preferential oxidation of  $^{12}\text{CH}_4$  over  $^{13}\text{CH}_4$ . Authigenic calcite forms from several centimeters below the sediment-water interface down to the methane hydrate layer, which encompasses the zone of anaerobically oxidized methane and sulfate reduction. Aerobic oxidation is likely a minor process, because the site is located near the base of the



regional oxygen-minimum zone, where bottom-water O<sub>2</sub> contents are  $\leq 0.3$  ml L<sup>-1</sup> (Emery, 1960). However, bottom-water oxygenation may change from oxic to dysoxic on a millennial scale (Hagadorn et al., 1995).

Because the bivalves live at or near the sediment-water interface, their shells are expected to be less <sup>13</sup>C depleted (more seawater DIC) than the authigenic calcite if they both utilized the same two carbon sources. Given this, it still remains uncertain why the shell <sup>13</sup>C values are so much more negative than values determined previously. There are two possible explanations. If it is simply a matter of the proportion of methane-derived DIC (<sup>12</sup>C-rich food source) to seawater DIC (as much as 25% of carbon is derived from CH<sub>4</sub> assuming -75‰ for CH<sub>4</sub>), then the Santa Monica Basin site must produce much more methane-derived DIC (extreme methane flux and oxidation rates) compared to other sites. This would imply a high rate of replenishment of seawater sulfate, unless other abundant oxidized species were available to form redox couplets with methane. Another explanation for the very negative <sup>13</sup>C values of shells would involve atypical kinetic and metabolic fractionations and symbionts (e.g., McConnaughey et al., 1997), because model calculations indicate that metabolic carbon fractionation occurs only to ~7‰ lighter than the DIC used (Tanaka et al., 1986), but is usually <2‰ lighter (McConnaughey et al., 1997). We favor the former explanation, because the southern California borderland is a major hydrocarbon-producing region that offers an abundant deep-seated source of gas. We propose that extreme methane fluxes and oxidation rates bathe the shells in isotopically light DIC, which directly contributes to their <sup>13</sup>C-depleted isotopic composition.

## CONCLUSIONS

1. Methane and hydrogen sulfide are venting at the seafloor above a shallowly buried methane hydrate that was sampled at the top of a mud volcano located offshore southern California.

2. Abundant authigenic calcite occurs down to the top of the gas hydrate, estimated to be from ~1.5 to 3.0 m subbottom. The calcite is <sup>13</sup>C depleted ( $\delta^{13}\text{C} = -46\text{‰}$  to  $-58\text{‰}$ ), indicating that carbon produced by anaerobically oxidized methane is the main source.

3. The <sup>13</sup>C values of bivalve shells (aragonite) from both living and dead specimens indicate that they used, in part, carbon derived from anaerobically oxidized methane. The <sup>13</sup>C values are highly variable, but most are -12‰ to -19‰. We propose that a much higher supply of methane-derived DIC compared to other sites and variable fluxes from several methane sources explain these unusual

<sup>13</sup>C-depleted shells. This is the first study to document the occurrence of such strongly <sup>13</sup>C-depleted marine macrofauna shells.

4. Mollusks in the geologic record with <sup>13</sup>C-depleted shells, especially if they show a wide range of  $\delta^{13}\text{C}$  values, may reflect paleo-cold-seep-hydrate systems rather than being products of diagenesis.

5. High concentrations of metals in mud volcano sediment are supplied from a deep-seated source by fluids circulating along an underlying fault, which also supplies abundant fossil methane to the seep-hydrate system.

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## Geology

### Methanogenic calcite, $^{13}\text{C}$ -depleted bivalve shells, and gas hydrate from a mud volcano offshore southern California

James R. Hein, William R. Normark, Brandie R. McIntyre, Thomas D. Lorenson and Charles L. Powell II

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