

Stable Isotope Profiles of the Fossil Mollusks from Marginal Marine Environment: Is Carbon from the Seasonal Methanogenesis?

BOO KEUN KHIM*, KATHY W. BOCK AND DAVID E. KRANTZ

College of Marine Studies, University of Delaware, Lewes, DE 19958, USA

**Research Institute of Oceanography, Seoul National University, Seoul 151-742, Korea*

Stable isotope profiles with fine-scale resolution were constructed from the fossil mollusk shells, *Mercernaria mercernaria*, obtained from the late Pleistocene transgressive deposits of Gomez Pit, Virginia, USA. Incremental sampling were made along the axis of maximum growth to provide high-resolution $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records. The $\delta^{18}\text{O}$ shell profiles exhibit a series of pronounced cycles in the overall amplitude, corresponding to strong seasonal variations in temperature, which is apparently positive environmental variable. Contrasts between the patterns of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles reflect the relationship influencing the seasonal carbon cycling in the shallow marine environment. Positive anomalies of the $\delta^{13}\text{C}$ values during the summer were observed to be out of phase with the $\delta^{18}\text{O}$ profile. Such relatively heavier carbon source may be alternated due to seasonal methanogenesis during the summer. A hypothesized methane-based system may be operated in the shallow and marginal marine environment, resulting in a $\delta^{13}\text{C}$ -enriched bicarbonate pool, in which the heavier isotope seems to be incorporated to the shell carbonate.

INTRODUCTION

The underlying assumption for application of stable isotopic geochemistry to mollusk shells is that ^{18}O and ^{13}C are incorporated into shell carbonate in equilibrium with ambient seawater. As a result of this equilibrium process, the isotopic geochemical compositions of the shells record the dynamics of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ fractionation influenced prominently by temperature (Epstein *et al.*, 1953; Mook and Vogel, 1968). Detailed sampling of mollusk shell at closely-spaced interval reflects the seasonal activity of isotopes over the lifespan of the animal. Therefore, information from stable isotope profiles, resolved to an annual level, has permitted both environmental and physiological variables, such as seasonal temperature cycles, transient salinity events, biomineralization associated with ontogeny, and other hydrographic conditions (Williams *et al.*, 1982; Arthur *et al.*, 1983; Krantz *et al.*, 1987; Romanek and Grossman, 1989; Geary *et al.*, 1992; Khim *et al.*, 1996).

Seasonal temperature ranges as well as modes of seasonal carbon cycling have been further inferred through the combined interpretation of oxygen and carbon isotope profiles in mollusk shells. The dominant signal preserved in the $\delta^{18}\text{O}$ profiles of

mollusk shells is the seasonal temperature change, which has been observed and documented in a number of recent studies (Arthur *et al.*, 1983; Geary *et al.*, 1992; Bock, 1994), including some of the classic and pioneering works (Urey *et al.*, 1951; Epstein and Lowenstam, 1953). However, the complete range of ambient seawater temperature variation is usually not recorded in the shell profile because of reduction of growth rate or complete cessation of shell growth (Arthur *et al.*, 1983; Krantz *et al.*, 1987).

Interpretation of $\delta^{13}\text{C}$ profiles is more complex than for oxygen, due to the interaction of potential variables, both environmental and biological, on $\delta^{13}\text{C}$ fractionation (Grossman and Ku, 1986; Romanek *et al.*, 1987). Regardless, the $\delta^{13}\text{C}$ profiles from mollusk shells provided potential clues to environmental conditions, possibly including a record of seasonal carbon cycling. Existing models for interpreting seasonal variations in the $\delta^{13}\text{C}$ of mollusk shells as a reflection of ambient seawater conditions (Killingley and Berger, 1979; Arthur *et al.*, 1983) suggest the following patterns: (1) heavier $\delta^{13}\text{C}$ values during the spring when phytoplankton blooms selectively remove ^{12}C from the dissolved bicarbonate reservoir during photosynthesis to produce isotopically light organic matter

(approximately -20‰); (2) progressively lighter $\delta^{13}\text{C}$ values through the summer as decomposition of organic matter releases ^{12}C into sediment pore-water and bottom-water ΣCO_2 ; and (3) back to the initial state following destratification and mixing of the water column in the fall and winter.

In contrast to this expected $\delta^{13}\text{C}$ cycle in the shallow water areas, we observed distinctly an unexpected more positive $\delta^{13}\text{C}$ values with prominent positive anomalies in the summer season in fossil shells of *Mercenaria mercenaria* collected from a late Pleistocene transgressive unit in Gomez Pit, Virginia, USA. Presented here are the results of a detailed study using the stable oxygen and carbon isotopic composition of well-preserved mollusk shells.

MATERIALS AND METHODS

The fossil specimens, *Mercenaria mercenaria*, were collected from the late Pleistocene transgressive unit in Gomez Pit, Virginia, USA (Fig. 1). Specimens GP-180 and GP-181 were collected from the middle layer (*Mercenaria* layer I) of the outcrop between the oyster biostrome and serpulid zone whereas specimen GP-276 was taken just below serpulid layer of the stratigraphically higher posi-

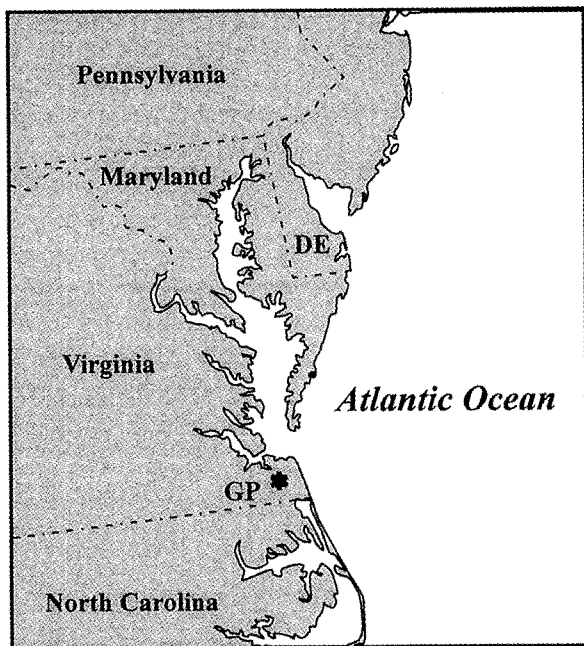


Fig. 1. Map showing the study area. GP stands for Gomez Pit where the late Pleistocene marine transgressive strata was exposed. The mollusk specimens, *Mercenaria mercenaria*, were collected from this area.

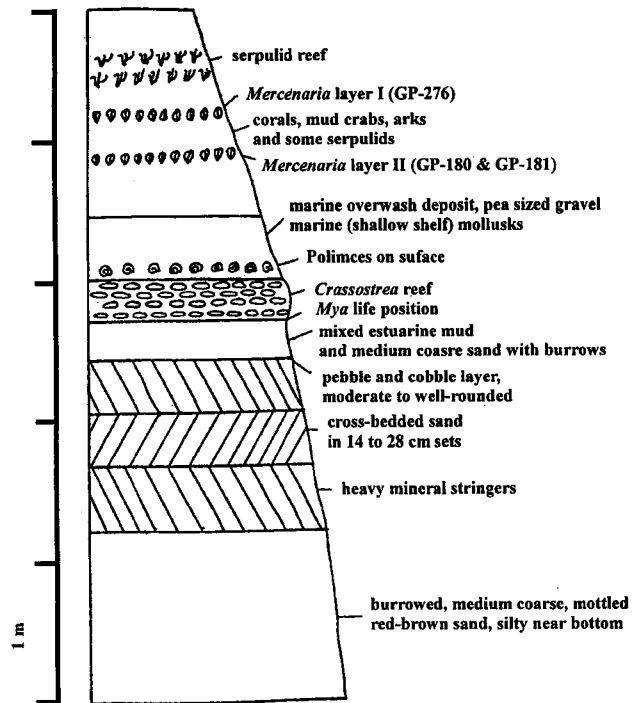


Fig. 2. General cross section of the Gomez Pit study site and sampling position of specimen *M. mercenaria* fossil mollusks (after Bock, 1994).

tion (*Mercenaria* layer II; Fig. 2).

The sedimentary sequences of the U.S. Atlantic Coastal Plain record the major transgressions of the late Tertiary and Quaternary. In this area, the Quaternary deposits are represented by a series of nearshore marine and marginal marine strata bounded by unconformities (Peebles *et al.*, 1984). The preserved stratigraphic sequences of at least four middle to late Pleistocene sea-level highstands have been designated as the Tabb Formation (Johnson, 1972; Mixon, 1985). The unit of interest, the Sedgefield Member of the Tabb Formation, indicates deposition in an estuarine to marginal marine environment during late Pleistocene highstand of sea level correlated with Oxygen Isotope Substage 5e (Toscano and York, 1992; Bock, 1994). The Sedgefield Member comprising the estuarine/lagoon sand and sandy silts contains several abundantly fossiliferous layers (Spencer and Campbell, 1987).

The sample preparation and analyses to produce $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ mollusk profiles follow the standard procedure employed in previous studies (Krantz *et al.*, 1987). The shells were sectioned along the axis of the maximum growth line with a low-speed diamond saw. Before drilling, the outer surface of

each valve was scraped off to remove organic debris or encrusting organisms. After the removal of the shell exterior, the individual carbonate powder samples were obtained incrementally from the outer shell layer avoiding the inner shell layer with a dental drill. Shell carbonate samples were taken approximately one millimeter apart over the years; generally years two through four or five are sampled due to the very thin prismatic layer of year one.

Carbonate powder samples were stored in pharmaceutical gel capsules and sent to mass spectrometer facilities at Rice University for the stable isotopic analyses. Approximately 0.5 mg of each carbonate powder was roasted at 350°C *in vacuo* to remove the organic components of the shell matrix. Samples then were reacted in purified phosphoric acid under vacuum and the evolved CO₂ gas was analyzed on the mass spectrometer to measure the relative ratios of ¹⁸O/¹⁶O and ¹³C/¹²C in each sample. Oxygen and carbon isotopic values are reported in standard δ-notation in permil (‰) relative to the Pee Dee Belemnite (PDB) international standard as below.

$$\delta^{18}\text{O} (\text{‰}) = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \right] \times 1000$$

$$\delta^{13}\text{C} (\text{‰}) = \left[\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \right] \times 1000$$

Analytical precision for both δ¹⁸O and δ¹³C was ±0.1‰ or better based upon duplicate analyses of internal standard and samples.

Stable isotope profiles of fossil Mercenaria mercenaria

The oxygen and carbon isotope profiles of *M. mercenaria* fossil specimens (GP-180, GP-181, and GP-276) are shown in Fig. 3. The δ¹⁸O values measured from mollusk shell carbonate can be used to calculate the temperature range during shell deposition because ¹⁸O is kinetically fractionated as a function of temperature (Epstein *et al.*, 1953). The δ¹⁸O profiles are very similar each other and clearly exhibit seasonal cycles, as would be expected by typical annual variation in seawater temperature. More positive (heavier) δ¹⁸O values are consistent with colder winter temperature, and more negative (lighter) values coincide with warmer summer temperature. However, in the present paper, the detailed paleotemperature estimate was not discussed.

The δ¹⁸O profile of specimen GP-180 shows a

series of four distinct annual cycles (Fig. 3a). Such a series of fluctuation confirms the isotopic variation of shell carbonate in accordance with seasonality (Epstein *et al.*, 1953). The annual cycles display an amplitude in δ¹⁸O ranging from approximately -1.5 to 0.5‰. The δ¹³C profile are not as discernible as the δ¹⁸O profile, but during the summer corresponding to the lighter δ¹⁸O values, the δ¹³C values are relatively a little positive. The δ¹³C values only range from about 0.25 to 0.75‰ over the entire seasonal cycles.

The δ¹⁸O profile of the specimen GP-181 shows a similar cyclic variation to that of specimen GP-180 (Fig. 3b). Up to approximately 75 mm shell height, specimen GP-181 has δ¹⁸O range of -1.5 to 0.4‰ representative of the typical temperature trend compared to that of specimen GP-180. The lighter δ¹⁸O values towards the shell margin from 75 mm shell height most likely represent the result of slow growth. Such ontogenic effects seem to dampen the amplitude of the seasonal cycles in the isotopic profiles, which record the partial range of δ¹⁸O values compared with the younger part. This general trend towards lighter values during ontogeny was also discussed with respect to the onset of reproductive activity in the physiological change (Krantz *et al.*, 1987; Romanek *et al.*, 1987).

The overall δ¹³C values of specimen GP-181 are slightly heavier by 0.5 to 0.7‰ than specimen GP-180 (Fig. 3). Specimen GP-181 shows cyclic variations with seasonal trends in δ¹³C profiles, which is different from that of specimen GP-180, representing relatively lighter δ¹³C values during the summer and heavier excursions occurring in the spring. This may follow the typical model for δ¹³C variation resulting from formation, buildup, and oxidation of isotopically light organic matter to change the δ¹³C of bicarbonate pool in seawater (Arthur *et al.*, 1983).

The δ¹⁸O and δ¹³C profiles of specimen GP-276 are shown in Fig. 3c. The oxygen isotope values of specimen GP-276 range from -2.0 to 0.5‰ but each annual cycle of the δ¹⁸O profile represents the unequal amplitude due to the interannual variability of seasonal temperature. At about 45 mm shell height, a transient peak in δ¹⁸O profile occurs with a roughly corresponding peak in δ¹³C profile. It is interpreted as an apparent reduced-salinity event largely due to freshwater input bringing not only isotopically light carbon into the system to shift the δ¹³C values of the shells towards negative in a more

sense but also a negative $\delta^{18}\text{O}$ transient spike. The $\delta^{13}\text{C}$ profile of specimen GP-276 fluctuates from -0.8 to 1.5‰ (Fig. 3c). While it is a fairly normal range for carbon, the $\delta^{13}\text{C}$ signals are relatively heavier in summer time on the basis of the $\delta^{18}\text{O}$ values controlled primarily by temperature.

Examination of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles within each shell specimen can aid the interpretation on the variation of the environmental condition. Specimen GP-181 has shown a typical in phase variation bet-

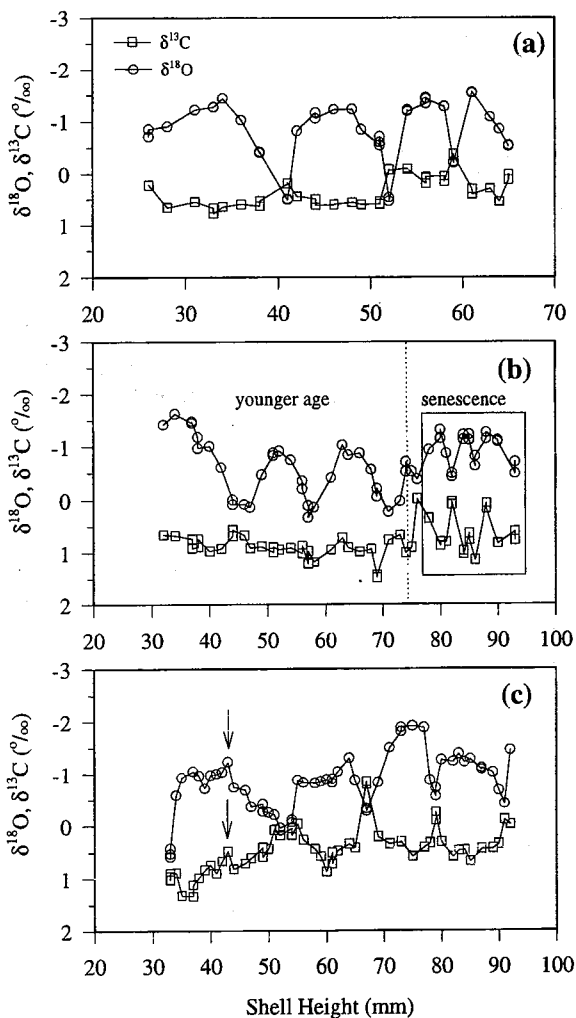


Fig. 3. Stable oxygen and carbon isotope profiles of fossil mollusk shells *M. mercenaria*. (a) specimen GP-180. The $\delta^{18}\text{O}$ profiles exhibit seasonal cycles in seawater temperature becoming "warmer" towards the top of the vertical scale. The scale of horizontal axis is in mm to measure from the umbo. (b) specimen GP-181. The lighter $\delta^{18}\text{O}$ values towards the shell margin from 75 mm shell height most likely represent the senescence of shell growth resulting from slow growth rate. (c) specimen GP-276. At about 45 mm shell height, arrows show that a transient peak in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles is interpreted as an apparent reduced-salinity event due to freshwater input.

ween $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles during the summer months of younger age (Fig. 3b). By contrast, in the stable isotope profiles of GP-180 and GP-276, the $\delta^{13}\text{C}$ curve seems to be out of phase with the $\delta^{18}\text{O}$ curve, departing from each other as summer approaches (Fig. 3a and 3c). The $\delta^{18}\text{O}$ profiles in these cases show the "expected" cycle; the isotopically lightest values occur during the summer, while the winter values are isotopically heavier. Moreover, the $\delta^{13}\text{C}$ values remain relatively positive throughout the summer months. This may suggest a potential alternate source of the elevated $\delta^{13}\text{C}$ during the summer if the existing model was compared for interpreting seasonal variations in the $\delta^{13}\text{C}$ of mollusk shells as a reflection of ambient seawater conditions (Killingley and Berger, 1979; Arthur *et al.*, 1983).

Although the carbon isotopic composition in the ambient seawater varies, as it has many sources and sinks, none of the conventional aerobic pathways could account for this relatively positive shift in $\delta^{13}\text{C}$ values during the summer. The *Mercenaria* specimens were living in a back-barrier lagoonal environment characterized by diaerobic conditions probably sometimes during the mid-summer. One possibility is that the seasonal methane production within the sediments plays a role in providing ^{13}C -enriched carbon for the mollusk shells during the summer growth. Such a methane-based biogeochemical system operates in the shallow marine environment in the summer time (Martens *et al.*, 1986; Whiticar *et al.*, 1986). Because isotopic fractionation during methanogenesis is extreme (-100 to -50‰) and the $\delta^{13}\text{C}$ value of methane is isotopically light, isotopically light carbon in the methane-based biogeochemical system is released directly to the atmosphere as methane bubbles, which can leave a relatively ^{13}C -enriched dissolved bicarbonate pool in the sediment porewater. This remaining heavy $\delta^{13}\text{C}$ pool could be incorporated into mollusk shell production, making the shell $\delta^{13}\text{C}$ values a little more positive and out of phase with the $\delta^{18}\text{O}$ profile. This effect would be expected to occur most frequently in the summer as dissolved oxygen concentrations in the lagoon reached a minimum as a result of density stratification of the water column. Since summer marks an increase in methane production, the relatively more enriched $\delta^{13}\text{C}$ values would occur at this time.

Incorporation of heavy carbon from seasonal methanogenesis

The active microbially-mediated reactions of sedimentary organic matter account for the generation of methane in anoxic sediments below the zone of sulfate depletion (Whiticar *et al.*, 1986; Faber *et al.*, 1990). In this situation, the sedimentary organic matter is fermented through two primary metabolic pathways; acetate fermentation and CO₂ reduction (Fig. 4). Both of these pathways are operated in shallow marine system; however, CO₂ reduction is the dominant mechanism. Carbon dioxide is produced through either methyl conversion or decarboxylation from the organic matter, represented by $\text{CH}_3\text{COOH} \Rightarrow \text{CH}_4 + \text{CO}_2$. The reduction of this produced CO₂ is continued in the saline environment by hydrogen to form methane and water, proceeded by $\text{CO}_2 + 8(\text{H}) \Rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$. This stepwise process is dominant in the sulfate-free zone of marine sediments, allowing the accumulation of methane in the shallow sediments. During the summer months when methane production peaks, the sulfate-reducing zone is quite shallow, ranging less than 10 cm below the sediment-water interface (Kipphut and Martens, 1982). Below the sulfate-free zone, these depths correspond to the onset of methane accumulation, which would affect the chemistry of biological calcium carbonate deposition of the indigenous infauna, i.e., shell formation in *M. mercenaria*.

According to Whiticar *et al.* (1986), the $\delta^{13}\text{C}$

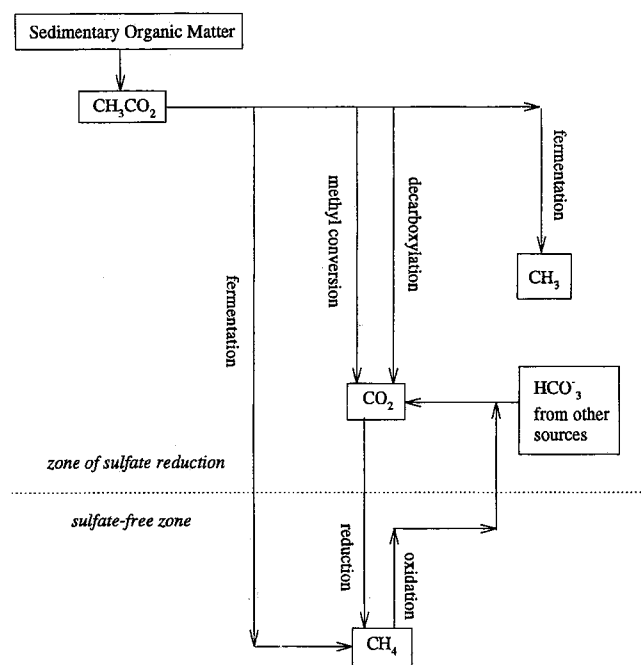


Fig. 4. Schematic diagram showing the pathways of methane production by acetate fermentation and CO₂ reduction in the marine environment (after Whiticar *et al.*, 1986).

value for methane is very negative, with $\delta^{13}\text{C}$ values ranging generally either between -110 and -65‰ for the formation through the CO₂ reduction or between -65 and -50‰ for the formation through the fermentation. The $\delta^{13}\text{C}$ values of methane obtained by Martens *et al.* (1986) at Cape Lookout Bight, North Carolina confirm these isotopically light $\delta^{13}\text{C}$ values. The corresponding $\delta^{13}\text{C}$ values of ΣCO_2 in seawater vary between about -11 and -3.0‰ with the summer values averaging between -10 and -8‰. Additionally, $\delta^{13}\text{C}$ values for CO₂ coexisting with bacterially-produced methane ranged from -20 to +10‰.

Since the solubility of methane is low, methanogenesis must play an important role in the formation of bubbles in the submerged anoxic layer. Because of the large fractionation during methanogenesis, the dissolved carbon remaining in the sediment porewaters would be enriched in ¹³C after the methane bubbles out to the atmosphere. The $\delta^{13}\text{C}$ ranges of the remaining ΣCO_2 in methanogenic sediments have been observed to be between -20 and +10‰ (Faber *et al.*, 1990) and between 0 and +5‰ (Reeburgh, 1982).

By contrast, following oxidation of sedimentary organic matter in the sulfate zone, utilization of concurrently-produced methane as a carbon source by sulfate-reducing bacteria would result in the isotopically light ΣCO_2 released from methane oxidation. In this case, the $\delta^{13}\text{C}$ value of interstitial carbon dioxide in the sediment porewater would lead to negative $\delta^{13}\text{C}$ values. However, high temperatures during the summer season is likely to prevent conversion of methane in the sediment porewater before ebullition to the atmosphere.

Some previous works have demonstrated the distinct seasonal variation of biogenic methane production under wet anoxic environments (Martens *et al.*, 1986; Whiticar *et al.*, 1986). The possible cause of the observed seasonal variation of methane production could be changes in methane production mechanisms. Such variations appears to be driven by seasonal temperature changes because the rate of decomposition of organic matter is proportional to increases of temperature as the summer approaches. This previous work indicates that methane production is highly seasonal with a marked increase from May to October (Martens *et al.*, 1986).

SUMMARY

From the observation of the $\delta^{13}\text{C}$ positive ano-

malies in the isotope profiles constructed from the fossil mollusk shells *Mercernaria mercernaria*, we hypothesize that seasonal methanogenesis occurred in the shallow marine substrate below the zone of sulfate depletion, in which the mollusks lived. This microbial mechanism would have utilized isotopically light carbon to generate the isotopically light methane and $\delta^{13}\text{C}$ -enriched bicarbonate pools. However, it must be substantiated for the recent corresponding environments that the $\delta^{13}\text{C}$ distribution in such pore fluids is explainable seasonally by the strong positive $\delta^{13}\text{C}$ -shift.

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REFERENCES

- Arthur, M.A., D.F. Williams and D.S. Jones, 1983. Seasonal temperature-salinity changes and thermocline development in the Mid-Atlantic Bight as recorded by the isotopic composition of bivalves. *Geology*, **11**: 655-659.
- Bock, K.W., 1994. Paleoenvironmental interpretation of the Late Pleistocene of Gomez Pit, Virginia. M.S. Thesis, University of Delaware, Lewes, Delaware, 123 pp.
- Epstein, S. and H.A. Lowenstam, 1953. Temperature-shell-growth relations of recent and interglacial Pleistocene shoal water biota from Bermuda. *J. Geol.*, **61**: 424-438.
- Epstein, S., R. Buchsbaum, H.A. Lowenstam and H.C. Urey, 1953. Revised carbonate-water isotopic temperature scale. *Geol. Soc. Am. Bull.*, **64**: 1315-1326.
- Faber, E., W.J. Stahl and M.J. Whiticar, 1990. Carbon and hydrogen isotope variations in marine sediment gases. In: *Facts of Modern Biogeochemistry*, edited by V. Ittekkot.
- Geary, D.H., T.A. Brieske and B.E. Bemis, 1992. The influence and interaction of temperature, salinity, and upwelling on the stable isotopic profiles of strombid gastropod shells. *Palaios*, **7**: 77-85.
- Grossman, E.L. and T. Ku, 1986. Oxygen and carbon isotope fractionation in biogenic aragonite: Temperature effects. *Chem. Geol.*, **59**: 59-74.
- Johnson, G.H., 1972. *Geology of the Yorktown, Poquoson West, and Poquoson East Quadrangles, Virginia*. Va. Div. Min. Res. Rept. Invest., **41**, 72 pp.
- Khim, B.K., T. Nobuhara and D.E. Krantz, 1996. Stable isotope records of the Pliocene fossil *Akebiconcha kawamurai* (Bivalvia: Vesicomysidae) from the Tamari Formation, Central Japan: Indication of chemoautotrophic symbiosis. *Trans. Proc. Palaeont. Soc. Japan*, **182**: 448-453.
- Killingley, J.S. and W.H. Berger, 1979. Stable isotopes in a mollusk shell: detection of upwelling events. *Science*, **205**: 186-188.
- Kipphut, G. and C.S. Martens, 1982. Biogeochemical cycling in an organic-rich coastal marine basin- 3. Dissolved gas transport in methane-saturated sediments. *Geochim. Cosmochim. Acta*, **46**: 2049-2060.
- Krantz, D.E., D.F. Williams and D.S. Jones, 1987. Ecological and paleoenvironmental information using stable isotope profiles from living and fossil molluscs. *Palaeogeog., Palaeoclim., Palaeoecol.*, **58**: 249-266.
- Martens, C.S., N.E. Blair, C.D. Green and D.J. Des Marais, 1986. Seasonal variations in the stable carbon isotopic signature of biogenic methane in a coastal sediment. *Science*, **233**: 1300-1303.
- Mixon, R.B., 1985. Stratigraphic and geomorphic framework of uppermost Cenozoic deposits in the southern Delmarva Peninsula, Virginia and Maryland. *U.S. Geol. Surv. Prof. Pap. 1067-G*, 53 pp.
- Mook, W. and J.C. Vogel, 1968. Isotopic equilibrium between shells and their environment. *Science*, **159**: 874-875.
- Peebles, P.C., G.H. Johnson and C.R. Berquist, 1984. The middle and late Pleistocene stratigraphy of the outer coastal plain, southeastern Virginia. *Vir. Min.*, **30**: 13-22.
- Reeburgh, W.S., 1982. A major sink and flux control for marine sediments: Anaerobic consumption, In: *The Dynamic Environment of the Ocean Floor*, edited by K.A. Fanning and F.T. Manheim, Lexington Books, Lexington and Toronto.
- Romanek, C.S. and E.L. Grossman, 1989. Stable isotope profiles of *Tridacna maxima* as environmental indicators. *Palaios*, **4**: 402-413.
- Romanek, C.S., D.S. Jones, D.F. Williams and D.E. Krantz, 1987. Stable isotopic investigation of physiological and environmental changes recorded in shell carbonate from the giant clam *Tridacna maxima*. *Mar. Biol.*, **94**: 385-393.
- Spencer, R.S. and L.D. Campbell, 1987. The fauna and paleoecology of the late Pleistocene marine sediments of southeastern Virginia. *Bull. Am. Paleontol.*, **92**: 1-124.
- Toscano, M.A. and L.L. York, 1992. Quaternary stratigraphy and sea-level history of the U.S. Middle Atlantic Coastal Plain. *Quat. Sci. Rev.*, **11**: 301-328.
- Urey, H.C., H.A. Lowenstam, S. Epstein and C.R. McKinney, 1951. Measurement of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark, and the southeastern United States. *Geol. Soc. Am. Bull.*, **62**: 399-416.
- Whiticar, M.J., E. Faber and M. Schoell, 1986. Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation: Isotope evidence. *Geochim. Cosmochim. Acta*, **50**: 693-709.
- Williams, D.F., M.A. Arthur, D.S. Jones and N. Healy-Williams, 1982. Seasonality and mean annual sea surface temperatures from isotopic and sclerochronological records. *Nature*, **296**: 432-434.