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Stable Isotopic Analyses of Selected Narragansett Bay Molecules

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STABLE ISOTOPIC ANALYSES OF SELECTED NARRAGANSETT BAY MOLLUSCS

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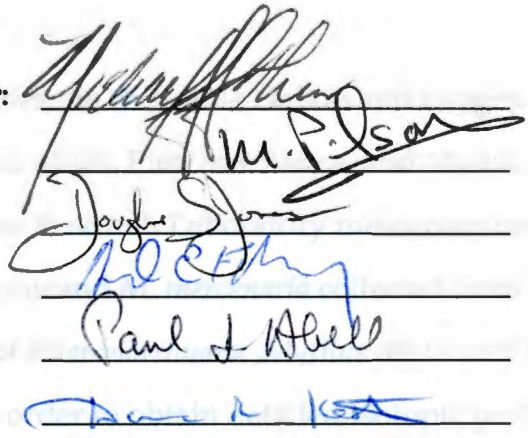

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THESIS ABSTRACT

Mollusc shells contain a potentially detailed record of both the life history and the environmental changes experienced by the mollusc during growth, and have been used to interpret past environmental conditions based on chemical analyses of the shell. Most of these previous studies, however, did not include detailed sampling of local environmental conditions during the time of shell growth to provide an important environmental database for direct comparison to the shell record. Thus, most geochemical interpretations of shell records presume reflection of environmental conditions, without rigorous testing of the accuracy of the relationship. The comparison of environmental conditions to the shell record is especially important if mollusc shells are to be used as reliable paleoenvironmental monitors.

This master's thesis examines the the stable carbon and oxygen isotopic signals from the shells of *Mytilus edulis, Pitar morrhuana,* and *Nucula annulata* grown in the Marine Ecosystems Research Laboratory mesocosm tanks at the Graduate School of Oceanography and *M. mercenaria* collected from Narragansett Bay, Rhode Island. The shells of *Pitar morrhuana ,Mytilus edulis* and *M. mercenaria* were incrementally sampled in order to obtain detailed isotopic profiles of the shell records. In this thesis I compare the isotope results from the shells to the observed shell growth patterns and to carbon and oxygen isotopic measurements of the water in Narragansett Bay . In addition, to develop a better understanding of ecological influences on growth rate, we set out to assess the suitability of *Pitar morrhuana, Mytilus edulis* and *M. mercenaria* as monitors of environmental conditions in the bay.

The isotopic analyses, in conjunction with the detailed data available from the MERL mesocosms, have enabled us to accurately interpret the $\delta^{18}O$ and $\delta^{13}C$

signals in the shells of these bivalves in terms of the seasonal timing of growth for *Pitar* and *Mytilus* and the known variations in the chemical and physical properties of the water in which they grew. The data indicate that the shells of both *Pitar* (aragonite) and *Mytilus* (calcite-outer layer only) appear to be forming at oxygen isotopic equilibrium with the ambient water and that the $\delta^{18}O$ profiles from these specimens are primarily controlled by variations in water temperature. The oxygen isotopes also indicate that in Narragansett Bay *Mytilus* has a longer growing season than *Pitar* by approximately one month at either end of the growing season.

The $\delta^{18}O$ analyses of shell samples of *M. mercenaria*, in conjunction with the water isotopic measurements, indicate that the shell of this species does not form in isotopic equilibrium with the surrounding sea-water. The measured $\delta^{18}O$ of the shell aragonite is typically 1.5‰ depleted relative to the values predicted with the aragonite–water isotopic fractionation equation of Grossman and Ku (1986). Although the isotopic fractionation is a problem for estimating absolute temperatures using the observed shell values, the oxygen isotopic profiles can be interpreted in terms of relative (high-low) seasonal temperature variations. The amplitude and cycles of $\delta^{18}O$ variations in the outer shell layer enable one to determine the seasonal timing of growth of *M. mercenaria* living in Narragansett Bay. These observations are verified by the analyses of samples taken from the outer shell edge of specimens collected during different times of the year. The growth history of the specimens, as revealed by the oxygen isotopes, indicates that the longest growing seasons occur during the years of fastest shell growth and it appears that with increasing age the growing season is restricted to warmer temperatures.

The influence of productivity on the $\delta^{13}C$ compositions of the *Pitar* and the *Mytilus* shell carbonate and possible associations with the carbon cycling in the

MERL tanks and Narragansett Bay were also noted. The different eutrophication levels of the mesocosms apparently had a profound affect upon the $\delta^{13}C$ composition of the *Nucula* shells. *Nucula* specimens from tanks with higher nutrient loadings (8x, 16x, and 32x) had much heavier shell $\delta^{13}C$ values than specimens from the normal nutrient level (control) mesocosms. Apparently much of the lighter carbon (C-12) was drawn out of the water column (and stored in the organic matter) due to the higher primary productivity in the tanks with increased nutrient loading.

The $\delta^{13}C$ measurements of the both the shell edge and the incremental samples from the *M. mercenaria* specimens do not exhibit any obvious seasonal trends. The $\delta^{13}C$ values obtained are much lighter than predicted, indicating that a portion of the carbon isotopic signal is probably derived from the uptake of isotopically light metabolic carbon during shell formation. This isotopically light metabolic carbon is most likely from the normal respiration occurring within the organism.

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The most important acknowledgement goes to my wife Carolyn (who didn't really know what she was getting into when we moved to Rhode Island), thanks for putting up with it all. I have appreciated all that you have done, far more than I can possibly express.

PREFACE

This master's thesis is written in the manuscript format and consists of two related papers. The first manuscript, Stable Isotope Records From *Pitar morrhuana, Mytilus edulis* and *Nucula annulata* Grown in an Experimental Mesocosm, examines the the stable carbon and oxygen isotopic signals from the shells of several species of molluscs grown in the Marine Ecosystems Research Laboratory mesocosm tanks at the Graduate School of Oceanography. The shells of *Pitar morrhuana* and *Mytilus edulis* were incrementally sampled in order to obtain detailed isotopic profiles of the shell records. The isotopic analyses, in conjunction with the detailed data available from the MERL mesocosms, have enabled us to accurately interpret the $\delta^{18}O$ and $\delta^{13}C$ signals in the shells of these bivalves in terms of the seasonal timing of growth for *Pitar* and *Mytilus* and the known variations in the chemical and physical properties of the water in which they grew.

The second manuscript, Isotopic Disequilibrium Observed in *Mercenaria mercenaria* From Narragansett Bay, Rhode Island examines the carbon and oxygen stable isotopic signals from the shells of *M. mercenaria* collected at different stations in Narragansett Bay. Carbon and oxygen isotopic measurements of the water in Narragansett Bay have allowed us to interpret the isotopic signals in the shells of *M. mercenaria* and to verify the seasonal nature of the observed variations of the shell. The $\delta^{18}O$ analyses of shell samples of *M. mercenaria*, in conjunction with the water isotopic measurements, indicate that the shell of this species does not form in isotopic equilibrium with the surrounding sea-water.

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STABLE ISOTOPE RECORDS FROM *PITAR MORRHUANA*, *MYTILUS EDULIS*, AND *NUCULA ANNULATA* GROWN IN AN EXPERIMENTAL MESOCOSM

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Abstract

The isotopic analysis of incremental shell samples from *Pitar morrhuana*, *Mytilus edulis* and *Nucula annulata* grown in mesocosm tanks demonstrates the utility of this method for determining shell growth patterns and reconstructing environmental conditions as recorded in the shell carbonate. The isotopic analyses, along with the detailed data available from the MERL mesocosms, have enabled us to accurately interpret the $\delta^{18}O$ and $\delta^{13}C$ signals in the shells of these bivalves in terms of known variations in the chemical and physical properties of the water in which they grew. We have determined the seasonal timing of growth for the bivalves *Pitar* and *Mytilus* by means of the range and cycles of the $\delta^{18}O$ variations. The data indicate that the aragonite shell of *Pitar* appears to be forming at oxygen isotopic equilibrium with the ambient water (as defined by the aragonite–water–temperature equilibrium equation of Grossman and Ku (1986)) and that the $\delta^{18}O$ profile from this specimen is primarily controlled by temperature changes. These data indicate that in Narragansett Bay *Mytilus* has a longer growing season than *Pitar* by approximately one month at either end of the growing season. *Mytilus* apparently ceases shell formation when the water temperature dips below about 4–6°C, whereas the critical temperature for *Pitar* is approximately 10 °C. Both species grow through the spring, summer and fall. *Nucula* has been shown to record mainly spring values of $\delta^{18}O$ in its shell, although this interpretation is based on whole shell analyses.

The influence of productivity on the $\delta^{13}C$ composition of shell carbonate and possible associations with the carbon cycling in the MERL tanks and Narragansett Bay was also noted. The *Pitar* specimen exhibited low amplitude cycles of $\delta^{13}C$ that seem to correlate with the observed phosphate cycling in the bay. The carbon isotopic results from the detailed sampling of *Pitar* and *Mytilus* indicates that both specimens are utilizing a depleted source of carbon for a

fraction of the total carbon incorporated into the carbonate. We suggest that in addition to the ambient dissolved inorganic carbon, these molluscs are incorporating metabolic carbon during carbonate precipitation. The effect of eutrophication on the shell carbonate of *Nucula* grown in tanks with nutrient addition was reflected in elevated values of $\delta^{13}C$ in the treated tanks.

INTRODUCTION

Mollusc shells contain a potentially detailed record of both the life history and the environmental changes experienced by the mollusc during growth, and have been used to interpret past environmental conditions based on chemical analyses of the shell. Recently the results of stable isotopic analyses of closely spaced, incremental samples taken along the axis of radial growth on mollusc shells have been used to draw inferences about environmental variablility (e.g., Killingley and Berger, 1979; Wefer and Killingley, 1980; Killingley, 1981; Jones et al., 1983; Arthur et al., 1983; Williams et al., 1982; Krantz et al., 1984; Romanek et al., 1986). The results of these studies demonstrate the utility of oxygen isotopes as a tool for estimating growth rate, age, and seasonality of shell growth, as well as their potential utility for addressing such diverse problems as history of coastal upwelling, environmental reconstruction, and interpretation of archeological sites. Most of these previous studies, however, did not include detailed sampling of local environmental conditions during the time of shell growth to provide an important environmental database for direct comparison to the shell record. Thus, most geochemical interpretations of shell records presume reflection of environmental conditions, without rigorous testing of the accuracy of the relationship. The comparison of environmental conditions to the shell record is especially important if mollusc shells are to be used as reliable paleoenvironmental monitors.

Mollusc shells collected from the experimental and control tanks at the Marine Ecosystems Research Laboratory (MERL) at the University of Rhode Island's Graduate School of Oceanography, offer a unique opportunity to compare the results of detailed isotopic analyses of molluscan shell carbonate with the environmental conditions in existence during growth. The temperature,

salinity, and water samples (collected for $\delta^{18}O_{water}$ and analyses of $\delta^{13}C$ of total dissolved carbon (TDC)) provide an environmental chronology for comparison to the oxygen and carbon isotope records of the shell. The use of different species of molluscs (grown in the same MERL tanks) allows for interspecies comparisons of growth rates, periods of maximum growth and seasonality of growth. The examination of several different species should assist in the recognition of an "optimum species" for use as an environmental monitor for future work in Narragansett Bay.

The objectives of this investigation were : 1) to measure the carbon and oxygen isotopic shell profiles of three common species of molluscs: *Pitar morrhuana, Mytilus edulis* and *Nucula annulata*; 2) to compare the measured carbon and oxygen isotopes of the shells of these molluscs with the results of the measured water values in order to verify the isotopic equilibrium formation of the shell carbonate (in terms of known aragonite and calcite water/temperature equilibria); 3) to characterize the resulting isotopic profiles in terms of molluscan growth and relationships to observed internal growth increments; and 4) to compare the isotopic results of the three species examined to isotopic investigations of other molluscan species.

PREVIOUS STABLE ISOTOPIC INVESTIGATIONS OF MOLLUSC SHELLS

Harold Urey suggested in 1947 that variations in the temperature of the water from which $CaCO_3$ is precipitated could lead to measurable variations in the $^{18}O/^{16}O$ ratio of the carbonate. The earliest oxygen stable isotope work by Epstein et al., 1951; Urey et al., 1951; Epstein and Lowenstam, 1953, and Epstein et al., 1953, was done on shell samples from molluscs grown in controlled tanks. In these initial experiments the shells of living molluscs were purposely damaged

by drilling or notching, and the subsequent calcite shell repair was examined isotopically, in conjunction with isotopic analyses of water samples from the same tanks. This work demonstrated the empirical relationship between the $^{18}O/^{16}O$ ratio of the shell carbonate and the temperature of the water, if the $\delta^{18}O$ value of the water was known. The original calcite-temperature (or paleotemperature) equation of Epstein et al. (1953) was modified slightly by Craig (1965). The earlier paleotemperature equations relating the equilibrium oxygen isotope fractionation as a function of temperature were for the calcite polymorph of calcium carbonate. Most molluscs, however, form shells of aragonite and some are bimineralic (Wilbur and Saleuddin, 1983). Grossman (1982) and Grossman and Ku (1981, 1986) have calculated equilibrium equations for the biogenic formation of the aragonite polymorph, based on molluscan and foraminiferal samples.

The utilization of modern mass spectrometers, requiring much smaller sample sizes, has enabled us to investigate the stable isotopic records of molluscan shells using detailed sampling methods. The more recent isotopic work involving molluscs generally involves closely spaced sampling of the outer shell in order to obtain a high-resolution isotopic record. These studies have revealed seasonal temperature and growth patterns using oxygen isotope compositions (Jones et al., 1983; Williams et al., 1982; Krantz et al., 1984; Romanek et al., 1986; Krantz et al., 1987), and have helped determine the initiation and/or cessation of seasonal growth. The investigation of Jones et al. (1983) used sequential isotopic samples to document the annual periodicity of the major shell increments observed in *Spisula solidissima*, as proposed earlier by Jones (1980). Other studies have demonstrated that coastal upwelling changes can be related to the carbon isotopic composition of the water as recorded in the molluscan shell (Killingley and Berger, 1979, Arthur et al., 1983). The oxygen isotopes of detailed

shell samples from archeological shell middens have also been used to determine the season of shell collection (Shackleton, 1973, Killingley, 1981). Work involving paleo-salinity reconstructions using the oxygen isotopic composition of mollusc shells as related to changes in salinity, rather than temperature, have been done in some areas where a wide geographic distribution of molluscs of the same age can be found (Eisma et al., 1976, Rye and Sommer, 1980).

ENVIRONMENTAL SETTING

Narragansett Bay

Narragansett Bay, Rhode Island, (Figure 1) is a weakly stratified, temperate estuary with strong tidal mixing and relatively low fresh water input (Pilson 1985a). Salinity variations in Narragansett Bay are relatively minor and are predominantly controlled by variations in the fresh water input. The tidal input into the bay is typically 250 times that of the fresh water (Hicks 1959). The annual precipitation (averaging 104.8 cm per year, from 1905 – 1981) to the drainage basin feeding Narragansett Bay is relatively constant, but the annual runoff is seasonal, with the greatest runoff usually occurring during January to April.

Salinities decrease from south (lower Bay) to north (upper bay) and from the bottom to the surface. The surface salinities in the lower part of Narragansett Bay fall within a fairly narrow range of 29‰ to 33‰ (Hicks 1959). The vertical salinity stratification in the lower bay is generally less than 3‰ during most of the year. The average bay (whole bay) to ocean salinity difference is typically 2.80‰, (Pilson 1985a). The water temperatures in lower Narragansett Bay, as measured at the Graduate School of Oceanography (GSO) dock and MERL laboratory (Figure 2), vary from a high of 22°-$\pm$1°C during July and August to a low of 1°-$\pm$1°C in January and February. A seasonal thermocline forms near the

Providence River in the upper bay during the summer, but is not usually present in the lower Bay.

MERL Mesocosms

The MERL mesocosm tanks are designed to mimic the conditions in mid-Narragansett Bay and to permit the alteration of those conditions for experimental work. The 14 outdoor tanks are constructed of fiberglass, measuring 1.8 meters wide by 5.5 meters tall, and are temperature controlled to within 2°C of the water temperature in the adjacent bay. The tanks operating with a sediment layer have approximately 30 cm of Narragansett Bay sediment and the associated bay biota, collected by box core from a mid-bay station 8 km northeast (41°35'N and 71°22'W) of the Graduate School of Oceanography (GSO). The seawater inlet system that feeds the MERL tanks originates 2 – 3 meters (depending on the tide) below the water surface, under the GSO dock. Water from the bay is continuously pumped into a header tank at MERL and fed from the header tank to the mesocosm tanks at regular intervals to maintain a turnover time of approximately 27 days in the tanks. Due to the continuous pumping, the header tank has a turnover time of approximately 15 minutes. The mesocosm tanks are mechanically mixed 4 times daily for a period of 2 hours (4 hours off, 2 hours on) with a vertical plunger that imitates tidal and turbulence conditions in the bay. The MERL conditions in the mesocosms have been shown (Pilson et al., 1980; Oviatt et al., 1981; Pilson 1985b) to mimic the magnitude and timing of the seasonal cycles of temperature, nutrients, production, and benthic respiration that occur in Narragansett Bay. During normal mesocosm operation the tanks are routinely monitored for temperature, salinity, seawater flow, light, pH, alkalinity, fluorescence, dissolved oxygen, total CO_2, total nutrients, and chlorophyll-a levels.

A sampling bias may be present when comparing water samples taken from the header tank and extrapolating the results to the other MERL tanks or the lower bay. Such a bias is possible because of the shallow depth of the sea-water intake for the MERL tanks and the difference in turnover times between the header tank and the other mesocosm tanks. At a depth of less than 3 meters, the intake only samples the surface water, which is warmer and lower in salinity (and hence lower values of $\delta^{18}O$) than the water near the bottom. The short turnover time of the water in the header tank (approximately 15 minutes) results in a sample of surface water near the intake averaged over only that time interval. Because of the much longer turnover time of the mesocosms tanks (27 days), many of the short term variations that are observed in the header tank water are damped out (to varying degrees) in the mesocosm tanks. This effect can be observed in the salinity measurements taken simultaneously from the header tank and tank 12 during 1984 and 1986 (Figure 3). Note that the average salinity for 1986 for both tanks is approximately the same (30.9‰). Measurements of the $\delta^{18}O$ of the header tank water would be expected to exhibit similar fluctuations that would also be more variable than measurements from the other tanks.

METHODS

$\delta^{18}O$ Water & $\delta^{13}C$ Dissolved Inorganic Carbon Samples

Water samples for the determination of $\delta^{13}C$ of dissolved inorganic carbon (DIC) and $\delta^{18}O$ water were collected from the MERL tanks between July 1986 and August 1987 (water samples were unavailable from the nutrient addition experiment time period– June 1982 - Sept. 1983). Samples were collected and stored in borosilicate glass vials (15 ml) and capped with rubber serum stoppers. Some samples were poisoned with a saturated solution of $HgCl_2$ (using 1 ml

$HgCl_2$ to 200 ml seawater), others were left unpoisoned. Approximately half of the samples were frozen after collection while the others were either analyzed immediately, stored at room temperature or stored under refrigeration at 3–4°C. The majority of the reported $\delta^{13}C$ DIC water samples were analyzed quickly after collection, usually less than 3 hours between sample collection and CO_2 extraction. Occasional leakage was apparent in the unfrozen samples because near atmospheric $\delta^{13}C$ values of –5 to –7‰ PDB were measured from several of the samples (both poisoned and unpoisoned). This leakage probably occurred around, or through, the rubber serum stoppers while the samples were stored at room temperature or refrigerated. $\delta^{13}C$ analysis of poisoned and unpoisoned samples collected simultaneously from the same tank, and immediately processed through the extraction line, revealed occasional contamination (much lighter values) of the poisoned samples. This probably occurred when the $HgCl_2$ solution was either not sealed properly during storage and/or not prepared with CO_2-free (distilled, boiled) water.

The dissolved inorganic carbon was extracted by acidification of the water sample with 100% phosphoric acid followed by stripping of the CO_2 from the sample using helium carrier gas, as described by R. Fairbanks (pers comm., 1986). The extraction line consisted of a stripping vessel equipped with a sintered glass frit and a replaceable serum injection port, two water separation traps (using a "slush" of isopropyl alcohol mixed with liquid nitrogen), a liquid nitrogen trap to collect the CO_2, and a metal bellows pump to recirculate the carrier gas. Samples were prepared as follows: the entire extraction line was evacuated with a rough pump, approximately 1 ml of acid was then added to the stripping vessel and pumped down, helium was let into the line to roughly 1 atmosphere pressure and the sample (usually about 10 ml in size) was injected using a glass syringe into the stripping vessel. The helium was pumped through the line for 20 to 25

minutes, after which the trapped CO_2 was purified and isolated for later analysis on the mass spectrometer. The best results were obtained when the phosphoric acid was pumped down just prior to a sample extraction. The storage of the samples prior to extraction was also important. Freezing the samples immediately after collection proved to be the most reliable method of storage. Unless otherwise noted, all oxygen and carbon isotopic ratios are given in the conventional delta (δ) notation as the per mil (‰) enrichment or depletion of ^{18}O, or ^{13}C, relative to the Pee Dee Belemnite (PDB) standard (Epstein et al., 1953), where: $\delta = (R_s/R_{ref} - 1) \times 1000$; R_s = isotopic ratio of sample gas and R_{ref} = isotopic ratio of the reference gas, all reported vs. PDB. The measured precision of duplicate water samples (free of contamination) using this extraction technique was $\pm$ 0.1‰ .

The $\delta^{18}O$ water samples were prepared following the method described by T. F. Anderson (pers. comm., 1987): a 1 gram sample of water is placed (using a glass syringe and Tygon tubing) in the rounded bottom of a 10 mm borosilicate tube. The water sample is connected to a vacuum line (using a Cajon Ultra-Torr fitting) and frozen with an isopropyl alcohol-liquid nitrogen trap (IPA trap). The water sample is then pumped down using a rotary vacuum pump to remove atmosphere and dissolved gases. The water sample is isolated from the pump, thawed under vacuum, refrozen and pumped down again. Approximately 50-100 micromoles of pure, dry CO_2 gas is frozen with the sample using liquid nitrogen. The sample tube is flame sealed and placed in a 25°C water bath for a minimum of 8 hours to allow for complete equilibration between the H_2O and CO_2. The equilibrated sample is reattached to the vacuum line and frozen with an IPA trap. The CO_2 is then trapped out with liquid nitrogen and purified for analysis on the mass spectrometer. All $\delta^{18}O_{water}$ values are reported in the delta (δ) notation relative to Standard Mean Ocean Water, or SMOW (Craig, 1961). The

SMOW values were corrected to PDB values (PDB = SMOW + 0.22‰) for use in the carbonate-temperature fractionation equations of Grossman and Ku (1986) and Epstein et al., (1953).

Molluscan Shell Samples

Shells of living *Mytilus edulis, Nucula annulata,* and *Pitar morrhuana* were collected from MERL tanks in September 1984. The shells had been growing in the tanks since June 1982, when they were collected as part of the sediment samples from Narragansett Bay. The MERL facility was conducting a eutrophication experiment (via inorganic nutrient additions) during this time, as described by Nixon et al., (1984) and Frithsen et al., (1985), with different mesocosm tanks subjected to: zero nutrient addition (control tanks), 2x, 4x, 8x, 16x and 32x the normal nutrient loading of Narragansett Bay. The shells of *Pitar* and *Mytilus* that we selected for detailed isotopic investigation were from the same mesocosm control tank (T-0), and the shells of *Nucula* were from the control tank, the 8x, 16x and 32x tanks. *Pitar morrhuana* is considered an interface feeder, *Nucula annulata* a subsurface deposit feeder, and *Mytilus edulis* is an epifaunal filter feeder.

The interiors of the molluscan shells were carefully cleaned of organic matter, then dried at room temperature. The right valves from a specimen of *Mytilus edulis* (length = 63 mm) and *Pitar morrhuana* (length = 42 mm) were sectioned along the radial growth axis (from the umbo to the ventral margin) using a diamond wafer blade on a variable speed sectioning saw. The periostracum of each shell was scraped or filed off prior to sampling. The individual samples for isotopic analysis were taken from the outer shell layer using a high speed drill and a 0.5 mm diameter carbide dental burr (Jones 1980,

Jones et al., 1983). Each powdered sample was ground off parallel to the growth bands in successive fashion across the external shell surface.

Samples for isotopic analyses were roasted under vacuum at 390°C for one hour and then reacted in 100% orthophosphoric acid at a constant temperature of 50°C to generate CO_2 gas. Gas samples were purified using low temperature isopropyl-liquid nitrogen baths to separate out the residual water and the resulting CO_2 gas was analyzed on a V. G. Micromass 602-D isotope ratio mass spectrometer. The isotopic data are given in the conventional delta (δ) notation relative to the PDB standard. NBS-20 was used at the start and end of each session on the mass spectrometer as the working standard. The analytical precision of the shell samples was $\pm$ 0.1‰ for both $\delta^{18}O$ and $\delta^{13}C$.

Several of the samples of *Pitar* were prepared as above at the University of Florida on an off-line reaction system for subsequent analysis on the mass spectrometer at GSO. A consistent fractionation between replicate samples and internal standards prepared on the off-line at the University of Florida and those reacted on line at GSO was observed; all off-line samples were corrected to the G.S.O. curve (see Table 3, Appendix I) by calculating the average of the amount of fractionation observed in 10 duplicate samples, prepared at both laboratories : –0.369 for $\delta^{18}O$ (1σ = 0.08‰) and –0.499 for $\delta^{13}C$ (1σ = 0.07‰).

Predicted $\delta^{18}O$ Water & Hydrographic Data

Because limited sampling for $\delta^{18}O_{water}$ was preformed in this study, we developed a simple two component mixing model that predicts the yearly variation of $\delta^{18}O$ of Narragansett Bay water, driven by the measured changes in the bay salinity. The oxygen isotopic values of the two end-members are based upon $\delta^{18}O$ measurements of Long Island Sound water and measurements of the regional riverine input by Fairbanks (1982). The seawater end-member has a

$\delta^{18}O$ value of –0.76‰ (SMOW) for a salinity of 32.5‰. The value of the freshwater end-member is taken as –9.5‰, which is an average of the monthly measurements from the rivers in this region, sampled during 1981.

$$\delta^{18}O_{water} = [S(-0.76‰) + (S - 32.5)(-9.5)]/32.5$$

The salinity measurements from a MERL control tank during the eutrophication experiment show a strong seasonality with a low of 27‰ in the spring and a summer to winter high of approximately 31‰ (Figure 3a), with little variation (±1‰) between the tanks (Frithsen et al, 1985). However, the eutrophication experiment salinity measurements are incomplete, running only from January 1983 to September 1983, less than half the duration of the experiment, with no data available for the header tank (the tank most closely equivalent to conditions in the bay). Figure 3b shows the most recent salinity data (courtesy of J. Frithsen, 1987) collected from 1984 to 1987, sampled from the MERL header tank and one of the mesocosm control tanks, on a weekly basis. These salinity data vary between 27.1‰ and 32.4‰, with more than 95% of the data within the range of 29.5 to 32.4‰. Unlike the salinity data measured during the eutrophication experiment, these data do not exhibit a strong seasonal signal. The more recent salinity data demonstrate that the MERL seawater inlet is close enough to the surface to reflect short term salinity fluctuations in the surface water, such as fresh water input during high runoff. The MERL mesocosm control tank, also shown in Figure 3b, does not show the same fluctuations as the header tank due to the much longer turnover time of the mesocosm tanks (27 days versus 15 minutes for the header tank).

Our predicted $\delta^{18}O_{water}$ values for control tank T–0 (1983) using the model are shown in Figure 4a. The values range between –2.2 and –1.2‰, with an average of –1.72‰ (SMOW). The 1984 to 1987 values for the header tank are shown in Figure 4b and range between –2.2 and –0.8‰(SMOW) with an average

of –1.19‰. The majority of the values for this tank exhibit a much smaller range. The calculated $\delta^{18}O_{water}$ values for salinities measured from a mesocosm control tank during 1985 to 1986 are between –1.47 and –0.92‰, with an average of –1.23‰. Thus, the calculated $\delta^{18}O_{water}$ values have a maximum range of approximately 1.4‰ (SMOW) which includes the sharp, short-term excursions observed in the MERL salinity data sets; the typical $\delta^{18}O_{water}$ range is less than 1‰ (SMOW). The observed vertical salinity gradients from surface to bottom rarely exceed 2‰ in the lower bay (Hicks, 1959; Pilson, 1985a) which would correspond to a vertical $\delta^{18}O_{water}$ gradient of approximately 0.5‰ using our model under constant temperature conditions. The results of our mixing model are very close to the results obtainable from the $\delta^{18}O$–salinity relationship of Fairbanks (1982) for water from the New York Bight.

Predicted $\delta^{18}O$ Calcite & Aragonite

We can now calculate the expected $\delta^{18}O$ (PDB) of aragonite and calcite precipitated in equilibrium with the bay water, using our modeled $\delta^{18}O_{water}$ values, an averaged MERL temperature record (an average of three years 1981 - 1983) and the aragonite paleotemperature equation of Grossman and Ku (1986, equation 3, for mollusc data only):

$$\delta^{18}O_{aragonite} = \delta^{18}O_{water} + [21.8 - T(°C)]/4.69$$

and the calcite paleotemperature equation of Epstein et al. (1953):

$$T(°C) = 16.9 - 4.2(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.13(\delta^{18}O_{cal.} - \delta^{18}O_{w})^2$$

$$\delta^{18}O_{calcite} = \delta^{18}O_{water} + [(4.38 - (19.18 - 0.4(16.9 - T)1/2]/0.20.$$

The predicted $\delta^{18}O$ carbonate results for both aragonite and calcite are shown in Figure 5a, using the measured temperatures and salinities from the 1981 to 1983 eutrophication experiment. The predicted aragonite values range from –1.2 to 3.45‰ while the predicted calcite values range from –2.4 to 2.9‰ (PDB). The results of the predicted isotopic values of aragonite and calcite using the 1984–1987 header tank salinity data are shown in Figure 5b. The aragonite isotopic values range from 3.7‰ (PDB) in the winter to –1.1‰ in the summer and the calcite values range from 3.25 to –2‰ throughout a year. The curves from both data sets reflect the distinct seasonal temperature variations observed in Narragansett Bay. The range of predicted $\delta^{18}O$ values for shell carbonate in the 1983 MERL data is very similar to the predicted values from the 1984–1987 MERL data set. Thus, a mollusc that precipitates aragonitic shell material in equilibrium with Narragansett Bay water during the entire year is predicted to have shell carbonate with a $\delta^{18}O$ range of approximately 4.8‰. Similarly, a mollusc forming a calcitic shell throughout the year would have a $\delta^{18}O$ range of approximately 5.3‰.

The sensitivity of the predicted $\delta^{18}O_{aragonite}$ can be tested by comparing the results of calculations done with the measured MERL control tank salinity of 1983 (Figure 3a) to calculations made using the average salinity value (29.0‰) of the same data set. The results are shown in Figure 6 and illustrate that the first order variation in the $\delta^{18}O_{aragonite}$ signal is due to seasonal temperature variations. The greatest consistent difference, 0.5‰, occurs in the late spring when the measured salinities were at a low for the year (Figure 3a). Overall, the observed 3 – 4‰ salinity variations can affect the $\delta^{18}O$ of the carbonate shells precipitated in the lower bay. Thus, for detailed isotopic work it is important to measure either the salinity or the $\delta^{18}O$ of the water in order to accurately use the isotopic–temperature equilibrium equations.

RESULTS

$\delta^{18}O$ Water & $\delta^{13}C$ Dissolved Inorganic Carbon

In order to interpret the shell oxygen isotope record in terms of temperature and timing of seasonal growth cycles, it is necessary to document the oxygen isotope variations of the water in Narragansett Bay. The results of the oxygen isotopic measurements of the water ($\delta^{18}O_{water}$) samples collected from the MERL header tank are shown in Figure 7 (and listed in Table 1, Appendix I). The measured $\delta^{18}O_{water}$ values range between –0.4‰ and –1.5‰ (SMOW), with a slight seasonal trend toward lighter values in the spring. The average of the measured $\delta^{18}O_{water}$ values was –0.98‰ (SMOW), with one standard deviation (1 σ) of all measurements equal to +0.32‰. This is approximately the same magnitude as the $\delta^{18}O_{water}$ variation predicted using our mixing model. The measured $\delta^{18}O_{water}$ values are, on average, slightly more positive (–0.98‰ versus –1.19‰) than the values predicted by our linear mixing model (Fig. 4a) based on the 1984 – 1987 header tank salinity data (Fig. 3b). The measured $\delta^{18}O_{water}$ values are quite a bit more positive than the values predicted using the 1983 MERL control tank salinity data, which had an average $\delta^{18}O_{water}$ equal to –1.67‰ (SMOW). The majority of this difference is due to the unusually low salinities observed in the spring of 1983, relative to spring conditions measured at other times (Fig. 3a). The use of the measured $\delta^{18}O_{water}$ values will generally result in slightly heavier predicted $\delta^{18}O$ values of shell carbonate than were estimated using the modeled $\delta^{18}O_{water}$ values.

The results of measurements of the $\delta^{13}C$ (PDB) of the total dissolved inorganic carbon in Narragansett Bay water collected from the MERL header tank are shown in Figure 8 (listed in Table 2, Appendix I). Samples were taken from August 1986 to September 1987 and the values range from 0.25 to 2.3‰ (PDB).

The average of all the data was 1.42 ± 0.42‰, with weekly variations of up to 0.5‰. The greatest change took place during late February to mid-March when an approximately 2‰ enrichment is observed in the data. The $\delta^{13}C$ values are increasingly lighter through the fall and into the winter, presumably due to the influx of lighter carbon (carbon-12) from benthic respiration and the low productivity occurring in the bay at this time (Pilson et al., 1980).

Shell Data

The oxygen and carbon isotope results from the incremental shell samples of *Pitar morrhuana* and *Mytilus edulis* are plotted in figures 9 and 10, respectively. The isotope data are plotted as the delta value (in per mil notation) versus the individual sample number drilled from the shell, roughly equivalent to shell height. The x-axis origin always represents the beginning of shell growth, the last sample on the x-axis is the shell edge sample, i.e., the last shell material formed prior to collection in September 1983. This method of plotting will introduce a bias toward those periods of faster growth, but has the advantage of "flattening" the shell such that the early shell growth is not lost due to the curvature of the shell in the umbonal region, better representing the incremental sampling technique. The delta (δ) values on the y–axis are plotted in the conventional carbonate isotope manner, with the negative (or lighter) values above the positive (or heavier) values (lighter $\delta^{18}O$ values often imply warmer temperatures for a constant $\delta^{18}O_{water}$.

Pitar morrhuana

A total of 47 successive incremental samples were removed from the right valve of *Pitar morrhuana* and examined isotopically. Most of these analyses were duplicated (76 separate analyses, listed in Table 3, Appendix I). This specimen

was collected from one of the MERL mesocosm control tanks that operated during the eutrophication experiment. The oxygen–isotope record (Figure 9) for this specimen of *Pitar* exhibits regular, high amplitude $\delta^{18}O$ cycles caused by the yearly seasonal temperature variations of Narragansett Bay water. The measured shell values range from 0.8 to –2.0‰, a range of 2.8‰. Based on the number of $\delta^{18}O$ cycles, this specimen is considered to have been approximately 4.5 to 5 years old at the time of collection.

This individual was approximately two years old when it was added to the MERL mesocosm in May of 1981. The specimen experienced the most rapid shell growth during the first two years with the second full year of shell growth exhibiting the greatest isotopic amplitude (2.8‰). The rate of shell growth apparently slowed dramatically after the first three years as the later $\delta^{18}O$ (annual) cycles are quite erratic. Slower shell growth results in more time-averaging for each incremental sample taken from the shell and consequent loss of resolution.

The carbon isotope record of the *Pitar* specimen does not exhibit the regular seasonal cycles observed in the oxygen isotope profiles. The seasonal range of values for the $\delta^{13}C$ of the shell samples is less than 1‰ with an overall increase in $\delta^{13}C$ for the first two and a half years from roughly –0.25 to 0.75‰ and then much more erratic variation for the last two years, from 0.75 to –0.2‰. Within a given year there seems to be a trend toward heavier values early in the (growth) year, followed by a jump of 0.25–0.5‰ to lighter values in mid to late summer, followed by a general increase in values through the fall.

Mytilus edulis

The specimen of *Mytilus edulis* we examined was collected from the same mesocosm control tank as the *Pitar* specimen. *Mytilus* is an epifaunal filter feeder

with a bimineralic shell, the outer layer of the shell (beneath the periostracum) is entirely calcitic and is the layer we sampled for the isotopic analyses. Samples from 52 successive intervals were analyzed isotopically with 9 replicate analyses (Table 4, Appendix I). Sample intervals were more widely spaced than those in *Pitar*. The shell height of this *Mytilus* specimen measured 62 mm .

The $\delta^{18}O$ signal from the *Mytilus* specimen (Figure 10) indicates strong seasonal temperature cycles recorded in the outer calcitic shell layer. The measured $\delta^{18}O$ values range from 1.5 to –2.3‰ (PDB), an overall range of 3.8‰. The $\delta^{18}O$ cycles, interpreted as representing annual temperature cycles, indicate that this *Mytilus* specimen was less than two years old at the time of collection, suggesting a very high rate of shell growth. The overall shape of the oxygen isotopic profile is somewhat different than that of the *Pitar* specimen with a predominant summer peak (consisting of 14 samples lighter than –2.0‰), and a greater overall range of isotopic values. Since this specimen is less than two years old, it must have entered the MERL seawater system in the planktonic larval stage.

The carbon isotope data from the *Mytilus* specimen are also shown in Figure 10. The measured values range between 1.6 and –1.3‰, with an amplitude of 2.9‰. The general trend of the carbon isotopes does not appear to be highly seasonal or to correlate in any way with the oxygen isotope cycles. The $\delta^{13}C$ values decrease steadily into the first summer, beginning at 1.6‰ and falling to –0.75‰ by mid-summer (timing inferred from the seasonal cycle of oxygen isotopes). After mid-summer the $\delta^{13}C$ values are more variable, generally becoming more positive (to approximately –0.5‰) into the fall. The $\delta^{13}C$ values decrease by 1‰ during the initial spring growth of the following year, level off at about –1 ‰, and then increase to –0.25‰ just prior to collection of this specimen.

Nucula annulata

The isotope data from the specimens of *Nucula annulata*, a small, sub-surface deposit feeder, are shown in Figure 11 (listed in Table 5, Appendix I). As previously discussed, some of the *Nucula* specimens were collected from the same MERL control tank as the *Pitar* and *Mytilus* specimens while other *Nucula* were collected from MERL tanks undergoing controlled nutrient additions of 8, 16 and 32 times the normal nutrient loading of Narragansett Bay. Because of their small size, these shells were not sampled incrementally. Instead, individual valves were ground up after removal of the periostracum. A few discrete samples were taken from the margins of the larger specimens. The $\delta^{18}O$ values generally fall between –0.1 and –1.2‰, indicating that the majority of the shell carbonate is deposited in the late spring (assuming that shell aragonite is deposited in equilibrium with the water). The specimens from the MERL control tank 0 generally exhibit more positive values (–0.1 to –0.6‰) than the specimens from the other tanks. The oxygen isotopic results of the shell margin samples are not significantly different from the whole shell results.

The whole–shell carbon isotopic records from the *Nucula* specimens have a wide range of variablility (Figure 11), apparently related to the degree of nutrient loading in the respective mesocosm tanks. The $\delta^{13}C$ shell measurements show a trend toward increasing $\delta^{13}C$ with increasing eutrophication (increasing nutrient addition level) of the mesocosm tanks. The specimens from the 32x tank (32 times the normal bay nutrient loading) have extremely heavy $\delta^{13}C$ values, ranging between 4.0 and 5.0‰, with one sample taken from the margin of a specimen measured at 5.8‰. The $\delta^{13}C$ values from the shells of specimens recovered from the 8x and 16x tanks overlap somewhat (see discussion below), ranging between 2.0 and 3.0‰. The $\delta^{13}C$ values of the control tank specimens are between 0.5 and 1‰. The 32x tank was observed (Frithsen et al., 1985b; Oviatt et

al., 1986) to have very low levels of dissolved oxygen (dropping occasionally to zero), high levels of chlorophyll a, and consistently low, but variable, levels of total CO_2. The heavy $\delta^{13}C$ values probably reflect the removal of carbon–12 during the sustained high primary productivity of this tank.

DISCUSSION

Oxygen Isotopes

A comparison of the predicted seasonal oxygen isotopic composition of shell aragonite precipitated in Narragansett Bay (Figure 5) to the measured oxygen isotopic composition of the *Pitar* samples (Figure 9), reveals: 1) the lightest measured values are slightly lighter than predicted, while, 2) the overall range of measured values is much less than predicted. If we compare the lightest measured $\delta^{18}O$ values from the last three annual cycles to the predicted $\delta^{18}O$ values (based on the maximum measured summer temperatures of 1981 (23°C), 1982 (21°C), and 1983 (22°C), our mixing model estimates of the $\delta^{18}O_{water}$ (–1.3 to –1.75‰ SMOW, Figure 4a) based on the salinity measurements of 1983, and the Grossman and Ku (1986) aragonite equation), we find that the measured $\delta^{18}O$ values are quite close to the predicted values. The predicted $\delta^{18}O$ value for the 22°C temperature maximum of August 1983 is –1.3‰ (salinity = 29.8‰, $\delta^{18}O_{water}$ = -1.45‰ SMOW) and the lightest measured value during the last annual cycle is -1.55‰, after a fractionation correction due to the effects of roasting aragonitic carbonate. The small discrepancy is probably due to either the estimation of the 1983 MERL $\delta^{18}O_{water}$ values (too heavy (by about 0.5‰; or, 2) uncertainties in the equilibrium water/temperature equation is incorrect.

Since no water samples from the 1981–1983 eutrophication experiment were available to us for isotopic analyses, we have tried to estimate the $\delta^{18}O$ of the

water at that time based on the 1983 salinity measurements and a mixing model, as described earlier. We have shown that the measured $\delta^{18}O_{water}$ values (Figure 7) collected from the MERL header tank during 1986 to 1987 are typically 0.2‰ (SMOW) heavier than were predicted using our $\delta^{18}O$ mixing model (results in Figure 4). Since the measured water values are heavier than the predicted values, it seems unlikely that the $\delta^{18}O_{water}$ values used in the aragonite temperature–water equilibrium equation are the reason for the isotopically light shell values. The measured $\delta^{18}O_{water}$ values for the 1983 summer would have to equal approximately –2.2‰ (SMOW) in order for the $\delta^{18}O$ aragonite values to equal (the observed) –2.0‰ (PDB).

It is possible that the temperature equation we are using for the equilibrium oxygen isotopic fractionation in aragonite is incorrect. This equation, from Grossman and Ku (1986), is relatively new and has not been independently tested. The earlier aragonite–temperature equation of Grossman and Ku (1982) predicts aragonite $\delta^{18}O$ values that are slightly lighter (by approx. 0.2–0.3‰) for summer temperatures and much heavier (by approx. 1‰) for winter temperatures (Figure 5). Thus, the earlier equation predicts aragonite values that are closer, but not quite equal to, the measured aragonite values. The validity of either aragonite equation cannot really be resolved with this data set, as the $\delta^{18}O_{water}$ values are primarily estimated.

The measured $\delta^{18}O$ amplitude of the *Pitar* specimen is slightly greater than half of the predicted $\delta^{18}O$ amplitude. The heaviest values sampled from this shell ($\delta \approx 0.5$ to 0.75‰) are lighter than the predicted values by more than 2‰, indicating that *Pitar* does not actively form shell material during the coldest part of the year. Based on the timing of the modeled values of $\delta^{18}O$ for aragonite (Figure 5a), it appears that this specimen of *Pitar* generally began forming shell material sometime in April or early May. The MERL temperature records (Figure

2) show that temperatures rise rapidly during April, increasing from 4 to 11°C in 1982, and from 5 to 13°C in 1983. The isotopic record of the *Pitar* specimen (Figure 9) also indicates that shell growth started earlier in the year and/or ended later in the year with increasing age, with the exception of sample #3, which apparently delineates two later growth (annual) cycles. The amount of shell material formed during the colder water temperatures must be fairly small, as the number of isotopic samples indicating low temperatures is very limited. Slower shell growth results in more time-averaging among incremental samples taken from the shell and subsequent loss of resolution. This sampling effect has been observed by others (e.g., Williams et al.,1982; Jones et al., 1983; Krantz et al., 1984,1987) in the isotopic investigations of various species of molluscs using detailed, incremental sampling techniques. Jones et al. (1983) discussed the consequences of unequal sampling of successive growth bands and concluded that the sampling effects were less important than the environmental effects as far as the overall amplitude of the isotopic signal, but that knowledge of life history of a bivalve species can be very important when trying to extract seasonality information using oxygen isotopes.

An "average" or bulk shell sample taken from this *Pitar* shell would probably indicate a temperature of approximately 17–19 °C, skewed toward the higher temperature range due to the greater number of warm temperature samples. This is actually much higher than the average annual bay temperature, which is roughly 10–11°C. Thus, temperature estimates using isotopic analyses of whole shell samples from this species of mollusc would indicate average temperatures much higher than the true value and would not be of much utility.

The *Pitar* oxygen isotopic profile can also be used to examine the relationship between the annual $\delta^{18}O$ cycles and the internal growth increments of this specimen. The internal growth increments can be observed as the dark

layer, or band, of shell material when viewing a radial cross section of the shell. These dark bands are generally thought to occur during periods of slow shell growth, the dark color arising from the relatively greater proportion of organic matrix material being incorporated into the shell during periods of slow growth (Jones, 1980, Lutz and Rhoads, 1980). The specimen of *Pitar* that we have examined isotopically has 5 dark bands, or growth increments that can be observed in the shell cross section. These 5 bands coincide with sample numbers 3, 8, 17, 32, and 45, which are the isotopically heaviest samples measured for each annual cycle (Figure 9). The internal growth increments are thus an excellent indicator of the age of the specimen.

The annual internal growth increments can be observed in a radial cross section of the shell as the alternation of thin dark layers (bands) with larger white increments of shell material. The dark bands are generally thought to form during periods of slow shell growth. The dark apperance arises from the dense, tightly-packed arrangement of the aragonitic crystallites which results in a translucent shell microstructure, contrasting with the white color of the typical (opaque) microstructure. The specimen of *Pitar* that we examined isotopically has 5 dark bands, or growth increments, that can be observed in the shell cross section. These 5 bands coincide with sample numbers 3, 8, 17, 32, and 45, which are the heaviest samples (isotopically) measured for each annual cycle (Figure 9) and formed each winter during the coldest period of shell growth. These annual internal growth increments are thus excellent indicators of the age of the specimen.

The age determination resulting from the $\delta^{18}O$ record of the *Pitar* specimen can also be used to construct a standard graph of shell height versus years of growth (Figure 12). The points on the graph correspond to the observed internal growth increment and to the isotopically heaviest (most positive) sample for each

observed annual cycle. The best fit to the von Bertalanffy growth equation is achieved with $SH_\infty = 44.22$, $k = 0.52$, and $t_o = 0.12$, such that the shell height (SH) at any time t, is equal to:

$$SH_t = 44.22\ (1 - e^{-0.52(t - 0.12)}).$$

This specimen of *Pitar* shows an average growth rate of approximately 9 mm per year, although the growth rate slows dramatically after the second year.

The *Mytilus* oxygen isotopic profile (Figure 10) exhibits a greater range of values and a slightly different shape to the annual cycles than the isotopic profile from the *Pitar* specimen (Figure 9). The *Mytilus* profile is characterized by a broader peak of isotopically light values than the *Pitar* profile, indicating a higher, more consistent rate of *Mytilus* growth during warm temperatures. The lightest measured $\delta^{18}O$ samples from the *Mytilus* specimen (Figure 10) match the predicted summer $\delta^{18}O$ values for calcite shell material (Figure 5a) quite well. This supports the validity of modeled $\delta^{18}O_{water}$ estimates. It is known that aragonite is enriched in ^{18}O relative to calcite, although there is some debate about the magnitude of the enrichment. Most of the current research (Ganssen, 1983; Grossman and Ku, 1981, 1986) indicates that the difference in aragonite – calcite fractionation is approximately 0.7‰. This suggests that the isotopic values measured from the *Pitar* specimen should be approximately 0.7‰ heavier than the *Mytilus* samples from the same time period, if both specimens were forming shell material in isotopic equilibrium with the surrounding water. If we compare the lightest measured values, as we can be most certain of the timing and temperature of these samples, we find that the lightest *Mytilus* and *Pitar* values vary by approximately 0.3‰, about one–half the accepted value. If we consider the fractionation that occurs due to the sample preparation techniques (roasting) we see that the lightest *Pitar* values are very close to 0.7‰ heavier than the

lightest *Mytilus* values. This indicates that the suggested value of 0.7‰ for the fractionation between calcite and aragonite (at 20–25°C) is very close to that observed using these two mollusc species.

The 14 sequential $\delta^{18}O$ samples (equally spaced) with values lighter than –2.0‰ indicate temperatures above 18°C. Thus, each sample represents (roughly) a week-long interval of time, given 3 months of temperatures above 18°C (Figure 2). In comparison, the *Pitar* specimen typically has only 3 to 4 samples with $\delta^{18}O$ values near –2.0‰, corresponding to approximately one sample per month during the summer.

The heaviest $\delta^{18}O$ values recorded by the *Mytilus* shell are approximately 1.5‰, nearly 1‰ greater than the heaviest values recorded by the *Pitar* specimen. Using the calculated values for the $\delta^{18}O$ of the water and the calcite paleotemperature equation of Epstein et al., (1953), we can estimate the temperature of formation for these heaviest samples. The calculated values correspond to shell formation at temperatures of approximately 5–6°C, or sometime during March, and the cessation of shell growth sometime in December for a typical seasonal cycle. This specimen of *Mytilus* formed shell material during much of the year, especially when one considers the time-averaging effect of the sampling technique.

The growth rate of this specimen of *Mytilus* was greater than 3 cm per year, which is quite high relative to most of the reported growth rates (e.g., Seed, 1969, Incze, 1980), although similar values have been observed by Incze et al. (1980) in the Damariscotta River estuary in Maine. This *Mytilus* specimen had no distinct disturbance bands on its outer shell layer, so we could not compare the disturbance ring method of age determination (e.g., Seed, 1969) to the isotopically determined age.

Carbon Isotopes

The degree of equilibrium ^{13}C fractionation between biogenic aragonite and seawater bicarbonate is not well established, although Grossman (1984a) has estimated it to be +2.40‰ at 25°C (revised from Rubinson and Clayton, 1969). Grossman and Ku (1986) have demonstrated a temperature dependence of the carbon isotopic fractionation between the dissolved inorganic carbon (DIC) and molluscan aragonite equal to –0.13‰ per°C, that is, less fractionation with increasing temperatures. Grossman and Ku (1986) suggested the following relationship:

$$\varepsilon^{13}_{moll} - DIC\ (‰) = 2.66 - 0.131(T°C)$$

to describe the fractionation between shell aragonite and dissolved inorganic carbonate. Earlier work by Emrich et al. (1970) with inorganically precipitated aragonite and bicarbonate indicated that the fractionation is in the opposite direction and is much smaller (+0.035‰ /°C). The results of both Emrich et al., (1970) and Grossman and Ku (1986) suggest the possibility of using carbon isotope variations as an indicator of temperature, similar to the oxygen isotopic temperature scale. Turner (1982) demonstrated that during inorganic calcite precipitation this fractionation (arag. – seawater) can vary with the rate of precipitation; slow precipitation resulted in greater fractionation (+3.4‰), whereas rapid precipitation resulted in lower fractionation (+0.4‰).

The relationship of Grossman and Ku (given above) predicts that at 20°C, the fractionation between the shell aragonite and the $\delta^{13}C_{DIC}$ should be 0.04‰, or virtually no fractionation at this temperature. The summer $\delta^{13}C$ values measured from the *Pitar* specimen vary from year to year, but range from approximately –0.25 to 0.25‰. These measured shell values are much lighter than predicted,

using the equation of Grossman and Ku (1986) and the 1986–1987 water values. The light shell $\delta^{13}C$ values may be due to the utilization of metabolic carbon by the mollusc, derived from internal respiration and thought to have an isotopic signature similar to the organic carbon in the tissues. Gearing et al., (1984) measured the carbon isotopic composition of the organic carbon in *Pitar* specimens collected from Narragansett Bay and found the value to be approximately –17.2‰ (PDB). Emrich et al. have measured the fractionation between bicarbonate ion and CO_2 equal to 8.38‰ at 20°C, that is, the bicarbonate ion is enriched relative to the CO_2. Thus, bicarbonate ion forming from the metabolic CO_2 has an isotopic value of approximately –8.82‰. If the summer seawater bicarbonate has a $\delta^{13}C$ value of roughly +1.2‰, and the measured summer (20°C) shell $\delta^{13}C$ value is 0.0‰ (e.g., the second year of growth observed in Pitar), then the contribution from the metabolic carbon pool must be approximately 12%,

[est. from: $0.0_{shell}‰ = -8.82_{metabolic}‰(x) + 1.2_{bicarbonate}‰(1-x)$] if there is no fractionation between the DIC and the shell aragonite. If the fractionation between the DIC and the shell carbonate is approximately 2.4‰, as suggested by Grossman (1984a), then the contribution from metabolic carbon pool would be roughly 45%. Tanaka et al., (1986) suggested that the contribution from the metabolic carbon pool ranged from 35–85%, with an average of 56% for several different species of molluscs collected in New Haven Harbor, Connecticut.

The variety of factors affecting the incorporation of carbon isotopes in shell carbonate make it very difficult to ascertain the causes of the observed $\delta^{13}C$ trends in the *Pitar* or *Mytilus* profiles. The first order trend in the $\delta^{13}C$ profile of the *Pitar* specimen (an overall increase in $\delta^{13}C$ for the first several years) may be related to physiological effects such as ontogenetic growth changes and/or sexual maturity. The increased variability in the record, beginning with sample #13

(Figure 9) could be related to the collection and containment of the specimen in the MERL mesocosm tank, which would have occurred at about this time. The increased variability could also be related to ontogeny, in particular the effects of slower, and probably more intermittent, growth. It is thought that the longer a shell is closed, the greater the build-up of metabolic carbon. This could have occurred at times represented by *Pitar* samples #3 and #8 (Figure 9) where light $\delta^{13}C$ values are associated with the heaviest $\delta^{18}O$ values. The first order trend in the *Mytilus* profile is exactly the opposite: the $\delta^{13}C$ values generally decrease with age. As mentioned earlier, the study by Turner (1982) has indicated that precipitation rates could have a drastic effect on the isotopic composition of the shell carbonate. Periods of fastest shell growth, generally spring to early summer, would form shell material with lower fractionation between the carbonate and the DIC than slow shell growth periods, if Turner's observations hold true for biogenically formed aragonite. The observed shell results are, however, more negative than the values that would be expected using Turner's estimates for rapid precipitation.

The second order trend observed in the carbon isotopic profile of the *Pitar* specimen may be related to the seasonal changes in phosphate in Narragansett Bay. Phosphate concentrations in Narragansett Bay have been observed to fluctuate on a seasonal basis (Figure 13), generally low in the early spring and high in the summer, as discussed by Pilson (1985b). These same changes in phosphate concentrations are also present in the MERL mesocosm tanks (Pilson et al., 1979; Frithsen et al., 1985b for the eutrophication experiment data). A negative correlation between $\delta^{13}C$ and PO_4 has been demonstrated by Broecker (1981) for ocean water, reflecting primary productivity changes as well as oxidation of organic matter in the water column. The slope of the relationship as calculated by Broecker is -0.93‰ $\delta^{13}C$/mm PO_4 for modern ocean water. The

typical seasonal range of dissolved phosphate observed in the MERL control tank 0 during 1981 to 1983 (Frithsen et al., 1985b) was approximately 1.6 mmol/liter. A 1.6 mmol phosphate range would correspond to a seasonal $\delta^{13}C_{DIC}$ range of approximately –1.5‰ using Broecker's relationship, with heavier $\delta^{13}C_{DIC}$ values in the spring and lighter values in the summer. This is roughly twice the seasonal $\delta^{13}C$ amplitude observed in the *Pitar* shell carbonate. Although the *Pitar* specimen did not form shell material all year, most of the observed phosphate change took place between April and September, during the presumed time of active shell formation. The phosphate – $\delta^{13}C$ correlation may not be valid for a temperate coastal estuary, especially considering the much stronger benthic coupling present in a shallow coastal ecosystem. The biologic production in Narragansett Bay is much greater than that of the open ocean per unit area, and with an average depth of only 8 meters, the oxidation of the majority of the organic matter occurs on the bottom (Durbin and Durbin, 1981, Nixon, 1983, Rudnick and Oviatt, 1986). In the open ocean the majority of the organic matter never reaches the bottom, but is oxidized in the water column.

There is no obvious relationship between the measured shell $\delta^{13}C$ values and the measured $\delta^{18}O$ values from the same samples for either *Pitar* or *Mytilus*. Such a relationship is suggested by the work of Grossman and Ku (1986) and to a lesser degree, by Emrich et al. (1970). This indicates that shell $\delta^{13}C$ values are either insensitive to temperature changes or that the carbon isotopic signal due to the temperature dependence is masked by other isotopic signals or inputs (e.g., changes due to metabolic carbon inputs or changes in the carbon isotopic fractionation due to growth rate variations). For either shell we have examined isotopically, it would be impossible to determine the temperature of shell formation given the $\delta^{13}C$ composition of the shell carbonate and the isotopic composition of the DIC.

Although shell growth for *Mytilus* begins approximately one month earlier than for *Pitar*, it does not begin soon enough to record the anticipated short term changes in the $\delta^{13}C$ of bay water as a result of the major seasonal (winter-spring) bloom in the bay. This bloom is mainly due to the production of the diatoms *Dentonula confervacea* and *Thalassiosira nordenskioeldii*. The effects of this bloom on the nutrients in the bay are not observed in the yearly data tabulation of Pilson (1985b) but may have been averaged out due to the method of reporting the data. The recent study by Rudnick and Oviatt (1986) indicates that time lags, on the order of months, are present between the deposition of the organic carbon from the winter-spring bloom and the remineralization of the (deposited) organic material.

The *Nucula* samples exhibit $\delta^{13}C$ values generally much more positive than the samples from either *Pitar* or *Mytilus*. The *Nucula* specimens collected from the MERL control tank have $\delta^{13}C$ values between 1.5 and 2.0‰ (PDB) (Figure 11). As sub–surface deposit feeders, *Nucula* are immersed in pore waters with very light $\delta^{13}C_{DIC}$ values, due to the oxidation of isotopically light organic carbon (McCorkle et al., 1985). This apparently has little bearing on the carbon isotopic composition of their shells. Differing levels of primary production (and hence the removal of lighter carbon from the DIC pool) between tanks must account for the observed difference between the *Nucula* samples. The data presented by Oviatt et al. (1986) demonstrate that the levels of apparent production and measured chlorophyll-a are more or less in line with the levels of nutrient addition. During periods of peak productivity (February – April) the 8x, 16x and 32x nutrient addition tanks commonly had chlorophyll a levels ten times higher than the control tanks. The observed high $\delta^{13}C$ values of *Nucula* shell carbonate are probably due to the storage of the light carbon isotope in the additional biomass (including accumulated organic matter) present in the nutrient addition tanks.

The observed increase in $\delta^{13}C$ with increasing nutrient addition is not a smooth trend. The $\delta^{13}C$ results of the *Nucula* collected from the 8x and 16x nutrient addition tanks are approximately the same (2 to 3‰), although distinct from either the control, or the 32x results. The $\delta^{13}C$ results from the control and 32x tanks indicate heavier isotopic values for the *Nucula* shells from the 16x tank than the 8x tank. Whether or not the similar 8x and 16x $\delta^{13}C$ values are due to factors operating between the tanks, or within the carbonate deposition mechanism of the mollusc, is very difficult to determine. There are a great number of factors affecting the isotopic composition of dissolved inorganic carbon and the incorporation of this carbon into shell carbonate. If the total biologic production was the same in both tanks, and the benthic organic carbon storage equal, then the draw-down of the lighter carbon isotope would have to be approximately the same, leading to the observed results. If we use the chlorophyll-a measurements as an indicator of production, we must conclude that the production in the 16x tank was almost always higher than the 8x tank, leading to higher $\delta^{13}C_{DIC}$ values in the 16x tank. The observed oxygen concentrations in the 8x tank had peak (spring-time) values that exceeded those of the 16x tank for brief periods of time, although the net seasonal production was greater in the 16x tank. On the other hand, the 8x tank had the greatest benthic biomass, including the greatest biomass of bivalves, of any of the mesocosm tanks at the end of the eutrophication experiment in 1983. This bentic biomass would 'lock–up' more of the lighter carbon, making the $\delta^{13}C_{DIC}$ in the 8x tank more positive than that in the 16x tank. The 8x tank was also the only tank to show a potential for a large net accumulation of organic matter (Nixon et al., 1986) and thus, the storage of the lighter carbon isotope relative to the 16x tank. If the benthic organic carbon regeneration in the 16x tank operated at a higher rate than that of the 8x tank, the isotopic effects of the production draw–down on

the $\delta^{13}C_{DIC}$ would have been balanced more quickly in the 16x tank. Further isotopic investigations are needed to resolve the relative contributions from these various sources.

CONCLUSIONS

The isotopic analysis of incremental shell samples from *Pitar morrhuana*, *Mytilus edulis* and *Nucula annulata* demonstrates the utility of this method for determining shell growth patterns and reconstructing environmental conditions as recorded in the shell carbonate. The isotopic analyses, along with the detailed data available from the MERL mesocosms, have enabled us to accurately interpret the $\delta^{18}O$ and $\delta^{13}C$ signals in the shells of these bivalves in terms of known variations in the chemical and physical properties of the water in which they grew. The data indicate that the aragonite shell of *Pitar* appears to be forming at oxygen isotopic equilibrium with the ambient water (as defined by the aragonite–water–temperature equilibrium equation of Grossman and Ku (1986)) and that the $\delta^{18}O$ profile from this specimen is primarily controlled by temperature changes.

We have determined the seasonal timing of growth for the bivalves *Pitar* and *Mytilus* by means of the range and cycles of the $\delta^{18}O$ variations. These data indicate that in Narragansett Bay *Mytilus* has a longer growing season than *Pitar* by approximately one month at either end of the growing season. *Mytilus* apparently ceases shell formation when the water temperature dips below about 4–6°C, whereas the critical temperature for *Pitar* is approximately 10°C. Both species grow through the spring, summer and fall. *Nucula* has been shown to record mainly spring values of $\delta^{18}O$ in its shell, although this interpretation is based on whole shell analyses.

The influence of productivity on the $\delta^{13}C$ composition of shell carbonate and possible associations with the carbon cycling in the MERL tanks and Narragansett Bay was also noted. The *Pitar* specimen exhibited low amplitude cycles of $\delta^{13}C$ that seem to correlate with the observed phosphate cycling in the

bay. The carbon isotopic results from the detailed sampling of *Pitar* and *Mytilus* indicates that both specimens are utilizing a depleted source of carbon for a fraction of the total carbon incorporated into the carbonate. We suggest that in addition to the ambient dissolved inorganic carbon, these mollusc are incorporating metabolic carbon during carbonate precipitation. The effect of eutrophication on the shell carbonate of *Nucula* grown in tanks with nutrient addition was reflected in elevated values of $\delta^{13}C$ in the treated tanks.

These observed seasonal variations in the carbon and oxygen isotopes also strongly caution against using whole shell analyses whenever possible. Both *Pitar* and *Mytilus* cease formation of shell material in the winter and hence the coldest temperature values are not recorded. Whole shell analysis of these same specimens would indicated that both species lived in water that was warmer than that observed and that *Pitar* lived in either a slightly warmer climate that *Mytilus* or precipitated its shell out of equilibrium with the surrounding water - assuming that the *Mytilus* shell values were "correct".

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FIGURES

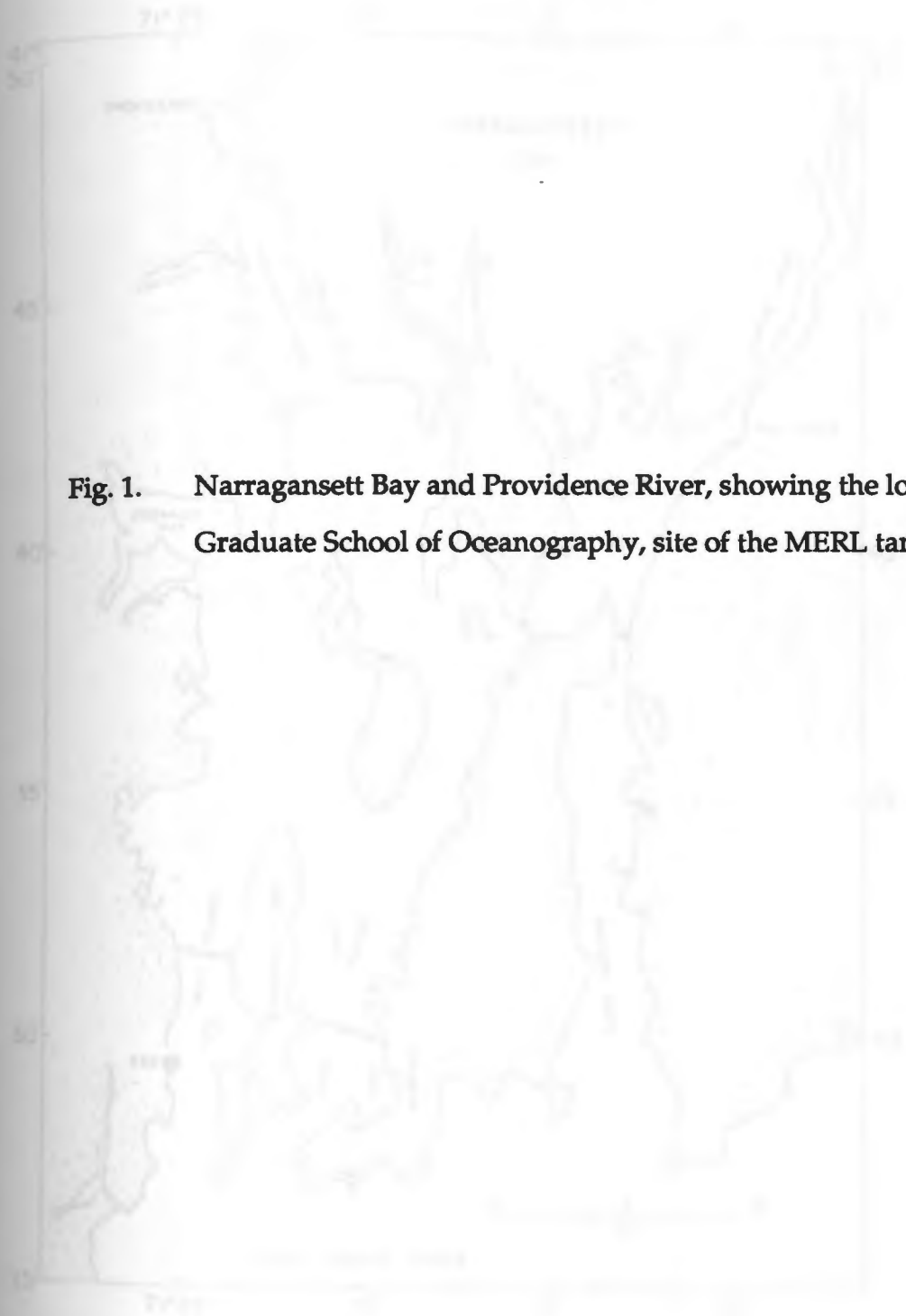
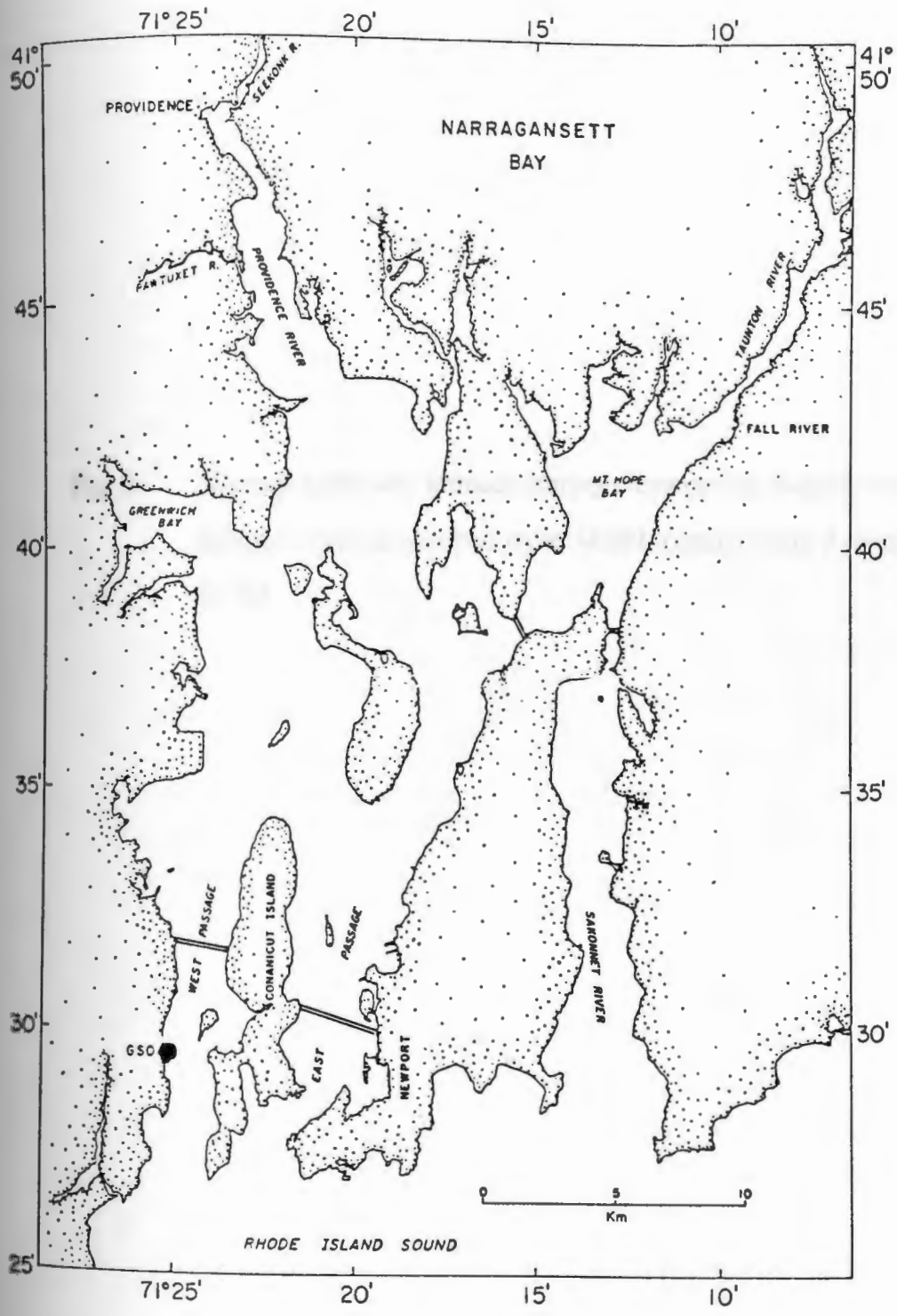


Fig. 1. Narragansett Bay and Providence River, showing the location of the Graduate School of Oceanography, site of the MERL tanks.


71° 25'
20'
15'
10'
41° 50'
45'
40'
35'
30'
25'
PROVIDENCE
SEEKONK R.
NARRAGANSETT BAY
FAN TUXET R.
PROVIDENCE RIVER
TAUNTON RIVER
FALL RIVER
MT. HOPE BAY
GREENWICH BAY
WEST PASSAGE
CONANICUT ISLAND
EAST PASSAGE
SAKONNET RIVER
NEWPORT
GSO
0 5 10
Km
RHODE ISLAND SOUND

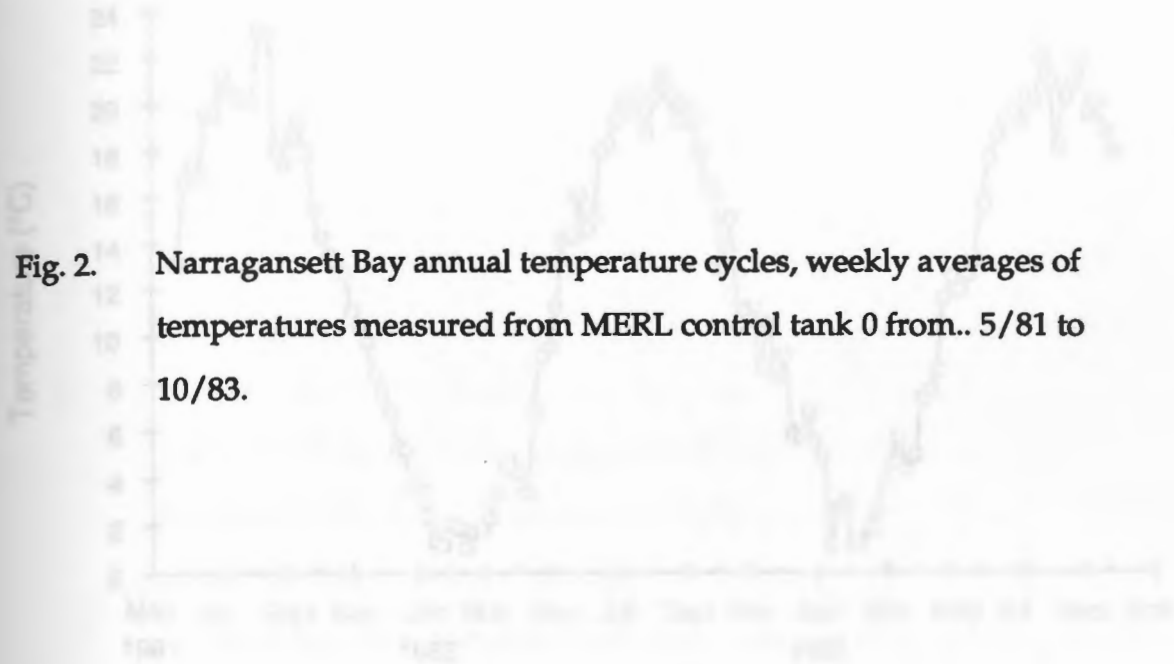


Fig. 2. Narragansett Bay annual temperature cycles, weekly averages of temperatures measured from MERL control tank 0 from.. 5/81 to 10/83.

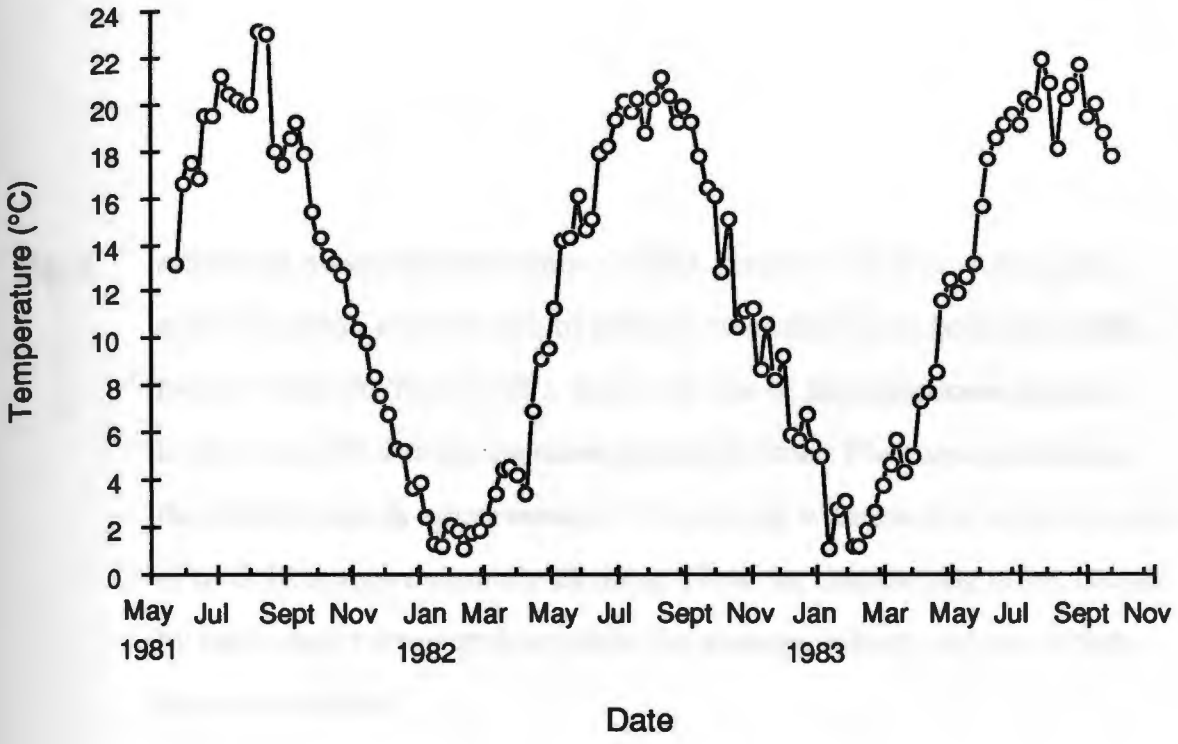
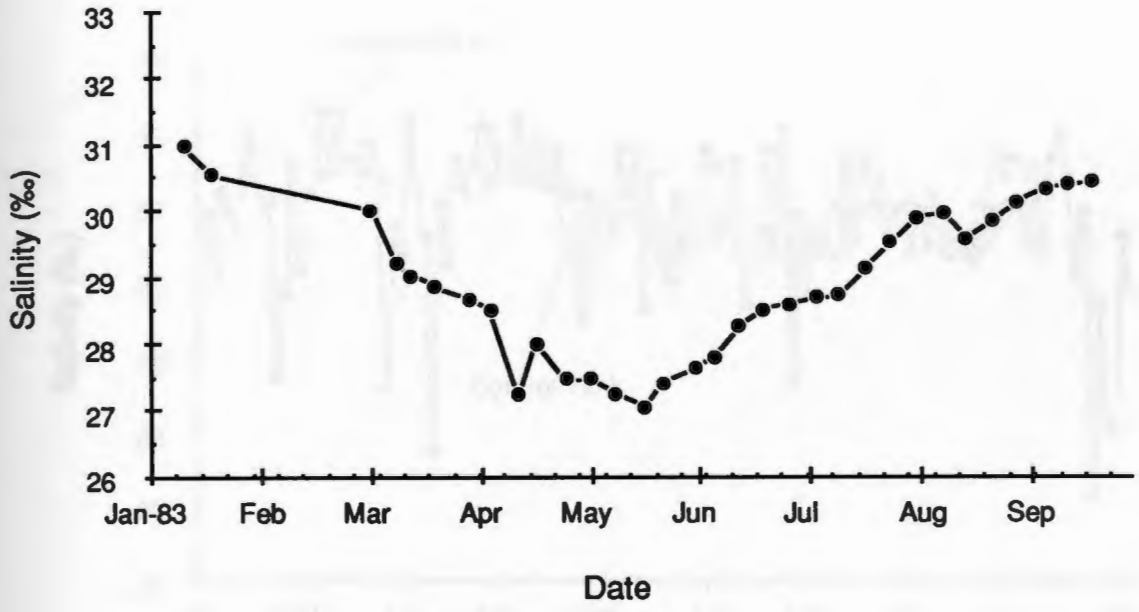

Temperature (°C)
24
22
20
18
16
14
12
10
8
6
4
2
0
May
1981
Jul
Sept
Nov
Jan
1982
Mar
May
Jul
Sept
Nov
Jan
1983
Mar
May
Jul
Sept
Nov
Date

Fig. 3. a)Salinity measurements from a MERL control tank #12 during the eutrophication experiment; b) salinity measured from both the MERL header tank (10/84 to 2/87), and from one of the mesocosm control tanks (tank 12) during the same period of time. The turnover time of the header tank is approximately 15 minutes whereas the turnover time of tank 12 is approximately 28 days. Note the dampening effect caused by the longer turnover time while the average salinity values of both tanks are similar.


33
32
31
30
29
28
27
26
Salinity (‰)
Jan-83
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Date

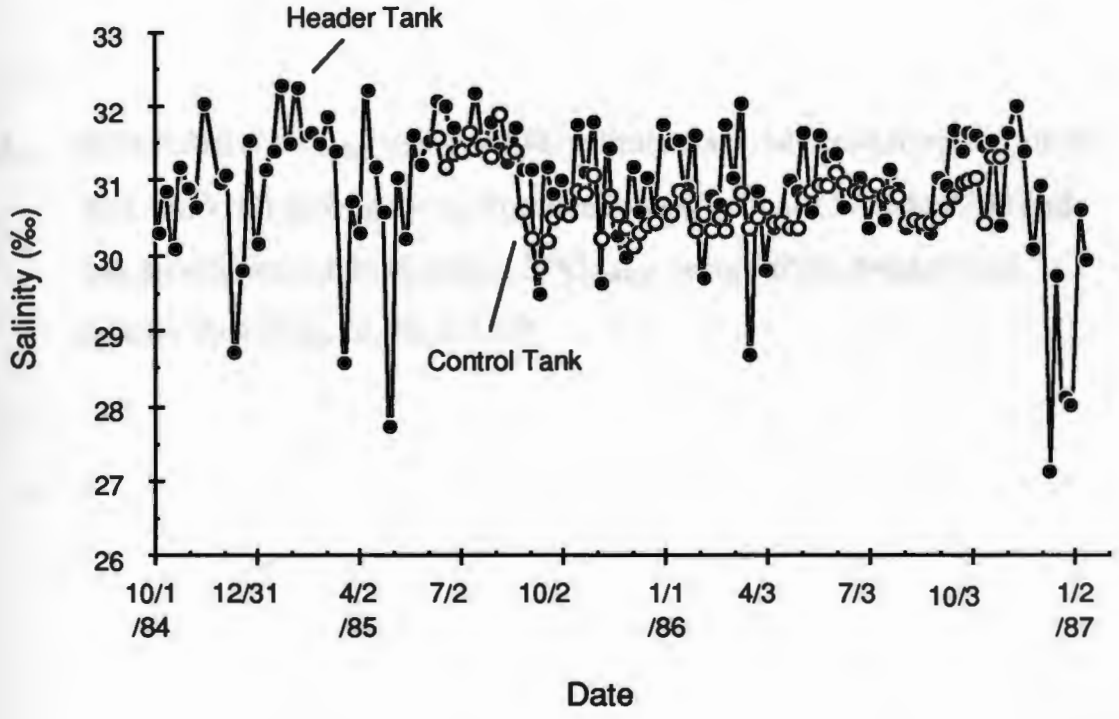
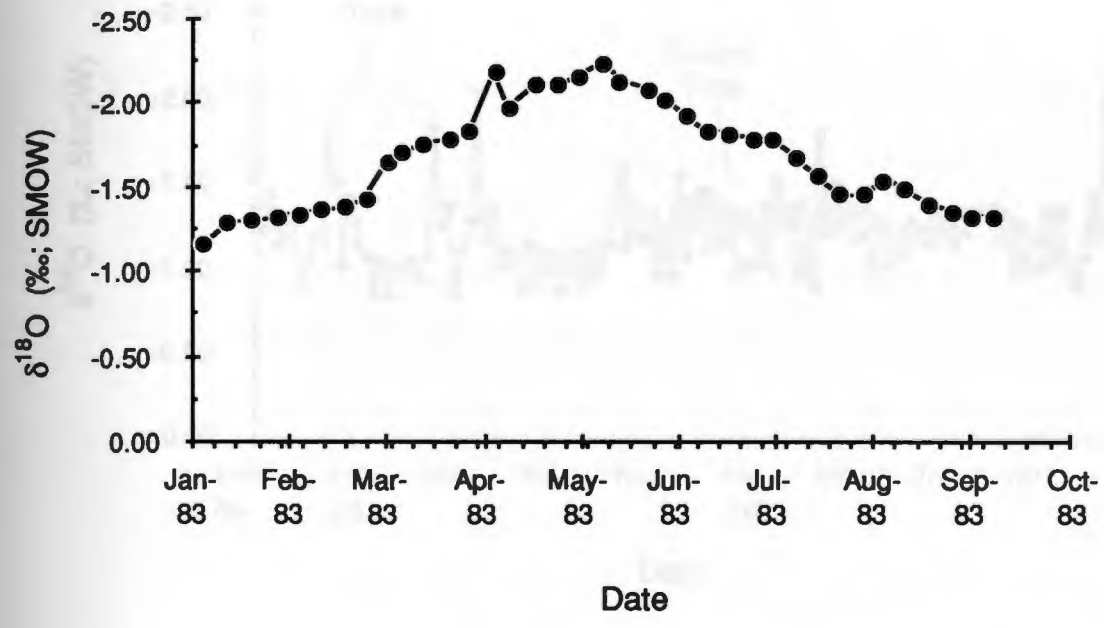

Header Tank
Control Tank
Salinity (‰)
33
32
31
30
29
28
27
26
10/1
/84
12/31
4/2
/85
7/2
10/2
1/1
/86
4/3
7/3
10/3
1/2
/87
Date

Fig. 4. a)Modeled $\delta^{18}O_{water}$ using MERL salinity data collected from a control tank (tank 12) during the eutrophication experiment 1/83 to 9/83 and our mixing model; b) modeled $\delta^{18}O_{water}$ using MERL header tank salinity data from 10/84 to 2/87.


-2.50
-2.00
-1.50
-1.00
-0.50
0.00
δ18O (‰; SMOW)
Jan-83
Feb-83
Mar-83
Apr-83
May-83
Jun-83
Jul-83
Aug-83
Sep-83
Oct-83
Date

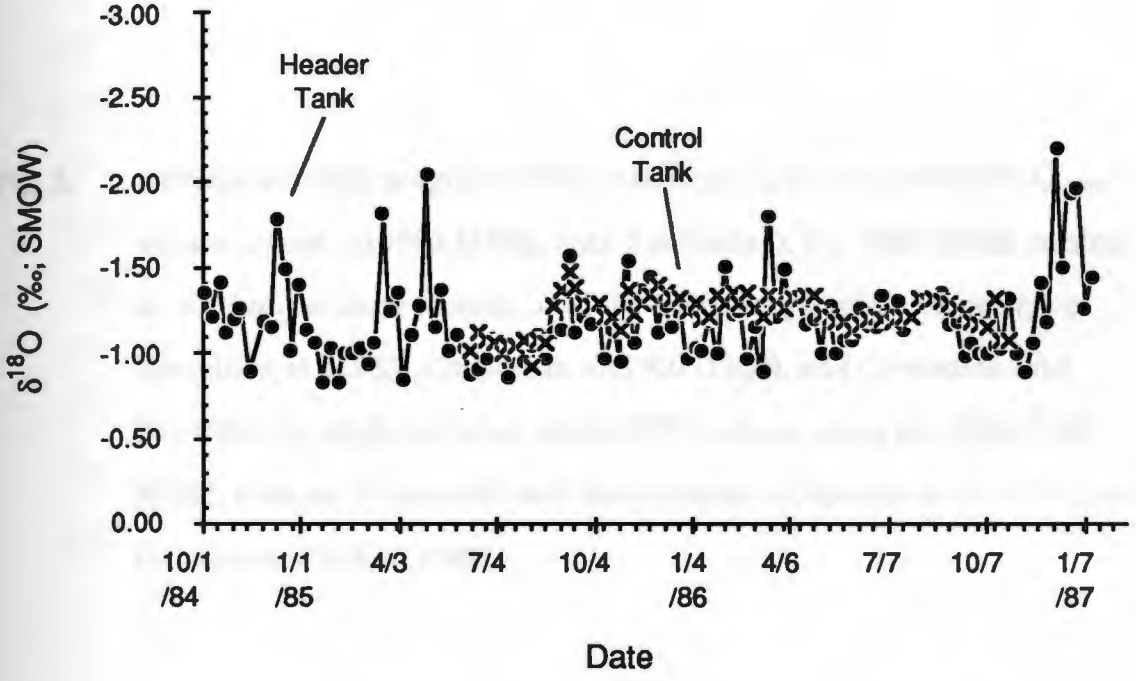
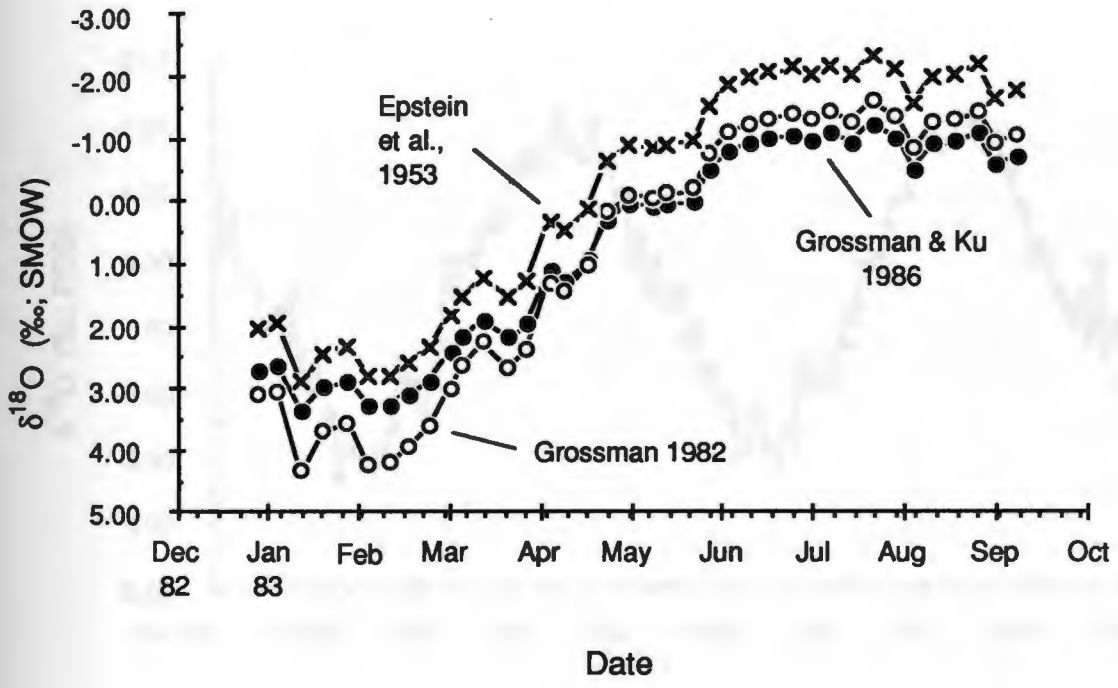

-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
Header Tank
Control Tank
δ18O (‰; SMOW)
10/1 /84
1/1 /85
4/3
7/4
10/4
1/4 /86
4/6
7/7
10/7
1/7 /87
Date

Fig. 5. a)Predicted shell aragonite $\delta^{18}O$ values using the modeled $\delta^{18}O_{water}$ values (based on 1983 MERL tank 0 salinities), the 1983 MERL control tank 0 temperature records, and the paleotemperature equations of Epstein et al. (1953), Grossman and Ku (1982), and Grossman and Ku(1986); b) predicted shell calcite $\delta^{18}O$ values using the 1984–1987 MERL data set (Figure 4b) and the equation of Epstein et al. (1953), and Grossman and Ku (1986).


-3.00
-2.00
-1.00
0.00
1.00
2.00
3.00
4.00
5.00
δ18O (‰; SMOW)
Epstein
et al.,
1953
Grossman & Ku
1986
Grossman 1982
Dec
82
Jan
83
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Date

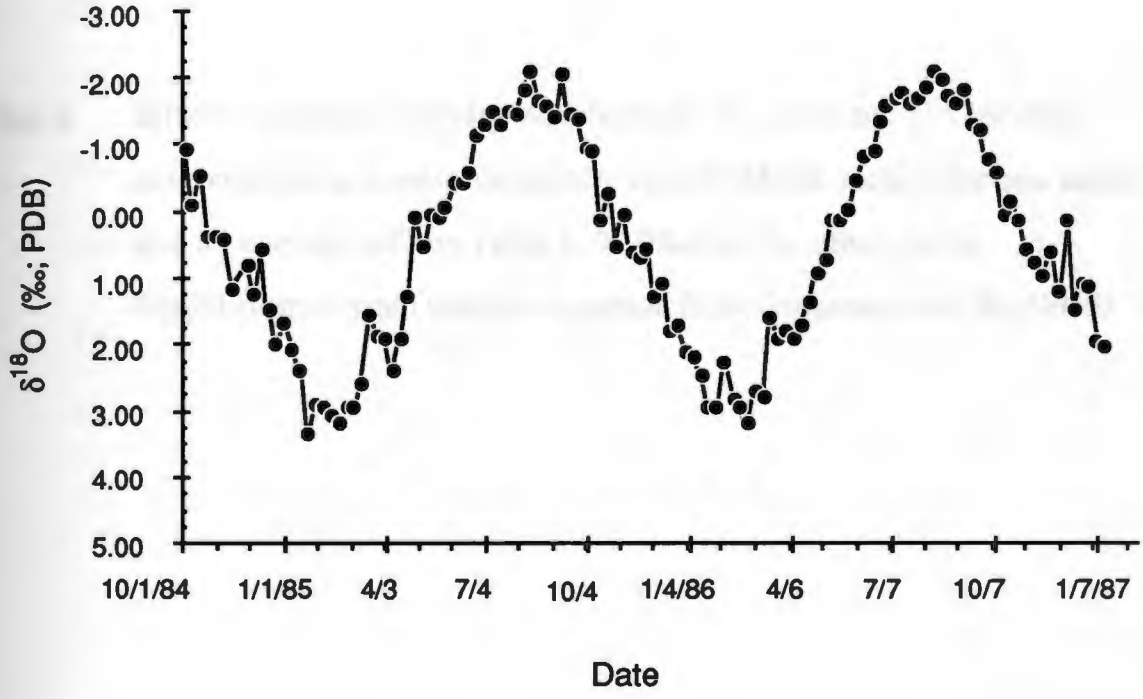
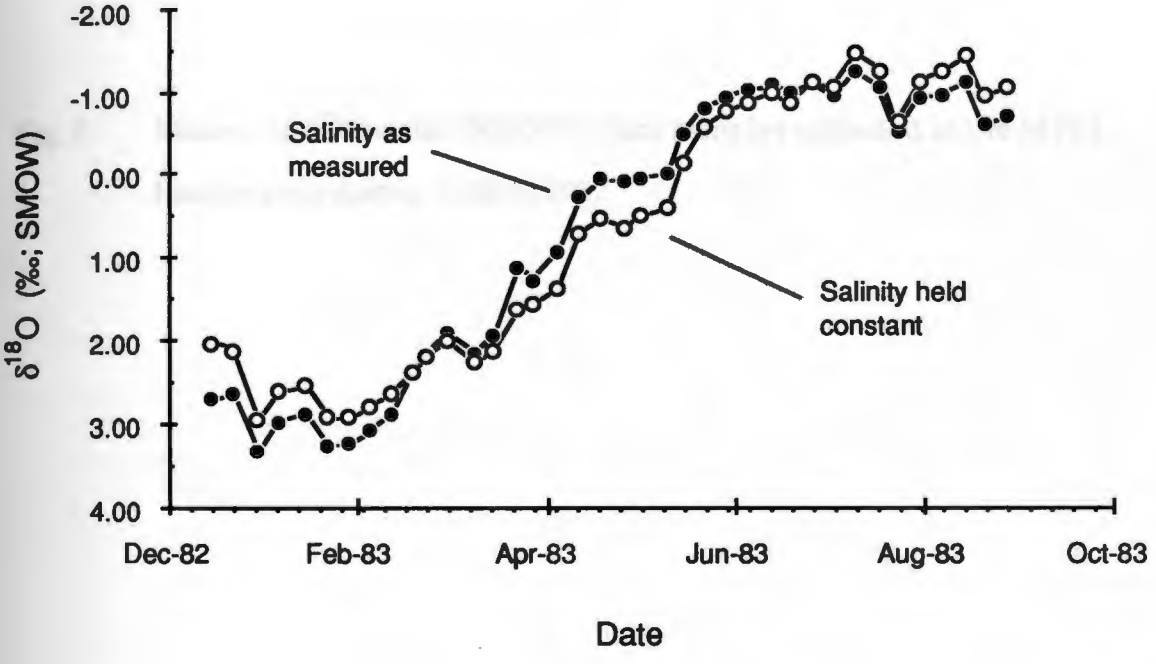

-3.00
-2.00
-1.00
0.00
1.00
2.00
3.00
4.00
5.00
δ18O (‰; PDB)
10/1/84
1/1/85
4/3
7/4
10/4
1/4/86
4/6
7/7
10/7
1/7/87
Date

Fig. 6. Effects of seasonal salinity variations on the predicted $\delta^{18}O$ of shell aragonite using a seasonal salinity record (MERL tank 0) for one curve and an average salinity value (= 29.0‰) for the other curve. Equilibrium oxygen isotopic equation from Grossman and Ku (1986).


-2.00
-1.00
0.00
1.00
2.00
3.00
4.00
δ18O (‰; SMOW)
Salinity as measured
Salinity held constant
Dec-82
Feb-83
Apr-83
Jun-83
Aug-83
Oct-83
Date

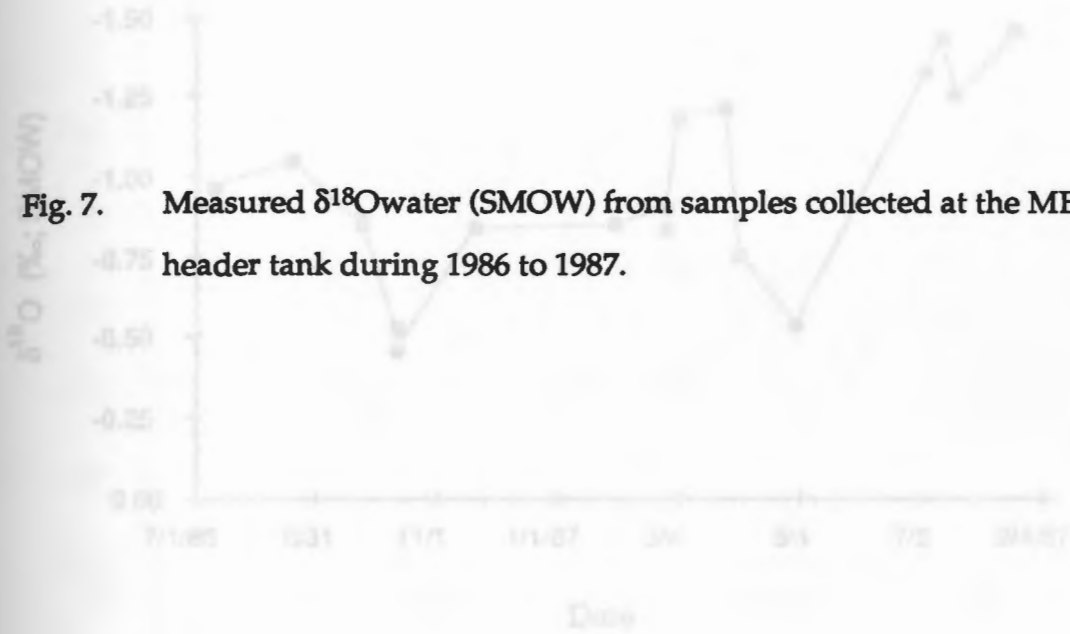
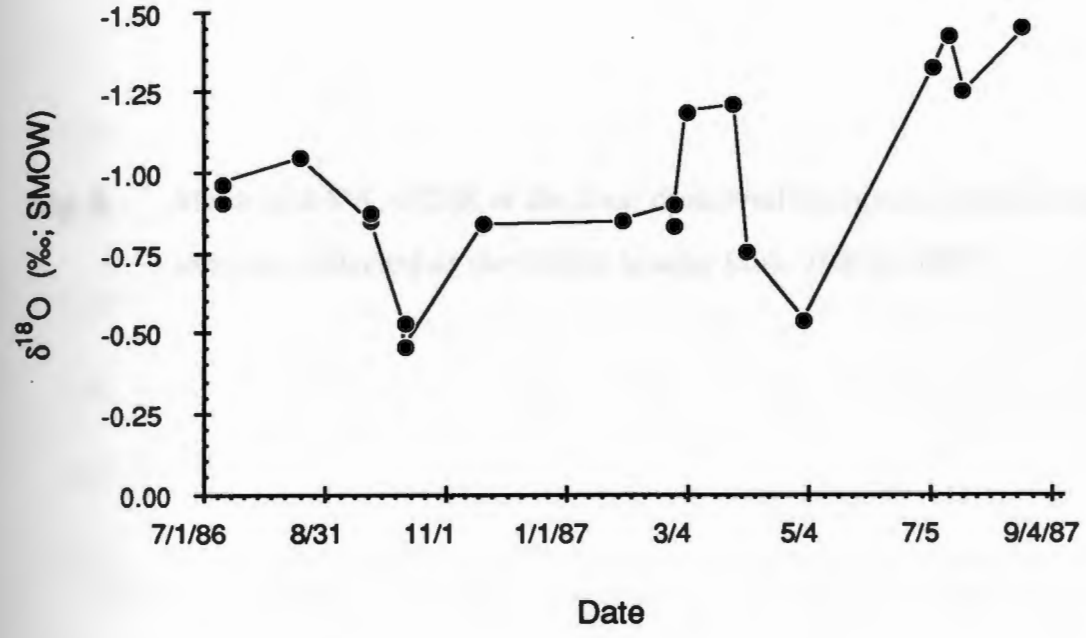


Fig. 7. Measured $\delta^{18}O$water (SMOW) from samples collected at the MERL header tank during 1986 to 1987.


-1.50
-1.25
-1.00
-0.75
-0.50
-0.25
0.00
δ18O (‰; SMOW)
7/1/86
8/31
11/1
1/1/87
3/4
5/4
7/5
9/4/87
Date

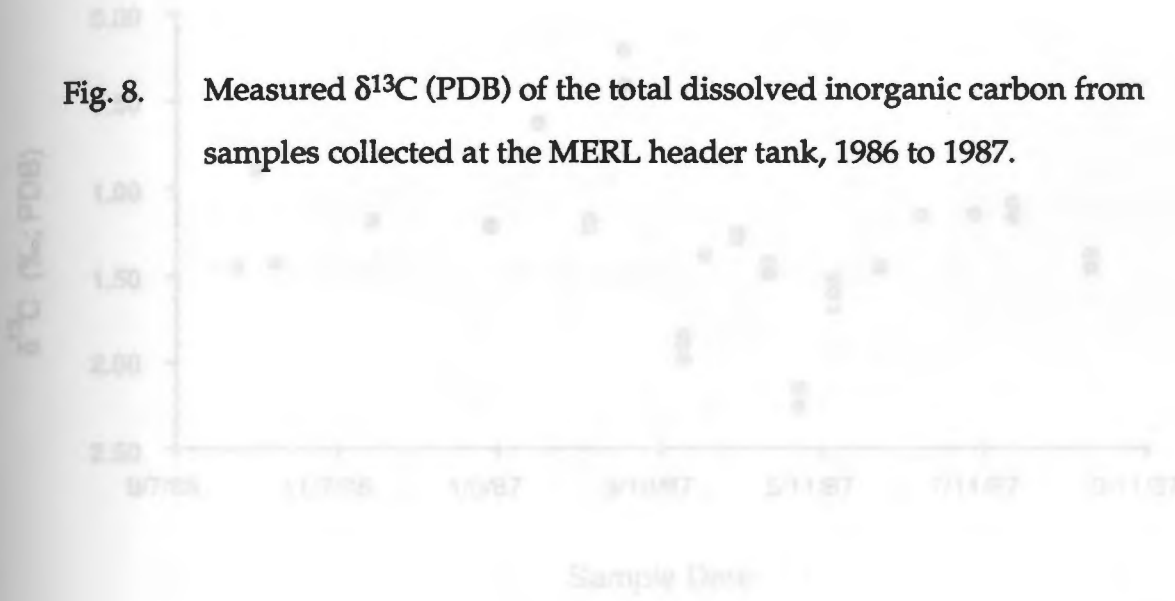


Fig. 8. Measured $\delta^{13}C$ (PDB) of the total dissolved inorganic carbon from samples collected at the MERL header tank, 1986 to 1987.

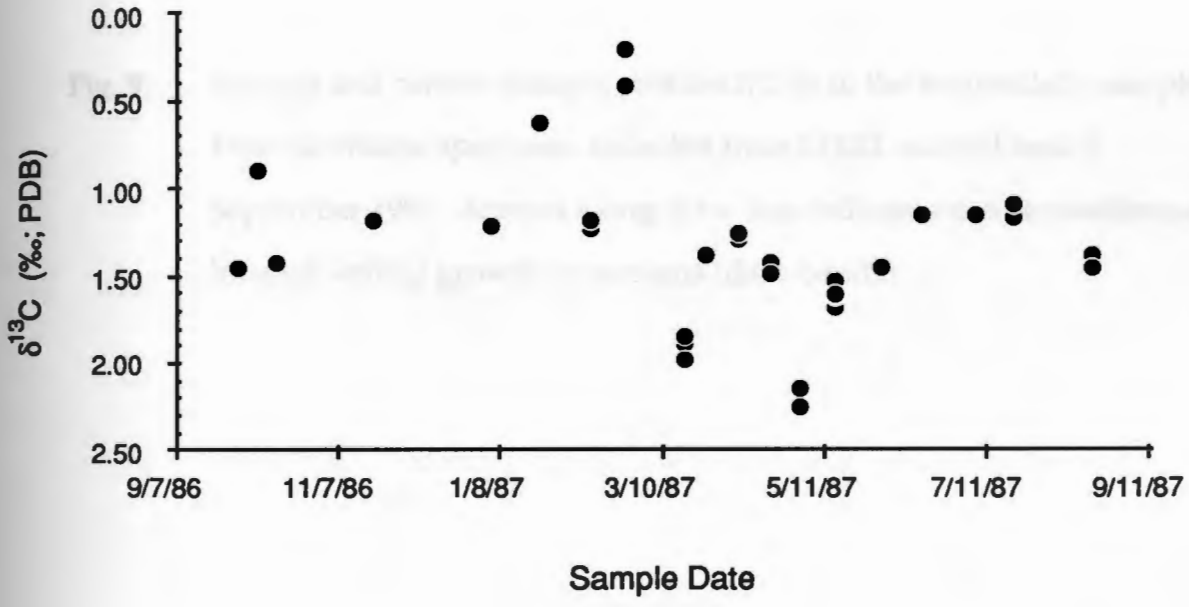
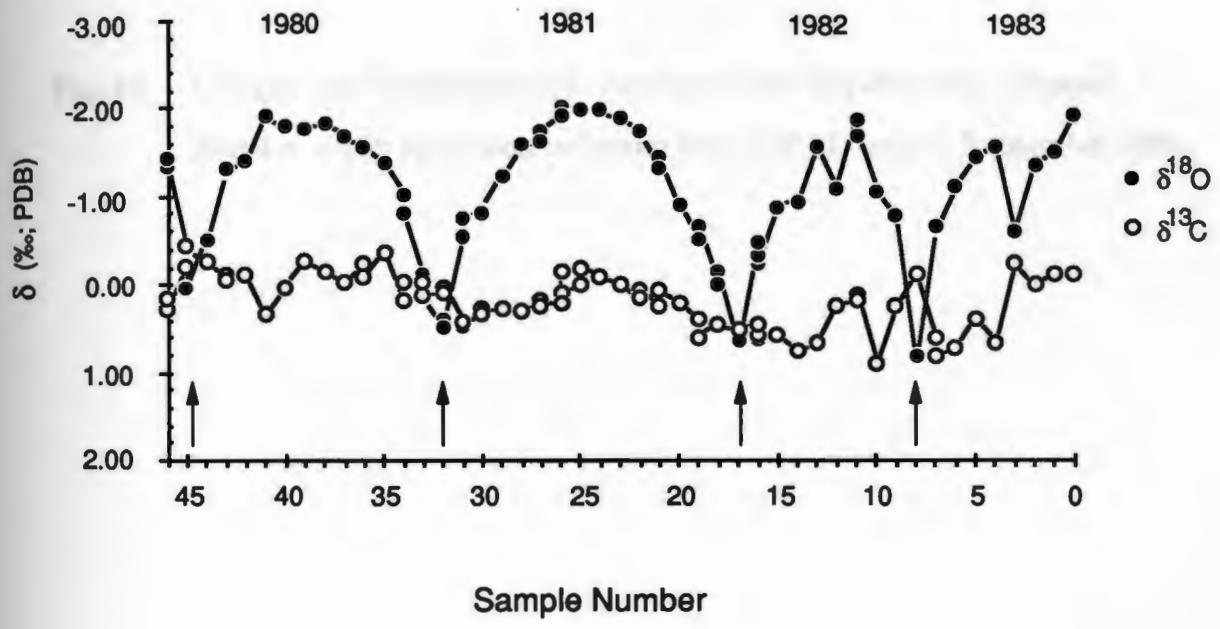

0.00
0.50
1.00
1.50
2.00
2.50
δ13C (‰; PDB)
9/7/86
11/7/86
1/8/87
3/10/87
5/11/87
7/11/87
9/11/87
Sample Date

Fig. 9. Oxygen and carbon isotopic profiles (PDB) of the sequentially sampled *Pitar morrhuana* specimen, collected from MERL control tank 0, September 1981. Arrows along the x-axis indicate relative positions of internal annual growth increments (dark bands).


-3.00
-2.00
-1.00
0.00
1.00
2.00
δ (‰; PDB)
1980
1981
1982
1983
45
40
35
30
25
20
15
10
5
0
Sample Number
δ18O
δ13C

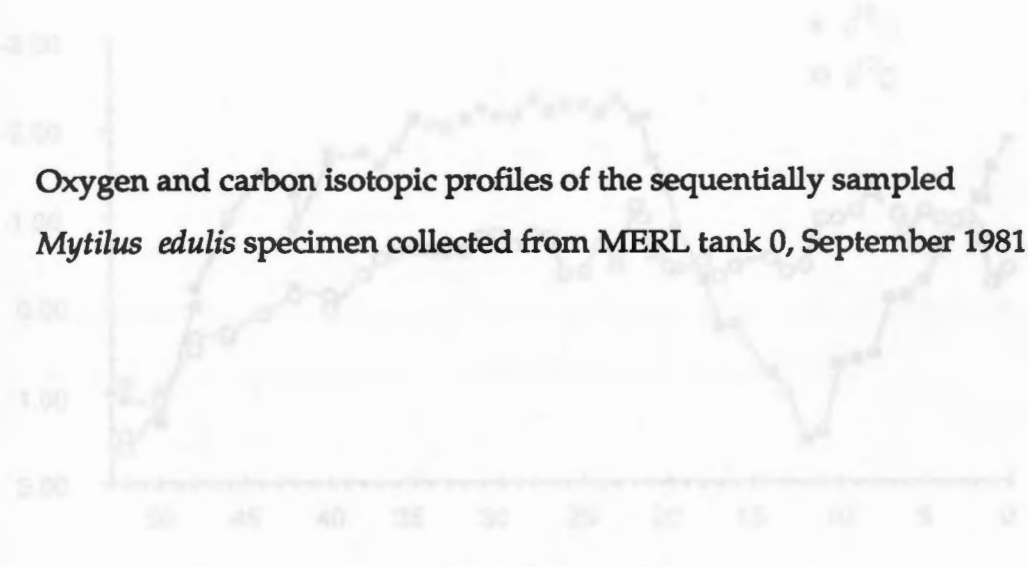
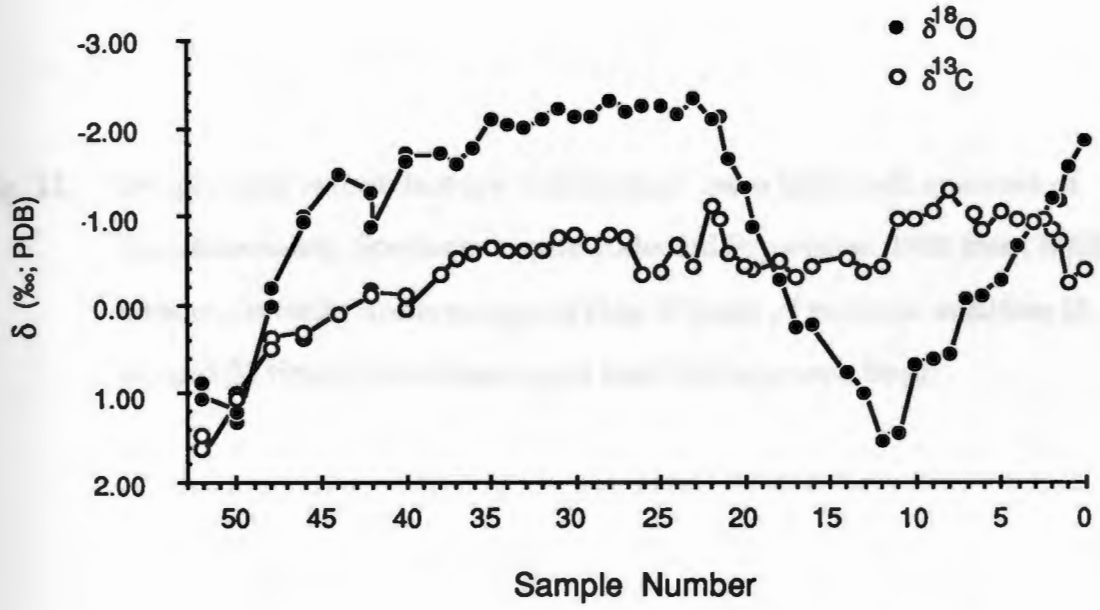


Fig. 10. Oxygen and carbon isotopic profiles of the sequentially sampled *Mytilus edulis* specimen collected from MERL tank 0, September 1981.


δ18O
δ13C
-3.00
-2.00
-1.00
0.00
1.00
2.00
δ (‰; PDB)
50
45
40
35
30
25
20
15
10
5
0
Sample Number

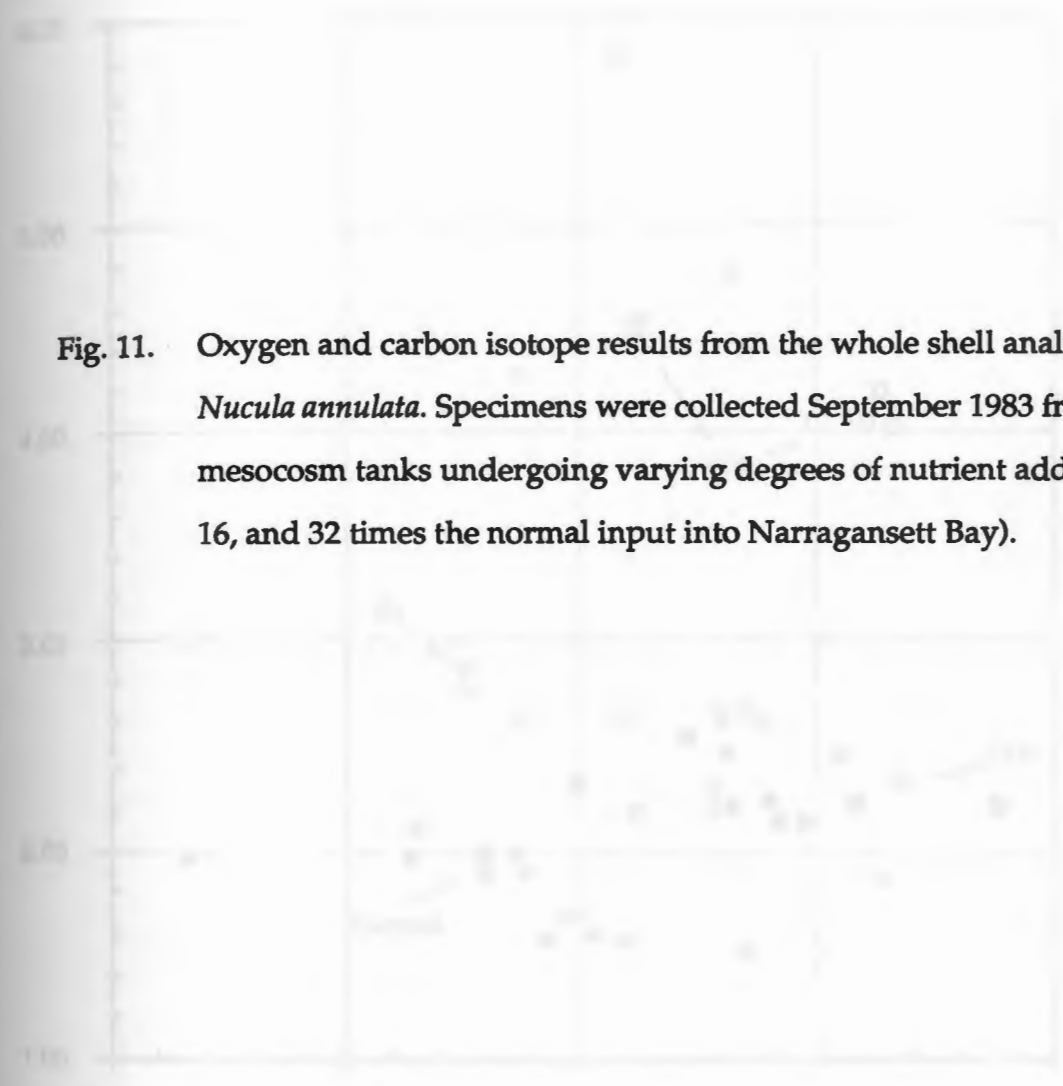


Fig. 11. Oxygen and carbon isotope results from the whole shell analyses of *Nucula annulata*. Specimens were collected September 1983 from MERL mesocosm tanks undergoing varying degrees of nutrient addition (8, 16, and 32 times the normal input into Narragansett Bay).

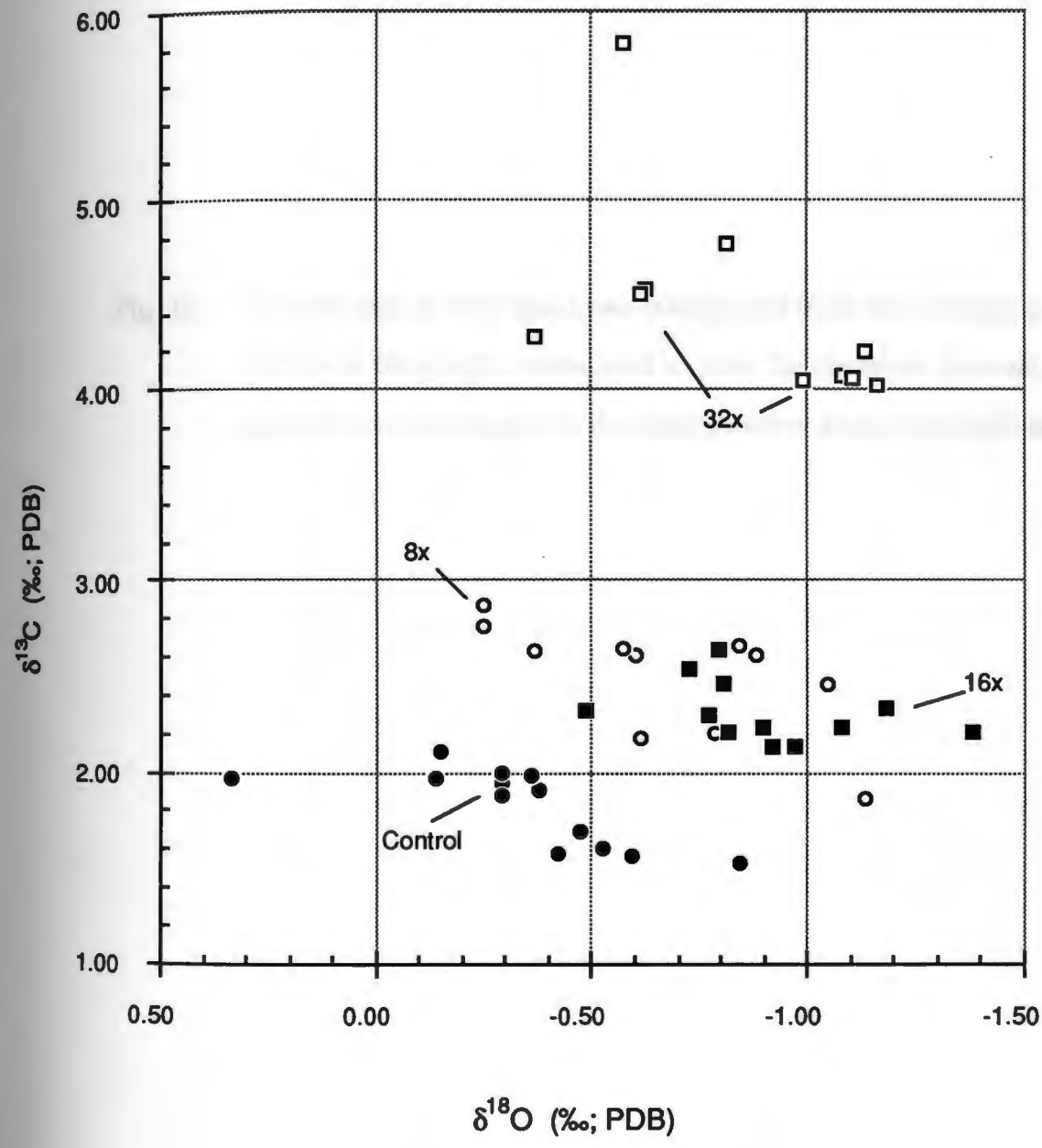
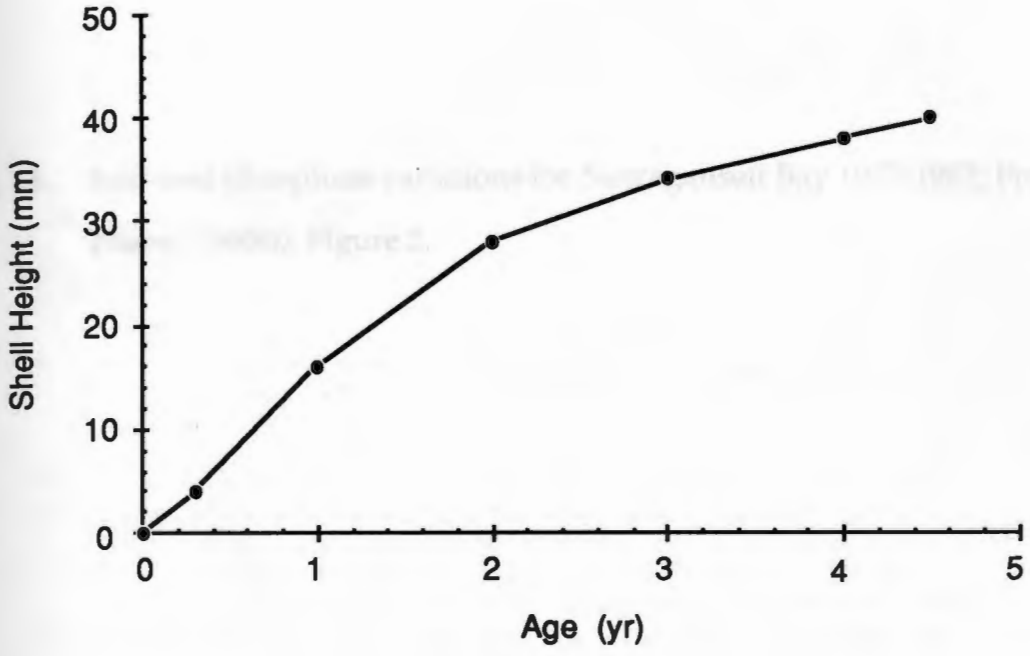

6.00
5.00
4.00
3.00
2.00
1.00
0.50
0.00
-0.50
-1.00
-1.50
δ13C (‰; PDB)
δ18O (‰; PDB)
32x
8x
16x
Control

Fig. 12. Growth rate of *Pitar* specimen interpreted from the isotopic profile. Points on the graph correspond to both the observed internal shell growth increments and to the most positive annual isotopic sample.


Shell Height (mm)
50
40
30
20
10
0
0
1
2
3
4
5
Age (yr)

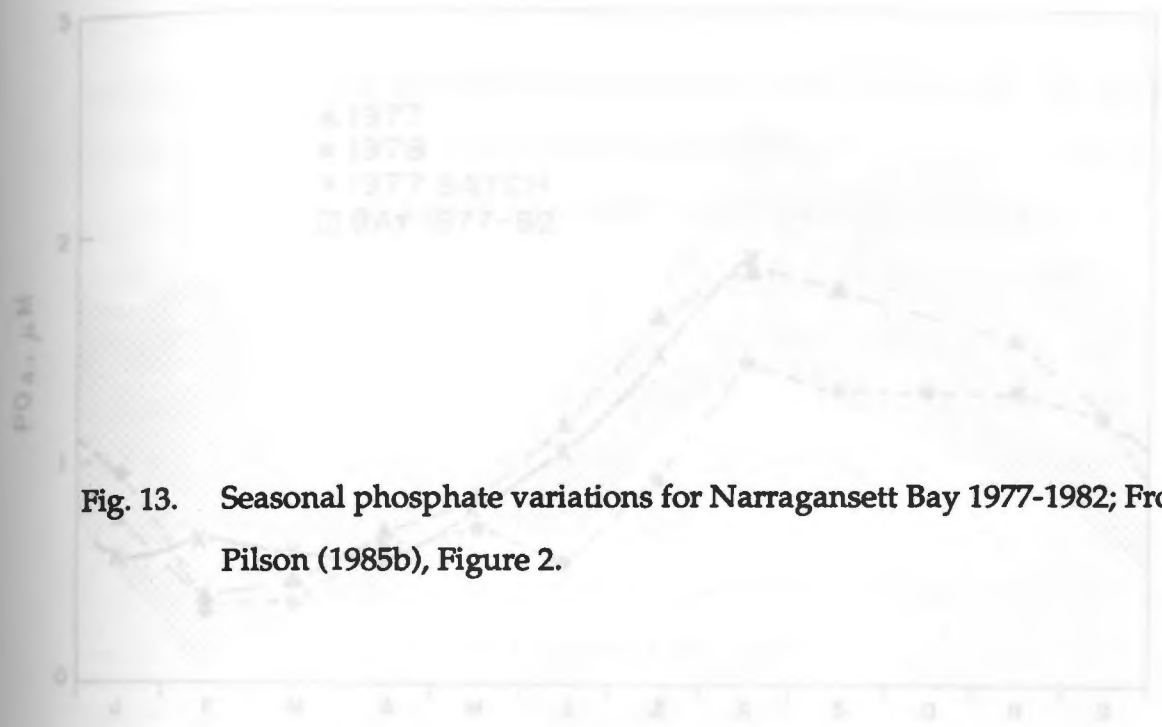


Fig. 13. Seasonal phosphate variations for Narragansett Bay 1977-1982; From: Pilson (1985b), Figure 2.

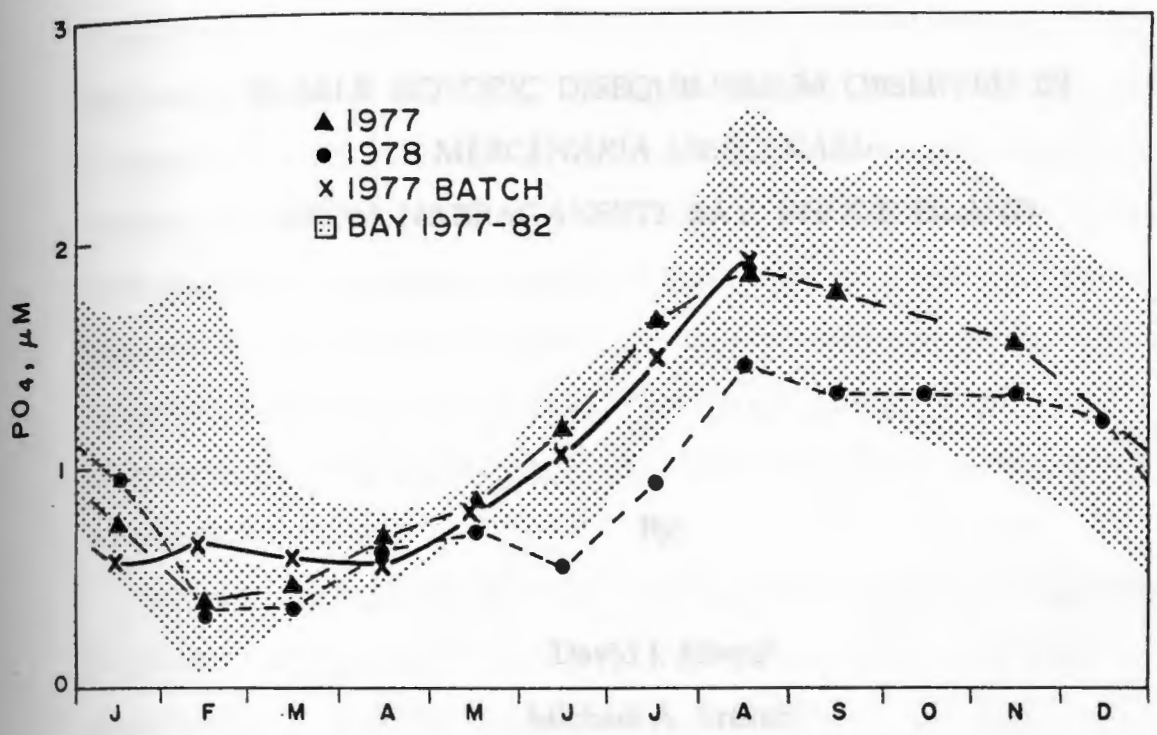


Fig. . Concentrations of phosphate in Narragansett Bay and in MERL tanks. The stippled area represents the field in which were found approximately 95% of the monthly means of weekly observations in lower Narragansett Bay, during a six-year period of observation. The two dashed lines connect the monthly means of weekly observations in three MERL control tanks during a two-year period. The solid line connects the monthly means of weekly observations in three tanks run in batch mode, with no sea water added during eight months of observation. (From Pilson, 1985b.)

STABLE ISOTOPIC DISEQUILIBRIUM OBSERVED IN *MERCENARIA MERCENARIA* FROM NARRAGANSETT BAY, RHODE ISLAND

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Abstract:

Carbon and oxygen isotopic measurements of Narragansett Bay water allow interpretations of the isotopic signals observed in the shells of *M. mercenaria* and verification of the seasonal nature of the shell $\delta^{18}O$ variations. These isotopic analyses of *M. mercenaria* indicate that the shell of this species does not form in isotopic equilibrium with the surrounding sea-water. The measured $\delta^{18}O$ of the shell aragonite is typically 1.5‰ more negative than the values predicted with the aragonite–water isotopic fractionation equation of Grossman and Ku (1986). Although the apparent isotopic disequilibrium is a problem in determining absolute temperatures, the oxygen isotopic profiles may indicate relative seasonal temperature variations.

Seasonal timing of growth of *M. mercenaria* was estimated by means of the amplitude and cycles of $\delta^{18}O$ variations in the outer shell layer. These observations are verified by the isotopic values of shell-edge samples of specimens collected during different times of the year. The growth history of the specimens, as revealed by the oxygen isotopes, indicates that greatest shell growth occurs between the second and fourth full years of growth, slowing dramatically after the fifth year. Years of greatest shell growth also represent the longest growing seasons and it appears that with increasing age the growing season is restricted to warmer temperatures.

There are no seasonal trends in $\delta^{13}C$ of either the shell edge samples or the incremental. The $\delta^{13}C$ values are more depleted than predicted, indicating that the carbon isotopic signal is influenced by the uptake of isotopically light metabolic carbon.

INTRODUCTION

Detailed isotopic analyses of the shell material of molluscs have revealed information about growth patterns of the molluscs as well as environmental conditions present during growth. When used in conjunction with growth increment analysis (Jones, 1981), a better understanding of factors such as growth rate and population size versus environmental influences, including temperature, salinity, pollution, and food availability, may be revealed. This study uses such techniques to examine the growth history and ecology of the hard clam *Mercenaria mercenaria* (Linné), collected from various locations in Narragansett Bay, Rhode Island (Fig. 1).

The hard clam is common along the east coast of the United States, ranging from the Gulf of Saint Lawrence to Florida and into the northern Gulf of Mexico (Saila and Pratt, 1973). *M. mercenaria* is a infaunal filter feeder that inhabits the intertidal and shallow subtidal zones of bays and estuaries, tolerating a wide variety of temperature and salinity regimes. Although *M. mercenaria* is geographically widespread and well studied, virtually no isotopic studies have been undertaken on the shells of this species. We believe that stable isotope studies can significantly improve the understanding of rate and season of shell growth. Extensive work has been done on the shell microstructure of this species (see Kennish, 1980; Grizzle and Lutz, in press), and in this paper we compare the isotope results from the shells to the observed shell growth patterns. In addition, to develop a better understanding of ecological influences on growth rate, we set out to assess the suitability of *M. mercenaria* as a monitor of environmental conditions in the bay. We hoped that these results, for example, could also be used to interpret the shell record of specimens collected from archeological sites in terms of environmental change. Many of the more recent isotopic studies of

molluscs have lacked the detailed sampling of the local growth environment that has such a strong influence on the isotopic record, relying instead on inferred relationships, often from differing environments. This study combines the detailed stable isotopic analyses of *M. mercenaria* specimens collected from Narragansett Bay with sampling of the bay water in order to determine the $\delta^{13}C$ of the total dissolved inorganic carbon and the $\delta^{18}O$ of the water.

ENVIRONMENTAL SETTING

Narragansett Bay is a weakly stratified, temperate estuary with strong tidal mixing and low fresh water input as described by Hicks (1959) and Pilson (1985a). The relatively minor salinity variations in the bay are predominantly caused by variations in fresh water input, most of which occur at the head of the bay. Salinities decrease from the entrance to the head of the bay. There is a low gradient in bottom water salinities (32 – 29‰), whereas the surface salinities gradient is usually more pronounced (31–27‰). The water temperatures in Narragansett Bay, as measured at the Graduate School of Oceanography (GSO) dock and Marine Ecosystems Research Laboratory (MERL) (Figure 2), vary from a high of 23°-$\pm$1°C during July and August to a low of 1°-$\pm$1°C in late January to early February.

Salinity values were obtained from the literature (Hicks, 1959, Kremer and Nixon, 1978, Pilson, 1985a), the MERL group (Oviatt, pers. comm., 1987) for the lower bay, and from Scott Nixon and Steve Granger at GSO (pers. comm., 1987) for the upper bay and Providence River. The majority (> 90%) of the (weekly) salinity measurements at MERL, which are essentially surface water values, fall within the range of 29.5 to 32.0‰, and are representative of the surface salinities in the middle and lower bay. Short-term, low-salinity excursions observed at

MERL (Fig. 3A) are probably due to periods of high runoff and related to the height (near sea-surface) of the MERL seawater intake. Figure 3a shows the weekly salinity measurements at the MERL header tank from October 1984 to January 1987 and from one of the MERL control tanks (tank–12) during part of that time period. The lower-bay surface salinity data presented by Hicks (1959) has a range of values similar to those measured at the MERL tanks (all years). Figure 3c is a time series of salinity measurements made by Steve Granger (of GSO) at the head of bay, near the Providence River. The surface salinities are much more variable at the head of the bay, especially in the late winter to early summer. The bottom-water salinity values are nearer to those measured in most other parts of the bay (29–32‰). Surface salinities in the upper bay decrease substantially during periods of high runoff (e.g. Hicks, 1959), although the low values probably do not persist for very long due to the increased flushing rate of the bay during periods of high runoff (Pilson, 1985a).

METHODS AND MATERIALS

The *M. mercenaria* shells for this study were selected from collections taken along a north-south transect of western Narragansett Bay and from the Providence River by the Rhode Island Department of Environmental Management (DEM) at their shellfish monitoring stations. The collection stations and the water depths of these stations are shown in Figure 1 (the second number is the water depth). The shells were collected during March 1984, July 1985, and December 1985. Selected specimens from the bay stations were analyzed in detail for stable oxygen and carbon isotopes, the remaining shells were sampled at their outermost edge for isotopic analysis. The Providence River specimens were collected in July, 1983 by Rick Crawford of the Coastal Resource Center at U.R.I.

Samples for the analysis of the oxygen isotopic composition of the water ($\delta^{18}O_{water}$) and the carbon isotopic composition of the total dissolved inorganic carbon ($\delta^{13}C_{DIC}$) were collected from the MERL mesocosm tanks during 1986 to 1987 at approximately two week intervals and prepared for isotopic analysis as per Allard et al. (submitted).

Shells were carefully cleaned of organic matter (viscera and periostracum) and dried at room temperature prior to sampling for isotopic analysis. The shells of several specimens were selected for detailed isotopic investigation. These shells were sampled using the method of Jones et al. (1983). The shell edge samples were filed from along the ventral margin. These samples represent the last shell material precipitated by the mollusc prior to collection. Incremental samples (generally 0.6 to 0.7 mm wide) are an average of all the shell material formed during the interval of time represented by the width of the sample increment. The width of this interval is variable depending on the rate of addition of shell material.

Samples for isotopic analyses were roasted under vacuum at 390°C for one hour and then reacted in "100%" orthophosphoric acid at a constant temperature of 50°C (±0.5°). The resultant CO_2 gas was subsequently analyzed on a V.G. Micromass 602–D dual collection isotope ratio mass spectrometer. The isotopic data are given in the conventional delta (δ) notation as the per mil (‰) enrichment or depletion in ^{18}O and ^{13}C relative to the Pee Dee Belemnite (PDB) standard (Craig, 1957). NBS-20 was used at the start and end of each session on the mass spectrometer as a standard. The analytical precision for the shell samples was ±0.1‰ for both $\delta^{18}O$ and $\delta^{13}C$ (standard deviation for the NBS–20 duplicates was the same).

We have found that roasting pure aragonite samples, such as the*Mercenaria* shell samples, under vacuum at 390°C results in an oxygen isotopic fractionation of –0.35‰ (1σ = 0.06‰), relative to the unroasted sample; a very slight carbon isotopic fractionation equal to –0.06‰ (1σ = 0.06‰) was also observed (see Appendix II). The values given in this paper have not been corrected for this observed fractionation.

We estimated the $\delta^{18}O$ of Narragansett Bay water using a two component linear mixing model, controlled by salinity changes (Fig. 3a) described by Allard et al. (submitted). The results of the modeled $\delta^{18}O_{water}$ (SMOW) are shown in Figure 4a for several different MERL tanks. The estimated $\delta^{18}O_{water}$ values (based on the salinity measurements) have a maximum range of approximately 1.4‰ (SMOW). The typical $\delta^{18}O_{water}$ range is less than 1‰ (SMOW) if the short-term salinity excursions observed in the MERL data sets are averaged out over time periods greater than 2 weeks. The observed vertical salinity gradients in the lower bay rarely exceed 2‰ (Hicks, 1959; Pilson, 1985a) which corresponds to a vertical $\delta^{18}O_{water}$ gradient of approximately 0.5‰ under constant temperature conditions. The vertical salinity gradients near the head of the bay can exceed

8‰ (Figure 3b) which corresponds to vertical $\delta^{18}O_{water}$ gradients of greater than 2‰. Most of the *M. mercenaria* samples came from water depths greater than 4 meters, which corresponds to a more limited $\delta^{18}O_{water}$ range.

The modeled $\delta^{18}O$ values of the water have been used to predict the oxygen isotopic composition of the shell aragonite formed by *M. mercenaria* during a typical year, using the paleotemperature equation of Grossman and Ku (1986, for mollusc data). Figure 5 shows the expected annual $\delta^{18}O$ compositions of shell carbonate formed by molluscs living in Narragansett Bay, using an averaged lower bay temperature record (from Figure 2b), the aragonite paleotemperature equation of Grossman and Ku (1986), and our calculated $\delta^{18}O_{water}$ values (Figure 4a). The variation between the curves in Figure 5 reflects typical yearly variations in salinity measured at MERL (weekly averages) for a given temperature. The predicted $\delta^{18}O$ aragonite curves are generally within 0.5‰ of each other at any given time and exhibit similar overall amplitudes with the greatest variation from year to year occurring in the spring. The salinities measured in the MERL (control) tank T-12 were about 4‰ lower than the salinities measured 3 years later, resulting in a difference in the expected $\delta^{18}O$ aragonite of approximately –1‰ (PDB). From the standpoint of estimating environmental temperatures using measured $\delta^{18}O$ values of shell aragonite, it is clear that a salinity change of 2‰, not uncommon in an estuary during any given week, could be incorrectly interpreted as a temperature change of approximately 2°C. As discussed below, short-term changes in salinity (and thus, changes in the oxygen isotopic ratio of the water as well) are probably not a problem in the isotopic interpretation of the shell carbonate, given the resolution of the shell sampling technique used in this study. Overall, the expected $\delta^{18}O$ range of *M. mercenaria* shell carbonate is approximately 4.5‰ for the yearly temperatures and salinities observed in Narragansett Bay.

The more commonly used aragonite–water equilibrium temperature equation of Grossman and Ku (1981) yields slightly different results than their more recent equation (Grossman and Ku, 1986). Most of the more recent work involving biologically formed aragonite (e.g., Jones et al., 1983, Krantz et al., 1987, Romanek et al., 1987) has used the earlier Grossman (1982) equation. The earlier aragonite equation was given in the same form as the calcite equation of Epstein et al. (1951, 1953) such that:

$$T(°C) = 20.19 - 4.56(\delta^{18}O_{aragonite} - \delta^{18}O_{water}) + 0.19(\delta^{18}O_{arag.} - \delta^{18}O_{w})^2$$

This equation predicts slightly lighter values of $\delta^{18}O_{aragonite}$ during warm temperatures (0.35‰ lighter) and more positive values of $\delta^{18}O_{aragonite}$ during cold temperatures (1.0‰ heavier). Thus, the predicted yearly range of $\delta^{18}O_{aragonite}$ using Grossman and Ku's (1981) equation is slightly less than 7‰. The majority of the difference between the two equations occurs at temperatures below approximately 5°C, corresponding to $\delta^{18}O_{aragonite}$ values greater than about 2.5‰ (PDB), using the conditions given above.

RESULTS

Water Oxygen & Carbon Isotopic Results

The results of the oxygen isotopic measurements of the water ($\delta^{18}O_{water}$) samples collected from the MERL header tank are shown in Figure 4b (listed in Appendix I, Table 1). The measured $\delta^{18}O_{water}$ values range between –0.4‰ and –1.5‰ (SMOW) with a slight seasonal trend toward lighter values in the spring. The average of the measured $\delta^{18}O_{water}$ values was –0.98‰ (SMOW) with one standard deviation (1 sigma) equal to 0.32 ‰. The measured $\delta^{18}O_{water}$ values are, on average, slightly more positive (–0.98‰ versus –1.19‰) than the values predicted by our linear mixing model (Figure 4a) based on the 1984 – 1987 header tank salinity data. As mentioned earlier, the header tank conditions are more variable than conditions below the surface of the bay or in the mesocosm tanks. The measured $\delta^{18}O_{water}$ values result in slightly heavier (approx. 0.2‰) predicted $\delta^{18}O$ values of shell carbonate than were estimated using the modeled $\delta^{18}O_{water}$ values.

The results of measurements of the $\delta^{13}C$ (PDB) of the total dissolved inorganic carbon in Narragansett Bay water collected from the MERL header tank are shown in Figure 6 (listed in Appendix I, Table 2). Samples were taken from August 1986 to September 1987 and the values range from 0.2‰ to 2.3‰ with an average value of 1.40‰ (PDB). The most noticeable changes occurred: 1) during late February to mid March of 1987 as a sharp increase in $\delta^{13}C_{DIC}$ of approximately 1.75‰; 2) during late April to early May as another sharp increase (1‰); 3) and from May through June as $\delta^{13}C_{DIC}$ values decreased by approximately 1‰.

Shell Edge Data

In an effort to define the timing of shell growth in *M. mercenaria*, we sampled the ventral margin of specimens collected from different Department of Environmental Management stations in Narragansett Bay and the Providence River during different seasons. These shell edge samples are much narrower than the drilled samples and therefore probably represent a shorter interval of time. The results of the shell edge sample analyses for the specimens collected July 23, 1984 and for the specimens collected December 17, 1984 are plotted in Figure 7 as $\delta^{18}O$ versus $\delta^{13}C$ (listed in Appendix I, Table 9). The $\delta^{18}O$ values of the summer specimens generally range between –2.7 and –4.0‰, excluding the Providence River stations which have values that range from –3.5 to –5.1‰. The $\delta^{18}O$ values of the majority of the winter specimens range from about –1.75 to –3‰ with a few lighter values that are discussed below. The data show a pronounced shift toward more positive $\delta^{18}O$ shell carbonate values from specimens collected in the summer compared to those collected in the winter, with very little overlap between the sets of values. It is apparent that the $\delta^{18}O$ of the shell margins becomes more positive (heavier) as the molluscs continue shell formation into the fall. The difference in $\delta^{18}O$ between the average shell edge values of specimens collected in summer and the average of those collected in winter is 1.4‰, this difference is somewhat lower than the seasonal amplitudes observed in the incrementally sampled specimens during the later stage of growth, as discussed below.

The lightest $\delta^{18}O$ values measured from bay specimens, presumably representing shell growth during the warmest temperatures or during periods of low salinity, are approximately 2 to 3.5‰ lighter than the predicted aragonite values for summer temperatures. Using the paleotemperature equation (given above) and an average measured $\delta^{18}O$ shell edge value of –3.5 ‰ (PDB), we can

estimate either the water temperature that this value represents (for a given $\delta^{18}O_{water}$), or the $\delta^{18}O$ of the water, for a given temperature. The measured oxygen isotopic composition of the water during the summer ranges from –0.75 to –1.25‰ (SMOW), with an average of –1.0‰. Converting the $\delta^{18}O_{water}$ value to PDB and inserting this value into the aragonite–water fractionation equation of Grossman and Ku (1986), a water temperature value of 34.6°C is predicted. This result is approximately 12°C above the normal summer water temperatures in the bay. Assuming that the light $\delta^{18}O$ shell values represent shell material formed during the summer in 20°C water, the same equation predicts that the $\delta^{18}O_{water}$ must have been equal to –3.68‰ (SMOW). The estimated salinity of this water, using the $\delta^{18}O$ – salinity mixing model, is equal to 20.4‰. A summer salinity value this low is highly implausible given the various sets of (bottom-water) salinity measurements made in Narragansett Bay over the years. It appears that the oxygen isotopic composition of the aragonitic shells of *M. mercenaria* are displaced from isotopic equilibrium, as defined by the equilibrium oxygen isotope fractionation equation of Grossman and Ku (1986) for aragonite and water.

The shell edge data from the Providence River *M. mercenaria* specimens collected on July 23, 1984 are also plotted in Figure 7a. These molluscs were forming shell material that was generally isotopically lighter (ave = -4.35‰) than that of the specimens in the bay, just to the south. The difference between the two sets of values (0.75‰) is probably due to either the decrease in salinity prevalent in the Providence River, or the slightly elevated temperatures that commonly occur in the river in the summer (Hicks, 1959). The literature data suggest that the salinity gradient is stronger than the temperature gradient at the head of the bay (e.g., Hicks, 1959; Pilson, 1985a) and it is likely that most of the observed 0.75‰ $\delta^{18}O$ shift in the shell carbonate is due to salinity variations rather than

temperature variations. A –0.75‰ change in the $\delta^{18}O$ of the water corresponds to a reasonable salinity change of approximately 3‰, using the mixing model described previously.

When the shell edge $\delta^{18}O$ values are plotted against the lengths of the specimens (Figure 8) we see that in general, the smaller specimens have heavier shell edge material than the larger specimens. This indicates that the smaller specimens, which are usually the younger specimens, are forming shell material in colder water than the larger (older) specimens. The smaller specimens apparently have a longer growth season than the larger specimens, judging by this data.

The measured shell edge $\delta^{13}C$ values also exhibit a seasonal shift toward heavier values from the summer specimens to the winter specimens. The measured $\delta^{13}C$ shell edge data range from approximately –1.5 to -5.5‰ in the specimens collected in the summer and from 0.5 to –4.5‰ in the winter specimens. The average shell edge value of specimens collected in the summer (excluding the Providence River specimens) was –3.52‰, whereas the average value of specimens collected in the winter was –1.16‰ (PDB). The difference between the $\delta^{13}C$ averages of the two collections is thus 2.56‰. This is almost twice the difference exhibited by the oxygen isotopic measurements from the same sample sets. Both averages are skewed by the data from the Wickford Breakwater specimens (station 12) which had significantly lighter $\delta^{13}C$ shell edge values than the other specimens measured. It is not clear why the $\delta^{13}C$ of the shell carbonate would shift in such a manner over the time period represented by these different collections. The work of Rubinson and Clayton (1969) and Grossman (1984a) suggest that the equilibrium fractionation between the $\delta^{13}C$ of the dissolved inorganic carbon and aragonite formed in that water should be approximately 2.4‰ (PDB) at 24°C (aragonite is enriched relative to the water).

This would suggest $\delta^{13}C$ values in the range of 3 to 4‰ (1.4 + 2.4‰) should be observed during typical summer/fall temperatures. The $\delta^{13}C$ values measured from the shell edge samples appear to be far out of equilibrium with respect to the known fractionation values between the dissolved carbon isotopes (CO_2, H_2CO_3, HCO_3^-, and $CO_3^=$) and aragonite.

Oxygen Isotopic Profiles

The $\delta^{18}O$ results of the sequentially sampled specimens of *M. mercenaria* collected from DEM stations 2A, 9, and 12 (north to south) are shown in Figures 9, 10, and 11, respectively (results listed in Tables 6, 7, and 8, Appendix I). The data for each specimen are plotted with the isotopic composition of each sample on the vertical axis versus the individual sample number (drilled from the outer shell layer) on the horizontal axis. Sample #1 is the first sample taken from the umbonal region and represents the earliest growth. The oxygen isotopic profiles of the specimens generally exhibit cyclic $\delta^{18}O$ fluctuations, with several longer, higher amplitude cycles followed by shorter cycles with slightly lower amplitudes. As with previous studies using incremental analysis techniques, each observed cycle of heaviest – lightest – heaviest $\delta^{18}O$ values is interpreted as representing a single annual temperature cycle, and thus, one year of growth (or growing season) for the mollusc. The annual cycles are more distinct during the early years of growth, indicating faster growth, as evidenced by the higher number of equally spaced samples taken per $\delta^{18}O$ cycle, or growth year. The later growth, characterized by higher frequency cycles and relatively few samples per growth year, indicates that a stage of slower shell growth occurs after the fourth or fifth full growth years. The seasonality in the isotope record of the specimen collected from station 12 (Wickford Breakwater) is not as distinct as the other shell records.

The isotopic compositions of the *M. mercenaria* shell samples range between approximately 0‰ and –3.25‰ (PDB). The specimen from station 12 has a mean $\delta^{18}O$ value of –2.19‰ while the specimen collected from station 9 has a mean value of –1.85‰ and the specimen from station 2A has a mean of –2.11‰. The lightest $\delta^{18}O$ values for a given specimen are fairly consistent from year to year whereas the heaviest measured values fluctuate from year to year. The range of oxygen isotopic values observed in the shell profiles during the later stage of growth is similar in magnitude to the range of values observed between the winter and summer shell edge samples. The heaviest oxygen isotopic profile values (for the last few years of growth) and the winter shell edge values are roughly the same.

The lightest shell values of $\delta^{18}O$ typically measured fell between 2.5 and 3.5‰, representing shell growth during the time of warmest water temperatures, and are approximately 1.0 to 2.0‰ lighter than the predicted summer temperature aragonite values. This offset is slightly less than that observed in the shell edge values described earlier. The oxygen isotope profiles obtained by the successive sampling method again indicate that the oxygen isotopic composition of the aragonitic shells of *M. mercenaria* is displaced from isotopic equilibrium. The repetitive, cyclic shape of the isotopic profiles indicates that seasonal water temperature information is apparently being recorded in the oxygen isotopic composition of the shell aragonite and that the fractionation offset is somewhat consistent. The actual values, however, do not fit current equilibrium models for temperature and aragonite–seawater dependence.

Individual Shell $\delta^{18}O$ Profiles

The oxygen isotopic record of the *M. mercenaria* shell collected from station 2A (Figure 9) indicates that the specimen was approximately seven years old at

the time of collection (seven $\delta^{18}O$ oscillations). The term year, or growth year, will be identified as a cycle on the isotopic profile beginning and ending with the most positive $\delta^{18}O$ value. The annual growth cycles are well defined for the first five years of growth, but become ambiguous for the last few years where a single sample may represent the only high or low points of the curve. The lightest measured shell $\delta^{18}O$ values are fairly consistent, approximately –3‰. The lowest $\delta^{18}O$ values recorded by the shell carbonate range from –0.3‰ to –2.5‰. The maximum $\delta^{18}O$ amplitude occurs during the third and fourth growth years and is slightly less than 3‰.

The specimen from station 2A apparently began growth in the summer, reaching a height of approximately 0.5 cm during the first calendar year. Shell growth reached a maximum in the third and fourth years (each of these growth years defined by 26 samples) representing approximately 1.8 cm of shell growth (height) during each of those years. The combination of greatest shell accumulation and the greatest $\delta^{18}O$ amplitudes during the third and fourth years leads to the conclusion that these years of maximum growth ocurred over the greatest temperature span. Growth rates may have been similar to previous years however shell formation continued later into the year for the third and forth years. The amplitude of the $\delta^{18}O$ values decreases in the last few years of growth although the overall values are still very light, indicating a change in the timing of the growing season that is restricted to the warmest part of the year. As the specimen aged (past its fifth year) overall shell growth decreased dramatically.

The first and second years of growth, represented by samples #1 to #8 and #8 to #24, respectively, were not the fastest growth years as is typical of most molluscs. The first two growth years are well defined in terms of $\delta^{18}O$ values and are similar in shape to the annual temperature pattern but the overall amplitudes are compressed, indicating steady, but slow, growth during those years.

The *M. mercenaria* specimen collected from station 9 has an oxygen isotope record (Figure 10) similar to the specimen from station 2A. The $\delta^{18}O$ data indicate that the station 9 specimen was approximately 8 years old at the time of collection. Shell growth was very limited the first year (only a partial growth year after the clam was spawned). Maximum shell growth (and $\delta^{18}O$ amplitudes) occurred during the second, third and fourth full years. The first full year of growth (samples #3 – #12) was not the year of greatest shell growth, as observed with the previous specimen. The lightest measured values of $\delta^{18}O$ are fairly consistent for the first 6 years, typically –2.75‰ PDB, then begin to get lighter and more erratic for the next 4 growth years. The heaviest $\delta^{18}O$ values become more positive for the first 3 (full) years of growth, starting at –1.1‰ and increasing to approximately 0‰ at the end of the third and fourth years. Then the values become increasingly lighter for the remaining 3 years of growth. As with the specimen from station 2A, the years with the greatest shell growth (most samples recovered from the shell per seasonal cycle) are also the years exhibiting the greatest range of $\delta^{18}O$ values. As this specimen matured, its growth pattern seems to have followed that of the specimen collected from station 2A: measured $\delta^{18}O$ values are generally lighter, fewer samples per year of growth, and overall yearly $\delta^{18}O$ amplitudes are compressed relative to those measured during years of faster growth.

The *M. mercenaria* specimen collected from station 12 has an oxygen isotope profile (Figure 11) that is quite different from the specimens previously described. The $\delta^{18}O$ record does not accurately track the regular, yearly temperature variations as one might expect and it is difficult to determine the exact age of this specimen based upon the isotopic evidence. The isotope profile exhibits fairly light $\delta^{18}O$ values overall and a trend toward even lighter values with increasing age. The heaviest seasonal $\delta^{18}O$ values are also lighter than recorded by the other

specimens. A few seasonal cycles such as the one from samples #62 to #77, and the one from samples #77 to #93, are pronounced. Yet, the amplitudes of these two cycles are less than 2‰ in contrast to the 3‰ amplitudes measured in the other specimens. These two cycles are represented by fewer samples than the fastest growth cycles of the other *M. mercenaria* , indicating overall slower growth in this specimen. There are several possibilities that may account for the observed isotopic record in the shell of this specimen. Collection station 12 is just outside of the Wickford breakwater in approximately 2 meters of water and this specimen is the largest of the *M. mercenaria* specimens sampled in detail. The environmental conditions at this site (DEM station 12) could be adversely affecting shell growth, leading to the erratic pattern recorded by the oxygen isotopes, and/or an overall lower rate of growth, compared to specimens collected from other stations.

Carbon Isotopic Profiles

The $\delta^{13}C$ records for each of the incrementally sampled specimens are plotted versus the sample number along with the respective oxygen isotope data in Figures 9, 10, and 11. The carbon isotope data from the *M. mercenaria* shells do not exhibit clear seasonal cycles as defined by the oxygen isotope data. The overall trend in the specimens collected from station 2A and station 9 involves initial shell formation with $\delta^{13}C$ values of approximately –1.0‰ for the first two years. This is followed by the uptake of slightly heavier carbon in the fastest growing years (values average 0.5‰) and finally by the incorporation of increasingly lighter carbon for the remaining years of growth. The $\delta^{13}C$ values can vary widely from sample to sample with the values recorded by the specimen collected from station 2A ranging from 0.4 to –1.75‰, although most of the values fall between 0.2 and –1.5‰. The values of the specimen collected from

station 9 range from 0.8 to –2.3‰, with most of the values falling between 0.5 and –1.5‰. The specimen collected from station 12 has $\delta^{13}C$ values ranging from 0.8 to –1.0‰ over most of the shell; but ,with increasing age, the shell $\delta^{13}C$ becomes increasingly lighter, ranging between –1.75 and –3.0‰ for the outermost shell. This mimics the trend observed in the oxygen isotope record during later growth in this specimen.

The equilibrium fractionation between aragonite and dissolved inorganic carbon (DIC) is somewhat uncertain. Rubinson and Clayton (1969) give a value of 2.7‰ (for a mixture of aragonite and calcite) at 25°C whereas Grossman (1984a) suggests a value of 2.40‰ between dissolved inorganic carbon and aragonite at 20°C. Grossman and Ku (1986) indicate that the ^{13}C enrichment (aragonite - DIC) is, under certain conditions, temperature dependent, suggesting the relationship:

$$^{13}\varepsilon_{mollusc\text{–}DIC}(‰) = 2.66 - 0.131\ T(°C).$$

Assuming that the $\delta^{13}C_{DIC}$ is equivalent to the $\delta^{13}CHCO_3^-$, the average expected $\delta^{13}C$ value of aragonitic shells precipitated in Narragansett Bay water should be approximately (1.4‰ave. DIC + 2.6‰ fractionation =) 4.0‰ (PDB). Clearly, the measured $\delta^{13}C$ shell values (generally between 0.5 and -1.5‰) are not in carbon isotopic equilibrium with the surrounding water, regardless of which of the above fractionation factors are used. The temperature dependence of the carbonate–DIC ^{13}C equilibrium fractionation (Grossman and Ku, 1986, for aragonite; Emrich et al., 1970, for calcite) would suggest a correlation between the measured $\delta^{18}O$ profiles of shell carbonate, which record mainly seasonal temperature cycle(s), and the $\delta^{13}C$ of the same samples. The lack of a correlation between the oxygen and carbon isotope samples (Figure 12), using the best defined growth years (years of fastest growth) of *M. mercenaria* from stations 2A

and 9, demonstrates that either the aragonite–DIC ^{13}C fractionation is not temperature dependent in this species of mollusc or that the carbon isotopic temperature signal is overwhelmed by other factors of the carbon cycle operating in the bay.

DISCUSSION

Growth Increments & the Oxygen Isotopic Records

Much of the recent work involving detailed isotopic analyses of mollusc shells (e.g., Arthur, et al., 1983; Jones, et al., 1983; Krantz, et al., 1984; Krantz, et al., 1987; Romanek, et al., 1987) has focused on the correlation between the isotopic record and the growth patterns that are observed on the exterior of the shell and/or the growth increments observed in a cross sectional view of the shell. The term growth increment can cover a wide variety of scales. The internal increment patterns that can be resolved with isotopes are usually seasonal or annual in nature whereas the growth increments that can be observed with the aid of a microscope have been ascribed to daily, bidaily, fortnightly and lunar-month growth periods (see Lutz and Rhoads, 1980; and Kennish, 1980 for a review) and are much too fine to be individually sampled for isotopic analysis.

Most bivalves are known to have internal growth increments of one kind or another (Rhoads and Lutz, 1980) and in many cases, such as observed with *Spisula solidissima* (Jones et al., 1978; Jones et al., 1983, Krantz et al., 1987), the more obvious internal growth increments have been shown to be annual in nature, allowing for quick and unambiguous age determinations. The exterior growth bands, or growth checks, common to many bivalves and often very distinct, are not always related to the annual (internal) growth increments (Jones, 1981; Krantz, 1984). Age estimates that make use of these exterior growth bands may not reflect the true age of the specimen. For the remainder of this paper the term growth increment will refer to the easily observable (with the naked eye), dark and light internal growth increment that is observed in a shell cross section.

The detailed isotopic analyses of the *M. mercenaria* shells allow for the comparison of the isotopic record (or profile) to the major growth increments

observed in these shells. The relative positions of the dark internal growth increments are marked with a small black arrow along the x axis in each $\delta^{18}O$ profile (Figures 9, 10, & 11). In the outer shell layer the dark growth increments may appear somewhat diffuse and will often split into thinner, multiple bands or a "packet" of bands, as they curve toward the external shell surface. The sharp, narrow, dark growth increments observed in the shells of the specimens from stations 2A and 9 generally appear to represent annual increments based on the oxygen isotope results. Because the dark increments usually split into multiple bands and intersect the outer shell layer at several different sampled intervals, it is difficult to pin down the actual timing of the initiation of these bands. For example, 4 individual dark bands, apparent as a single dark increment near the umbo, intersect the outer shell layer of the specimen from station 9 between samples #63 and #71. These samples have isotopic signatures that indicate summer through fall growth with the last, and sharpest, of the bands coinciding with the heaviest value recorded between two successive growth years. Counted separately, these 4 bands do not represent annual growth. When grouped together these packets occur in different growth years (as defined by the isotopic profiles). The first few dark increments (when the molluscs are less than 3 years old) are fairly distinct and are not always subdivided into multiple bands. These increments are also lighter and thinner than the dark increments that occur later. After the third or fourth year, the dark increments are always split into multiple bands and are darker than previous bands. This is probably indicative of more erratic growth in such years, a notion supported by the isotopic evidence and the number of samples taken per growth year. The isotopes indicate that after the third year, the multiple splits of a dark increment (a packet) begin appearing in the summer and occur through the fall. There is usually a thin (much thinner than any sample), sharp band that coincides with the heaviest value recorded.

Thus, the most obvious dark increments, or groups of finer increments, are not representative of slow, winter growth, but correspond to periods of erratic growth occurring throughout the summer and fall. These data indicate that the counting of the dark growth increments (counting each increment packet as one) in *M. mercenaria* will give approximately the correct age of the mollusc, although care must be exercised in correctly identifying all the increments and in using the dark increments to estimate the season of death of the specimen.

The specimen collected from station 12 exhibits a great number of dark growth increments (shown on Figure 11). Most of these increments are too thin to resolve with the sampling methods used here. The growth increments toward the ventral margin (those formed most recently) are too numerous to differentiate by eye, making the outer edge fairly dark in color. The inability to correlate the oxygen isotope record with any seasonal temperature fluctuations in this specimen precludes any determination of the timing of the dark increments.

The shell microgrowth patterns of *M. mercenaria* have been documented by a number of workers (e.g., Pannella and MacClintock, 1968; Rhoads and Pannella, 1970; Kennish and Olsson, 1975; Kennish 1978; 1980) as indicating nearly continuous shell growth during a year. These researchers have reported a hierarchy of growth patterns in the shell microstructure, ranging from subdaily to seasonal annual growth increments, as well as abrupt breaks in shell growth related to spawning, thermal shock (including freezing), and storm effects. Kennish (1980) reported that the daily growth increments of *M. mercenaria* range from 1 to 50 mm in winter, and from 15 to 150 mm during summer in specimens collected from a temperate New Jersey estuary (seasonal temperature range of –1.4 to 28.0°C).

Ansell (1968) concluded that*M. mercenaria* stops growing at temperatures below approximately 9°C, although temperature is apparently not the only factor

limiting growth. The work of Kennish (1980) indicates that shell growth in *M. mercenaria* is continuous for specimens collected from a temperate estuary in New Jersey but, the growth rate decreases rapidly below approximately 10°C. Although the isotopic evidence indicates that the aragonitic shells of *M. mercenaria* are out of equilibrium with the surrounding sea water, the relative amplitudes of the predicted shell aragonite curves and the measured shell values can be compared, assuming the offset is fairly constant. The general shape of the *M. mercenaria* oxygen isotopic profiles indicates that some seasonal temperature information is being recorded in the oxygen isotopic compositions. The expected range of aragonite precipitated in the bay is approximately 4.5‰ whereas the isotopic range measured from the *M. mercenaria* shells is typically less than 3‰. The heaviest isotopic values measured are much lighter than the values predicted (+3.5 ‰) for shell aragonite precipitated in the winter-time temperatures, even with the observed 1.5 – 2.0‰ offset toward lighter values. The isotopic evidence supports the observation that *M. mercenaria* either drastically slows or ceases deposition of shell material through the winter and during parts of the spring and fall. It would appear that at the level of detail used in the shell sampling techniques for this study, the utility of *M. mercenaria* as a monitor of annual geochemical variations or seasonal temperature amplitudes is somewhat limited.

The absence of measured $\delta^{18}O$ shell values indicative of low temperatures, or over the expected seasonal $\delta^{18}O$ range, could be due to the relatively coarse sampling method (average individual sample width is approximately 0.7 mm). This arguement is strengthened if comparisons are made relative to the fine detail of the shell microstructure when examined in thin section. If we use the growth rates given by Kennish (1980) then three months of continuous shell growth at 1μm per day would result in 0.12mm of total shell growth during the winter months, too small to be sampled with the sampling techniques used here. A shell

in its fastest growth years, growing continuously for three months at 10mm per day, would grow approximately 1.2μm in height over that period of time. Similarly, shell growth of 30μm per day would result in 3.6mm of shell growth recording winter temperatures values (when the $\delta^{18}O$ of the carbonate is examined). Both of these winter growth intervals would be nearly impossible to miss using the sequential shell sampling methods described above. It is possible that samples filed from the shell margin of smaller specimens (1 to 3 cm) could be used for a more accurate assessment of the total range of isotopic values. The shell edge samples have the advantage of being more detailed, due to their narrower (sampling) size.

The majority of the measured oxygen isotopic ratios are intermediate in value, indicating that the majority of shell growth in any well sampled year occurs in the spring and early summer. Previous studies (e.g., Rhoads and Pannella, 1970; Kennish and Olsson, 1975; Kennish, 1980) have indicated that the highest rate of shell growth in *Mercenaria* occurs in the summer, during times of elevated temperatures. Although the lightest $\delta^{18}O$ values are fairly consistent, they are quite limited in terms of the number of samples drilled for any given summer. This suggests slower total growth during the summer months (defined here as the 3 months with water temperatures above 18°C), relative to the growth occurring in the spring. If the summer months constitute the period of fastest overall growth, one would expect to see samples with similar (light) $\delta^{18}O$ values occurring in numbers greater than, or at least equal to, the number of samples with spring-time (intermediate) values. It is possible that the spring-time growth is merely the steadiest growth, occurring at a slower but more consistent rate than the growth rates observed in the summer in the studies cited above. If the rate of growth in the summer was faster but infrequent, or erratic, perhaps due to

the energy required for spawning or the availability of food, the result could be an isotopic profile similar to that observed.

Carbon Isotopic Disequilibrium

The $\delta^{13}C$ of the shell carbonate most likely reflects, or is regulated by, a wide variety of processes operating concurrently in the bay, including : phytoplankton production in the water column, regeneration of organic matter by the benthos, seasonal variations in ^{13}C input from fresh and/or oceanic water, the rate of growth, and the utilization of metabolic carbon by the molluscs, commonly refered to as the "vital effect". The seasonal phytoplankton production in Narragansett Bay is highly variable both in timing and in the quantity of biomass production (Karentz and Smayda, 1984; Oviatt et al., 1981). This seasonal primary production can alter the $\delta^{13}C$ of seawater bicarbonate by depleting the water in ^{12}C during periods of high productivity and some researchers (Killingley and Berger, 1979; Arthur et al., 1983) have attributed changes in mollusc shell $\delta^{13}C$ to this process. The degradation of this same organic biomass will eventually return much of the lighter carbon to the water column. Rudnick and Oviatt (1986) have shown that in Narragansett Bay this remineralization process lags the initial phytoplankton production by a few months. The starting point for their study was the Narragansett Bay winter–spring bloom which usually occurs in late January (plus or minus a few weeks) and is the strongest of the seasonal plankton blooms occurring in the bay. The water samples measured for $\delta^{13}C$ DIC do not show an increase in $\delta^{13}C$ values early in the year that might accompany this bloom. There are sharp changes in the $\delta^{13}C_{DIC}$ of the water in Narragansett Bay and there is a trend toward lighter values through the spring and summer.

Since *M. mercenaria* does not precipitate sufficient shell material to measure isotopically during the winter months, it is impossible to resolve the $\delta^{13}C$ signal

that might occur in the water column as a result of the winter–spring bloom. An examination of the isotopic record from any of the *M. mercenaria* shells sampled here (Figures 9, 10, and 11) reveals that there is little shell record of the remineralization of the organic carbon (a trend toward lighter values of $\delta^{13}C_{DIC}$, and hence, the $\delta^{13}C$ of aragonite) that might be expected during the spring and into the summer. There are a few instances of the $\delta^{13}C$ in the shell carbonate becoming lighter during the spring growth (samples 29 - 36 for the station 2A specimen and samples 14 – 19, and 55 – 62 for the specimen collected from station 9) but many of the growth years exhibit $\delta^{13}C$ changes in the opposite direction or show no change at all.

The shell edge $\delta^{13}C$ values of the *M. mercenaria* specimens collected in summer are much lighter than any of the samples measured from the three specimens samples in detail. This could be due to the age of the specimens, the growth environment – including conditions particular to 1984, or the different techniques used in obtaining the samples for isotopic measurement. Since the sizes of the specimens examined for shell edge samples and for incremental samples are similar, it is unlikely that the ages are drastically different. However, the specimens collected for shell edge analyses from station 12 are all larger than the specimen sampled in detail and this potential age difference could be significant isotopically, as the older shell growth exhibits much lighter $\delta^{13}C$ values.

The summer $\delta^{13}C$ values may indicate a fairly rapid rate of remineralization of the organic matter from the winter and spring blooms, as measurements in the bay (Pilson, 1985b) reveal higher levels of most nutrients throughout the summer. The same data also show high nutrient levels continuing from summer through the fall, which makes it difficult to postulate a mechanism that would draw down the lighter carbon-12, thus enriching the shell carbonate in carbon–13 as observed.

There is an established negative correlation between surface water phosphate levels and $\delta^{13}C$ values of total dissolved carbon (TDC) in seawater (Broecker, 1982) involving the uptake of phosphate and carbon–12 during photosynthetic production which depletes the surrounding water in ^{12}C relative to ^{13}C.

It has been suggested that a source of the isotopically light carbon observed in molluscan shell carbonate could be derived from the pore waters surrounding the (infaunal) organisms. It is well documented (e.g., Grossman, 1984a, McCorkle et al., 1985) that the carbon isotopic composition of pore waters decreases with increasing depth in the sediment, due to the bacterial remineralization (oxidation) of the isotopically light organic matter within the sediments. Organic-carbon rich sediments, such as those found in Narragansett Bay (Gearing et al., 1984), would be expected to have a more pronounced pattern of $\delta^{13}C$ depletion with depth than sediments from the open ocean and one might expect a higher advection rate of light $\delta^{13}C$ out of the sediment pore waters in this environment. Although $\delta^{13}C$ values from Narragansett Bay pore waters are lacking, it is doubtful that this is an important source of light carbon for *M. mercenaria*. As a large infaunal filter feeder *M. mercenaria* is probably capable of pumping water right through the benthic boundary layer. Considering the strong tidal circulation of Narragansett Bay, coupled with the additional (and constant) estuarine circulation, it seems that any advecting (isotopically light) pore waters would be rapidly mixed before uptake by *M. mercenaria* could occur.

The incorporation of metabolically derived carbon, depleted in ^{13}C, into the *M. mercenaria* shell carbonate is the most likely reason for the observed $\delta^{13}C$ disequilibrium. The idea that this process might be occurring is not new. McCrea (1950) proposed that molluscs' internal environment could cause the deposition of shell carbonate that was out of isotopic equilibrium with the dissolved bicarbonate of the water (e.g., Craig, 1953, Hammen and Wilbur, 1959;

Keith et al., 1964; Dillaman and Ford, 1982; Tanaka et al., 1984; Jones et al., 1986). Shell formation in molluscs is thought to occur entirely within the environment of the extrapallial fluid layer which is in contact with the shell surface and is a part of the mantle (see Wilbur and Saleuddin, 1983, for a recent review). The fluxes of Ca^{2+} and $HCO_3^=$ are thought to be bidirectional (Greenway, 1981a) through the mantle membranes and it has been suggested (Simkiss and Wilbur, 1977) that the $HCO_3^=$ is provided by direct ionic transfer from both the dissolved bicarbonate and from metabolic CO_2 (which includes that CO_2, produced (respired) by the body tissues and that produced under the pH control of the extrapallial fluid). The addition of a small amount of CO_2, derived from the molluscan tissue could alter the isotopic signature of the shell carbonate quite easily as the tissue carbon is much lighter (isotopically) than the dissolved bicarbonate in marine waters. Gearing et al. (1984) measured the $\delta^{13}C$ of organic tissue from various bivalve species in Narragansett Bay and found an average value of –18.5‰ (PDB), almost 20‰ lighter than the average $\delta^{13}C_{DIC}$ measured in this study. At 20°C and equilibrium conditions, CO_2, gas with a $\delta^{13}C$ value of –18.5‰ is in isotopic equilibrium with bicarbonate ion that has an isotopic composition of approximately -10‰ (Emrich et al. 1970). According to the fractionation factors used above, this –10‰ bicarbonate ion would precipitate aragonitic carbonate with a $\delta^{13}C$ value of approximately –7.4‰. To achieve a typical average shell $\delta^{13}C$ value of approximately –1.0‰, 36% of the shell carbonate would have to be derived from metabolic bicarbonate and 64% from the seawater bicarbonate. [calculated from: –1.0‰(shell $\delta^{13}C$) = (2.6‰HCO_3,)(X) + (–7.4 ‰metabolic)(1–X)].

This conclusion is similar to the results of Tanaka et al., (1986) and it is important to note that the use of different fractionation factors will yield different results. Values for the fractionation factors between the various components of the CO_2, – $CaCO_3$ system can be found in Friedman and O'Neil (1977), and more

recently in Grossman (1984a), Inoue and Sugimura (1985), Wannindhof, (1985), Grossman and Ku (1986), and Herczeg and Fairbanks (1987). It is not clear how molluscan metabolic carbon would vary from day to day, or over longer periods of time, as many factors can contribute to the quantity of metabolic CO_2, produced. There is apparently a change in the utilization of the metabolic carbon with increasing age (see below) and it has been demonstrated (Gearing et al., 1984; Peterson et al., 1985, Tanaka et al., 1986) that the organic carbon in molluscan tissue varies with the available food sources. The values for carbon isotopic fractionation between aragonite and bicarbonate and carbonate ion is poorly constrained. Considering the effects of metabolic–derived CO_2, on shell carbonate, and the problems involved in the separation of metabolic carbon from DIC, it is likely that fractionation factors derived from the study of biologic organisms will probably be in error.

Another possible source of light carbon results from the necessity of molluscs to maintain, or at least moderate, the pH of the extrapallial fluid during shell deposition. The precipitation of calcium carbonate from Ca^{2+} and $HCO_3^=$ produces hydrogen ion, or protons, which decreases the pH of the extrapallial fluid. It has been proposed (Wheeler, 1975) that carbonic anhydrase, which is present in the extrapallial fluid and is thought to act as a catalyst, catalyzes the reaction: $HCO_3^= + H^+ \rightarrow CO_2, + H2O$. The evolved CO_2, is expected to diffuse from the extrapallial fluid to the mantle and out to the body fluid (blood) and eventually to the surrounding medium. Crenshaw (1972) has shown that this pathway for the dissolved CO_2 would be down gradient, as total CO_2 in the extrapallial fluid of *M. mercenaria* is approximately twice that of the surrounding seawater. This method of maintaining the pH level of the extrapallial fluid could influence the bicarbonate isotopic composition within the mantle as the carbon dioxide (diffused out) is much lighter than the bicarbonate ion (pool) in the

mantle under nonequilibrium conditions that might exist in a mollusc actively depositing shell material. The pH of the mantle fluid can also change quickly with shell closure, decreasing as conditions become anaerobic within the shell. If the conditions continue long enough the pH may drop sufficiently to cause dissolution of recently deposited shell material (see Crenshaw, 1980, for a review). This dissolution would form bicarbonate ion with an isotopic value intermediate between that from seawater bicarbonate and from metabolic processes. Thus, the bicarbonate involved in this reaction could come from three sources: 1) seawater bicarbonate, with an average $\delta^{13}C = 1.4‰$ in the bay; 2) bicarbonate from metabolic CO_2 formed within the tissues of the mollusc, with $\delta^{13}C \approx -10‰$; and/or 3) bicarbonate from shell dissolution during shell closure and anaerobic conditions, with $\delta^{13}C \approx -3.4‰$ (based on a shell $\delta^{13}C$ value of $-1.0‰$ and Grossman's (1984a) estimate for fractionation between aragonite and bicarbonate of $-2.4‰$ at 25°C).

In addition to the overall light $\delta^{13}C$ values measured in *M. mercenaria*, there is also a distinct ontogenetic trend toward lighter values of $\delta^{13}C$ with increasing age in all of the isotopic profiles. A similar trend has been observed in other species, including *Spisula solidissima*, *Placopecten magellanicus* and *Tridacna maxima* (Jones et al., 1983; Romanek et al., 1985; Jones et al., 1986; Krantz et al., 1987). The trend toward lighter $\delta^{13}C$ values is usually concurrent with a change in the recorded $\delta^{18}O$ values. The oxygen isotopic values continue to change with seasonal temperature variations, but shell growth is apparently restricted to warmer temperatures as evidenced by the lower $\delta^{18}O$ amplitudes. The $\delta^{13}C$ trend has been attributed by Romanek et al. (1985 and 1987) to physiological changes occurring during the transition from a primarily juvenile stage to the adult stage and the resultant shift in energy from shell growth to gametogenesis.

Oxygen Isotopic Disequilibrium

The previous discussion on the sources and magnitude of the carbon isotopic fractionation and causes of disequilibrium may shed some light on the apparent oxygen isotope disequilibrium observed in *M. mercenaria*. The depleted shell $\delta^{18}O$ values can also be attributed to the incorporation of isotopically light oxygen, derived from metabolic sources that may have affected the carbon isotopic compositions (Keith and Weber, 1965; Weber and Woodhead, 1970; Buchardt and Hansen, 1977; Erez, 1978; Grossman, 1987). The carbonate formed by molluscs must be in isotopic equilibrium with metabolically derived sources of carbon dioxide and water, as well as the ambient, non–biogenic sources. The main sources of isotopically light oxygen that could be incorporated into molluscan shell carbonate are respired (metabolic) carbon dioxide and metabolic water, via the (highly simplified) reaction:

$$CH_2O + O_{2(dissolved)} = H_2O_{(metabolic)} + CO_{2(metabolic)}$$

(Grossman, 1987). The assumption is made that the respired water and carbon dioxide are in isotopic equilibrium with each other. Kroopnick (1975) has shown that the isotopic ratio of the respired oxygen is depleted relative to dissolved oxygen not used in the metabolic processes (dissolved oxygen is approx. +24‰ SMOW, or –7‰ PDB, respired oxygen is approx. +3‰ SMOW, or –28‰ PDB).

Grossman's model (1987) for the incorporation of metabolic oxygen into biogenic calcite predicts that a pure "metabolic" calcite, formed near the surface, will be depleted by 17‰ relative to an inorganic calcite precipitated in the same water. The values estimated for aragonite would presumably be enriched by approximately 1‰. The 1 to 1.5‰ $\delta^{18}O$ depletion that we observe in warmest *M. mercenaria* samples would be accounted for by the incorporation of 6–9% of the depleted metabolic oxygen source, using this model. This percentage range is

lower than that predicted using metabolic carbon (36%), which may indicate that 1) the metabolic oxygen isotope model developed by Grossman for calcite formation is incorrect; 2) the metabolic carbon model is incorrect; 3) the equilibrium fractionation factors between aragonite (both biogenic and inorganic) and the important chemical species (CO_2, $HCO_3^=$, CH_2O) are not known well enough for accurate modeling; 4) other processes are involved that moderate the contribution from metabolic oxygen (i.e., kinetic fractionation, ^{18}O re-equilibration with water); or 5) all of the above.

The kinetic fractionation of isotopes that may affect the oxygen isotopic composition of shell carbonate. The rate of carbonate formation will affect the isotopic composition of the shell, if kinetic fractionation is an important process, with faster precipitation rates resulting in depleted shell material. Turner (1982) has shown that precipitation rates affect the carbon isotopic composition of inorganic calcite–aragonite mixtures with slow rates of precipitation producing enriched carbonates (+3.4‰ PDB) relative to carbonates formed by fast precipitation (+0.4‰). Fritz and Poplawski (1974) examined the isotopic composition of mollusc shells cultured in tanks with different dissolved inorganic carbon $\delta^{13}C$ values ($\delta^{13}C$ DIC = +5.4, –13.1, and –35.5‰) and found that the mollusc shells grown in the tanks with the lightest $\delta^{13}C_{DIC}$ (–35.5‰) had carbonate values that were enriched relative to the DIC values. The enriched shell values indicate that the the molluscs had incorporated metabolic carbon (enriched in this case, relative to the $\delta^{13}C_{DIC}$) into their shells. The data from their mollusc culturing experiments indicate that the isotopic depletion due to the incorporation of metabolic carbon is more important than the contribution due to kinetic fractionation effects.

The isotopic exchange of metabolically derived oxygen with the oxygen of the ambient water is a process that could account for carbonates with near

equilibrium oxygen isotopic compositions, and disequilibrium carbon isotopic compositions (Grossman, 1987). This is an intriguing possibility, as a great number of biogenic carbonates are formed at, or near, oxygen isotopic equilibrium, but out of carbon isotopic equilibrium with respect to dissolved inorganic carbon. This process could occur within the extrapallial fluid or at the site of calcification.

CONCLUSIONS

Measurements of the oxygen isotopic composition of water and the $\delta^{13}C$ of the TCO_2 in Narragansett Bay have allowed us to interpret the isotopic signals in the shells of *M. mercenaria* and to verify the seasonal signal in the observed $\delta^{18}O$ variations along shell cross-sections. However, the isotopic analyses of shells samples of *M. mercenaria,* in conjunction with the water isotopic measurements indicate that the shell of this species does not form in isotopic equilibrium with the surrounding sea-water. The measured $\delta^{18}O$ of the shell aragonite is typically 1.5‰ more positive than the values predicted with the aragonite–water isotopic fractionation equation of Grossman and Ku (1986). Although the isotopic fractionation is a problem, the oxygen isotopic profiles can be interpreted in terms of relative seasonal temperature variations. The isotopic analyses of incremental and shell edge samples of *M. mercenaria* demonstrate the utility of this method for determining shell growth patterns.

The growth history of the specimens, as revealed by the oxygen isotopes, indicates that the greatest shell growth occurs between the second and fourth full years of growth, slowing dramatically after the fifth year. The longest growing seasons occur during the years of fastest shell growth and it appears that with increasing age the growing season is restricted to warmer temperatures.

The $\delta^{13}C$ values of both shell-edge samples and incremental samples do not exhibit any systematic seasonal trends. The $\delta^{13}C$ values obtained are much lighter than predicted, indicating that a large portion of the carbon isotopic signal is probably derived from isotopically light metabolic carbon, possibley from the organism itself.

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FIGURES

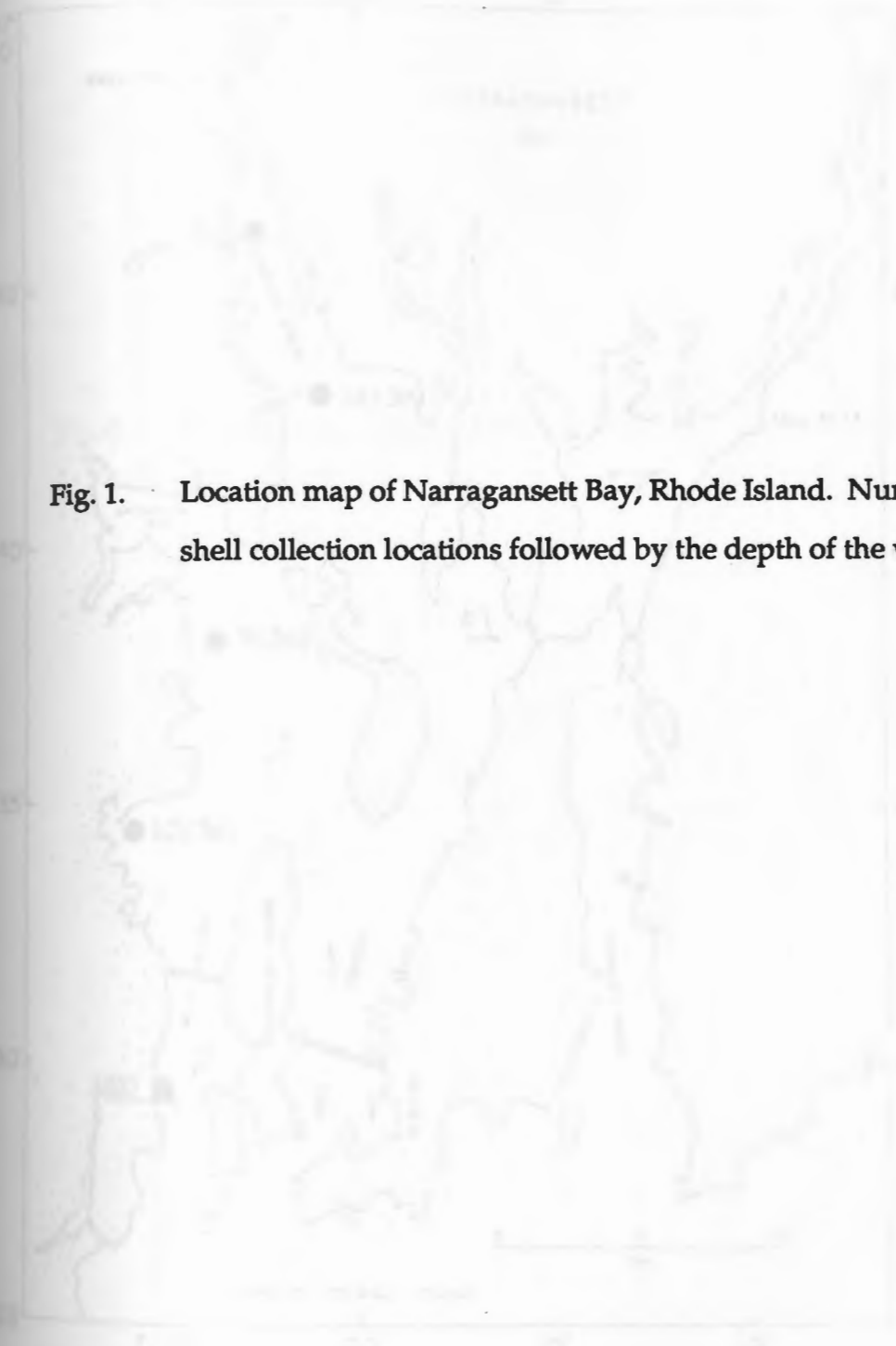


Fig. 1. Location map of Narragansett Bay, Rhode Island. Numbers indicate shell collection locations followed by the depth of the water in meters.

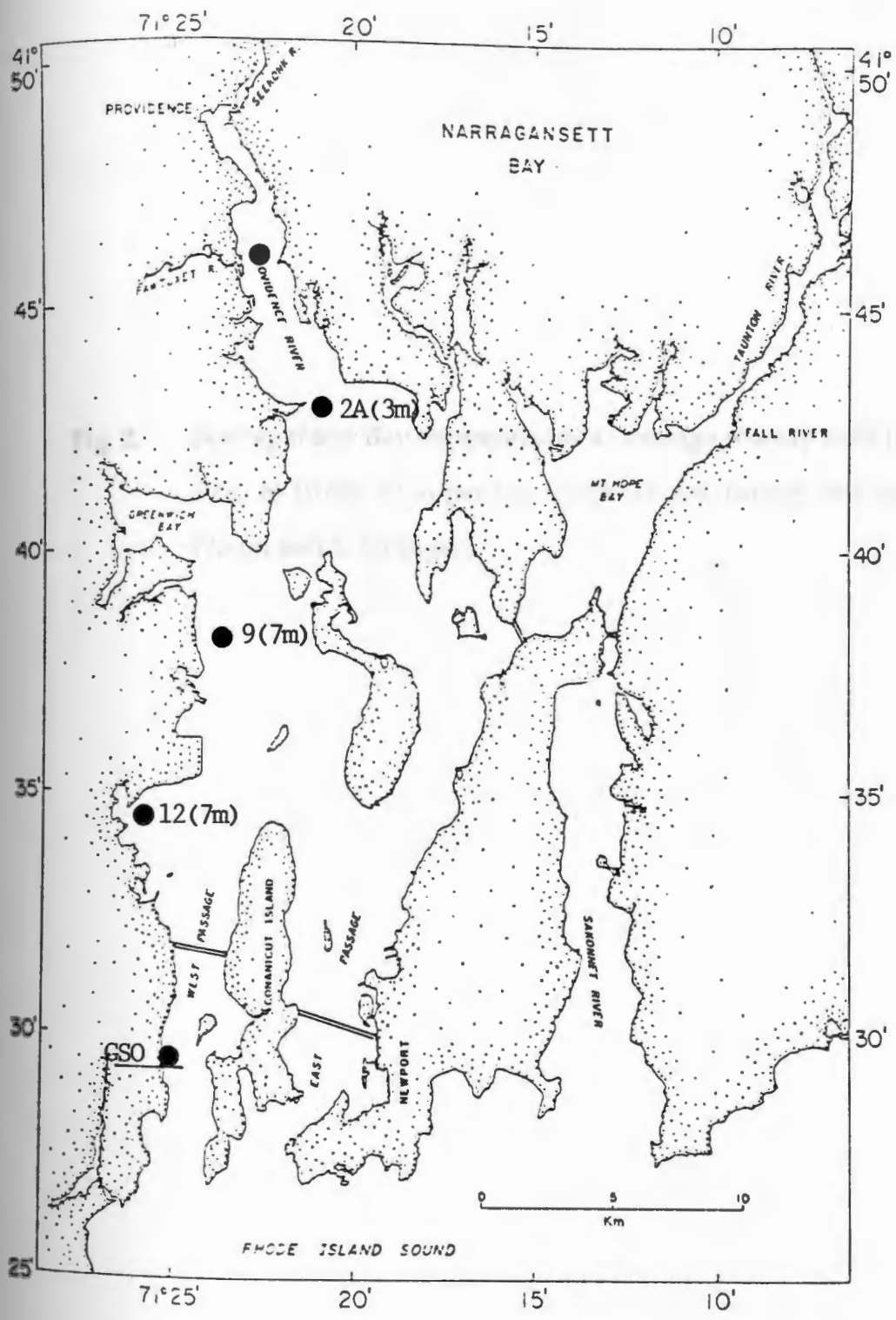
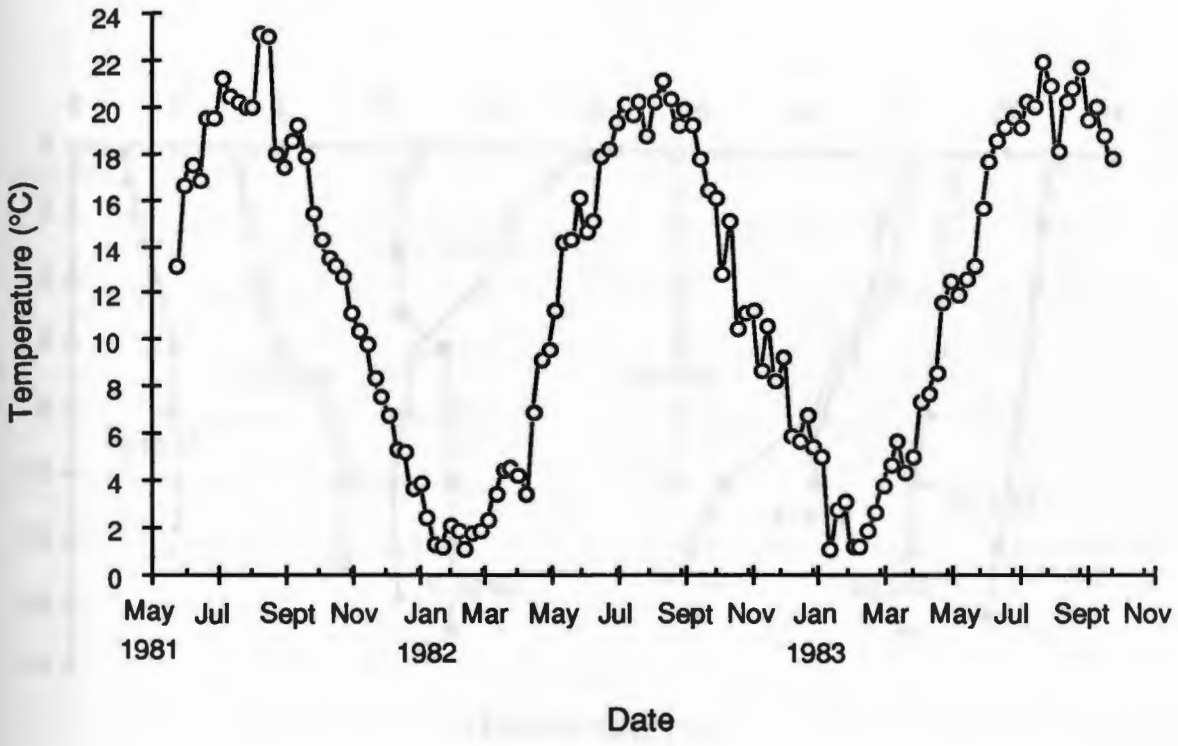

71°25'
20'
15'
10'
41°50'
45'
40'
35'
30'
25'
PROVIDENCE
SEEKONK R.
NARRAGANSETT BAY
PAWTUXET R.
PROVIDENCE RIVER
TAUNTON RIVER
FALL RIVER
MT HOPE BAY
GREENWICH BAY
2A(3m)
9(7m)
12(7m)
GS0
WEST PASSAGE
EAST PASSAGE
CONANICUT ISLAND
NEWPORT
SAKONNET RIVER
0
5
10
Km
RHODE ISLAND SOUND

Fig. 2. Narragansett Bay temperatures a) average weekly MERL record of 5/81 to 10/83, b) upper bay temperatures during 1983 (courtesy of S. Nixon and S. Granger).


Temperature (°C)
24
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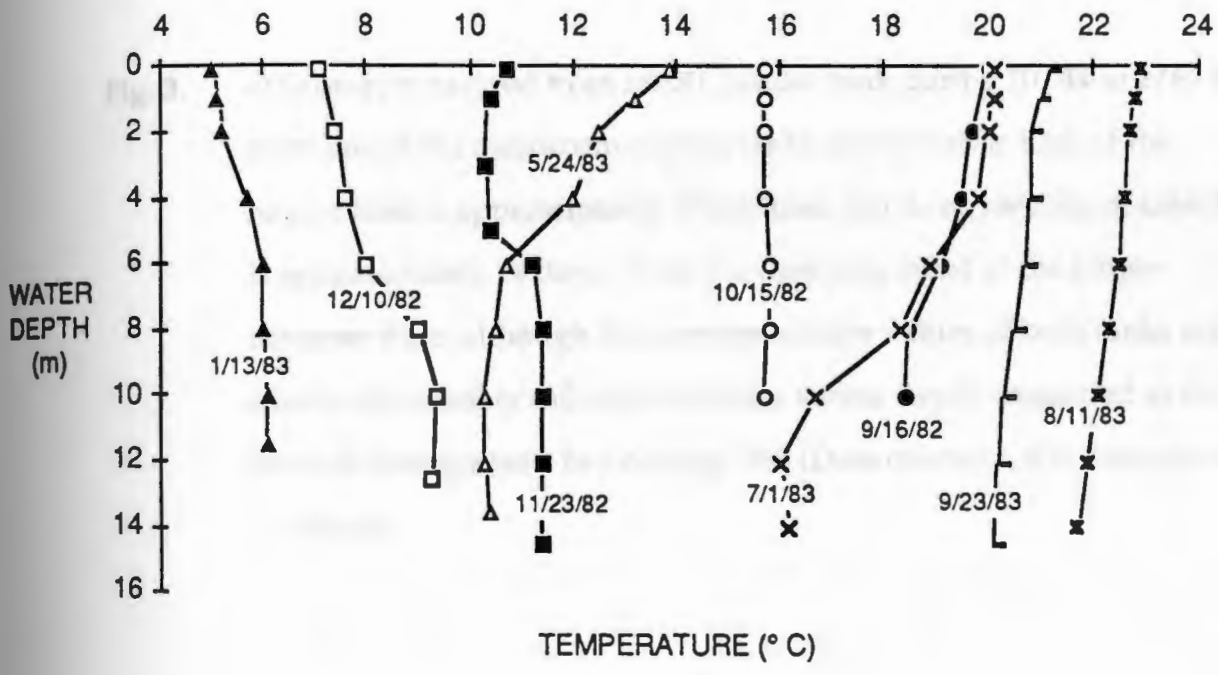
May Jul Sept Nov Jan Mar May Jul Sept Nov Jan Mar May Jul Sept Nov
1981
1982
1983
Date


4
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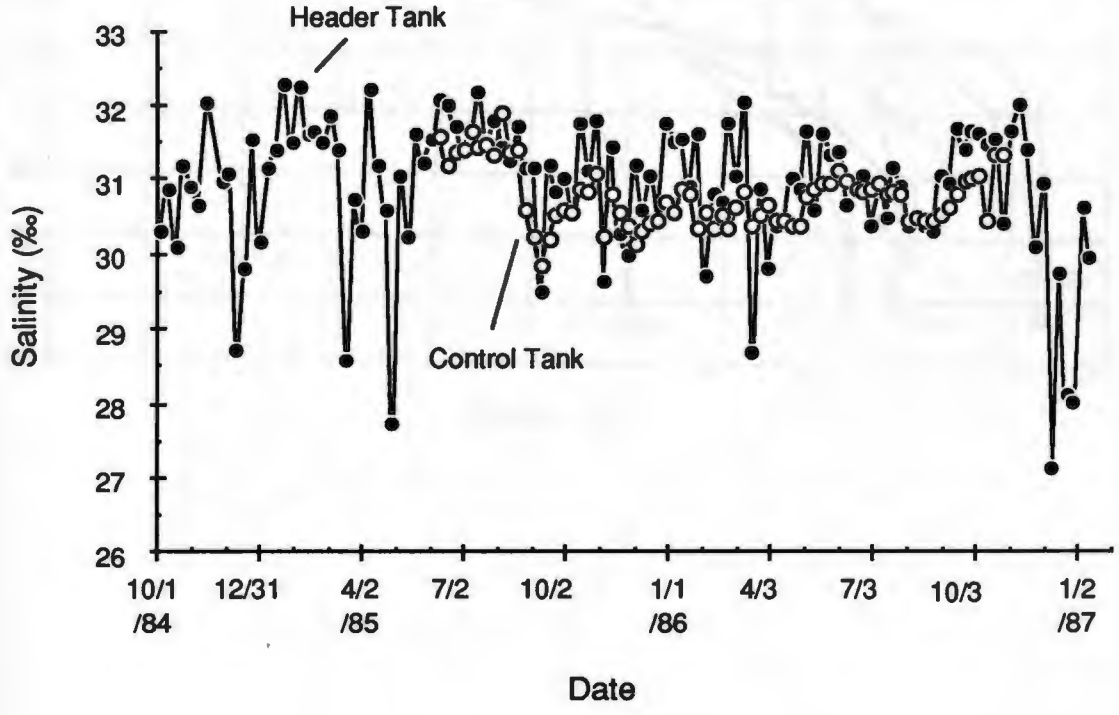
WATER DEPTH (m)
1/13/83
12/10/82
5/24/83
11/23/82
10/15/82
7/1/83
9/16/82
9/23/83
8/11/83
TEMPERATURE (° C)

Fig. 3. a) Salinity measured from MERL header tank during 10/84 to 2/87 and from one of the mesocosm control tanks; the turnover time of the header tank is approximately 15 minutes, the turnover time of tank 12 is approximately 28 days. Note the damping effect of the longer turnover time, although the average salinity values of both tanks are similar. b) monthly salinity variations versus depth, measured at the head of Narragansett Bay during 1983 (Data courtesy of S. Granger and S. Nixon).


Header Tank
Control Tank
Salinity (‰)
33
32
31
30
29
28
27
26
10/1
/84
12/31
4/2
/85
7/2
10/2
1/1
/86
4/3
7/3
10/3
1/2
/87
Date

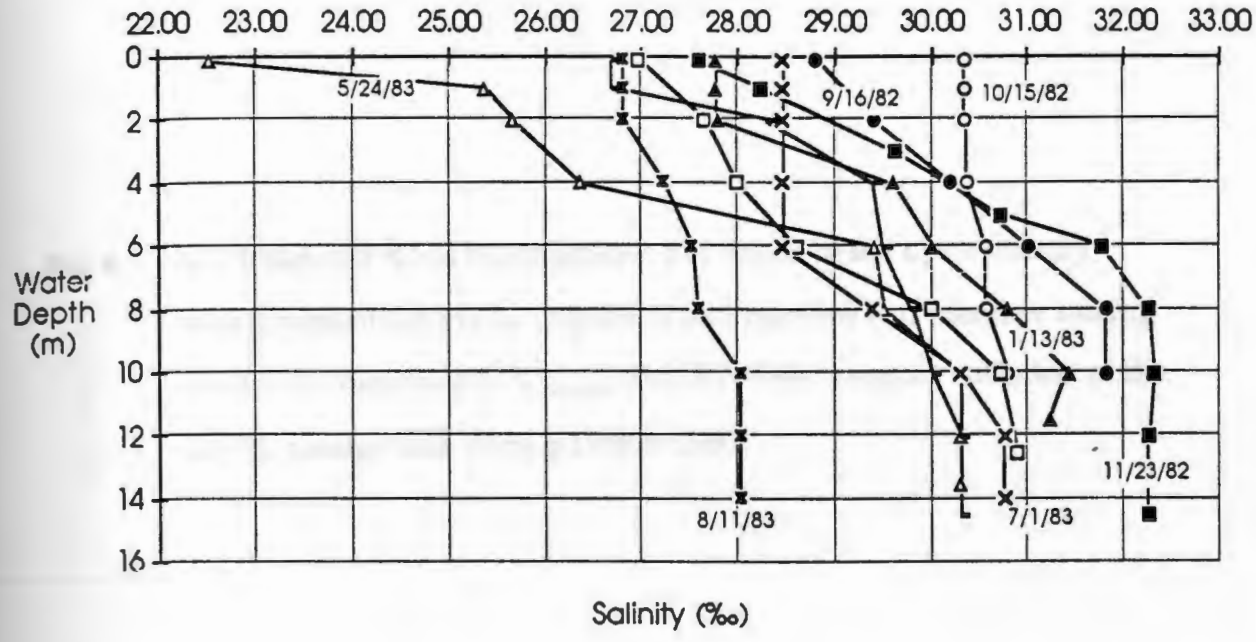
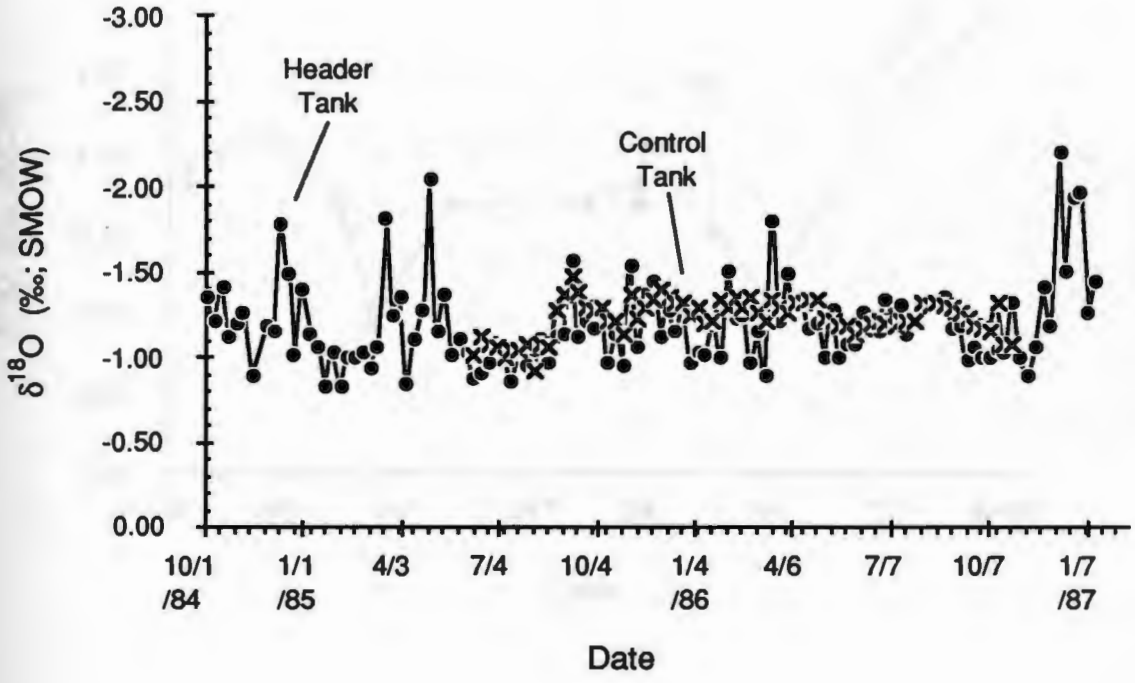

22.00
23.00
24.00
25.00
26.00
27.00
28.00
29.00
30.00
31.00
32.00
33.00
0
2
4
6
8
10
12
14
16
Water Depth (m)
5/24/83
9/16/82
10/15/82
1/13/83
11/23/82
8/11/83
7/1/83
Salinity (‰)

Fig. 4. a) Modeled $\delta^{18}O$ of Narragansett Bay water based upon salinity measurements at MERL (Figure 3) and our two end member mixing model; b) Measured $\delta^{18}O_{water}$ (SMOW) from samples collected at the MERL header tank during 1986 to 1987.


-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
Header Tank
Control Tank
δ18O (‰; SMOW)
10/1 /84
1/1 /85
4/3
7/4
10/4
1/4 /86
4/6
7/7
10/7
1/7 /87
Date

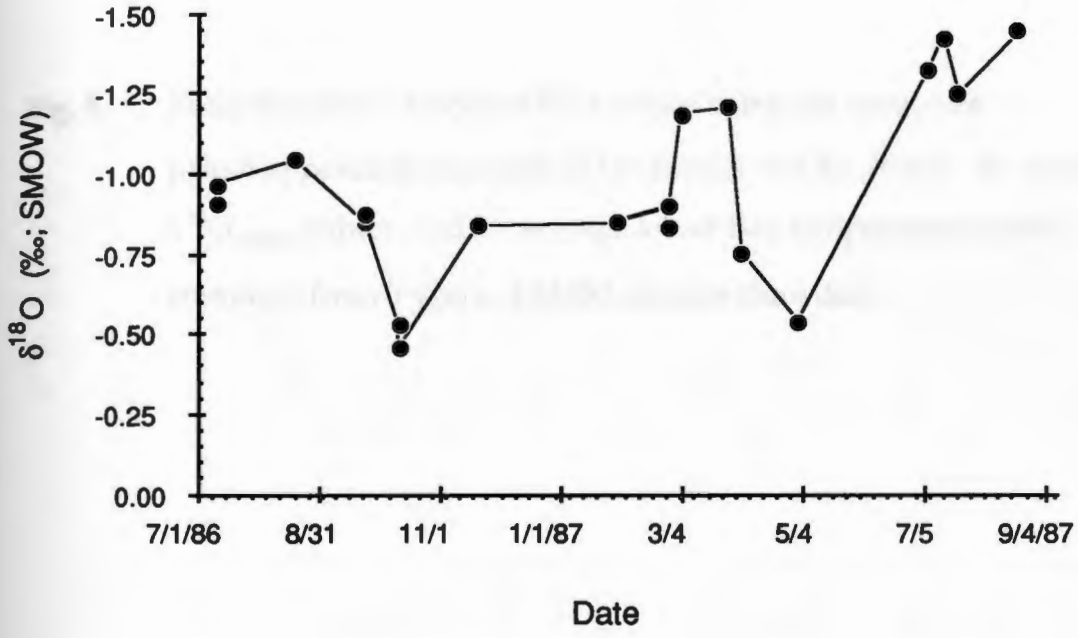

-1.50
-1.25
-1.00
-0.75
-0.50
-0.25
0.00
δ18O (‰; SMOW)
7/1/86
8/31
11/1
1/1/87
3/4
5/4
7/5
9/4/87
Date

Fig. 5. Predicted shell carbonate $\delta^{18}O$ values using the aragonite paleotemperature equation of Grossman and Ku (1986), the modeled $\delta^{18}O_{water}$ values, and an average lower Bay temperature record compiled from 3 years of MERL temperature data.

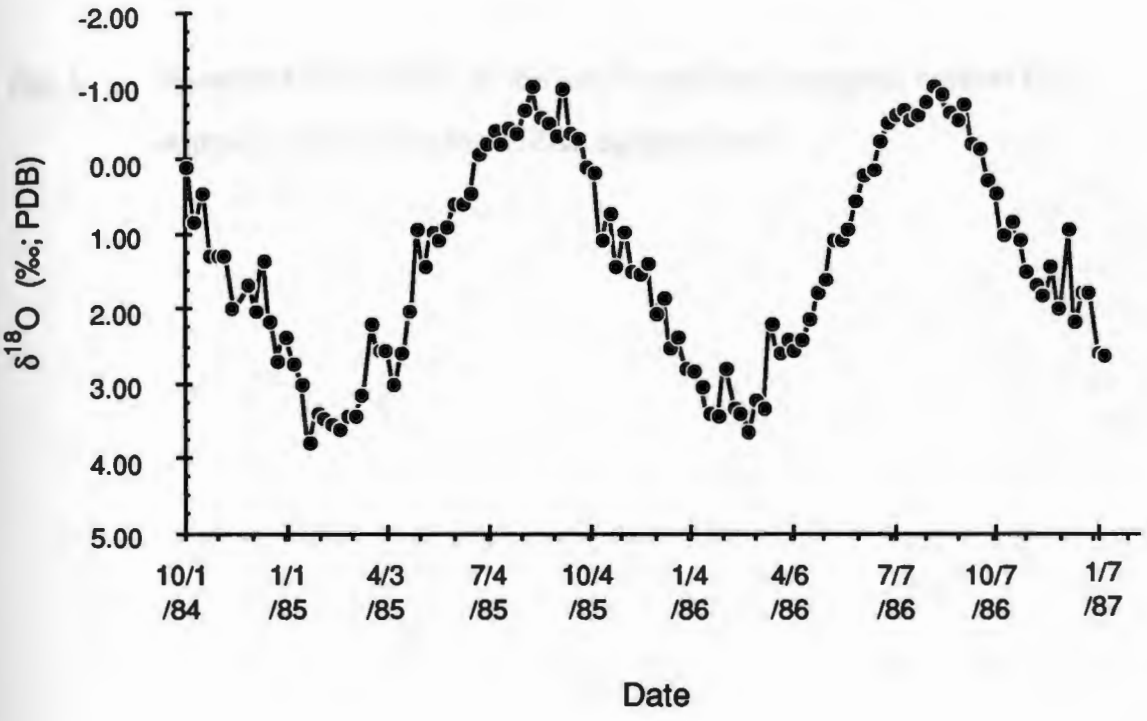
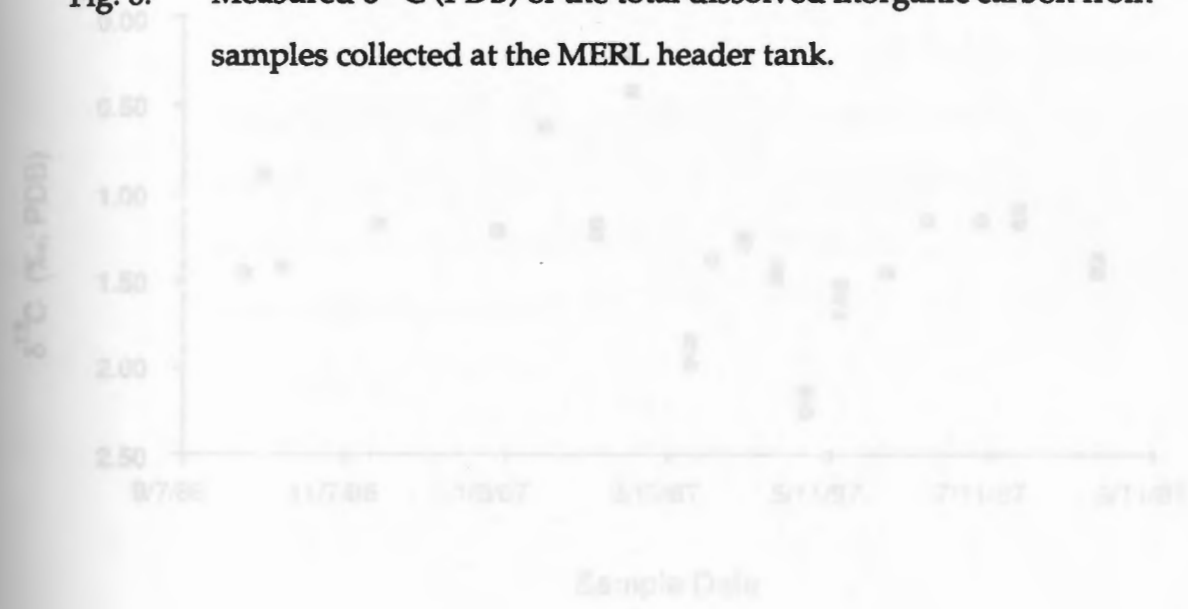

-2.00
-1.00
0.00
1.00
2.00
3.00
4.00
5.00
δ18O (‰; PDB)
10/1 /84
1/1 /85
4/3 /85
7/4 /85
10/4 /85
1/4 /86
4/6 /86
7/7 /86
10/7 /86
1/7 /87
Date

Fig. 6. Measured $\delta^{13}C$ (PDB) of the total dissolved inorganic carbon from samples collected at the MERL header tank.



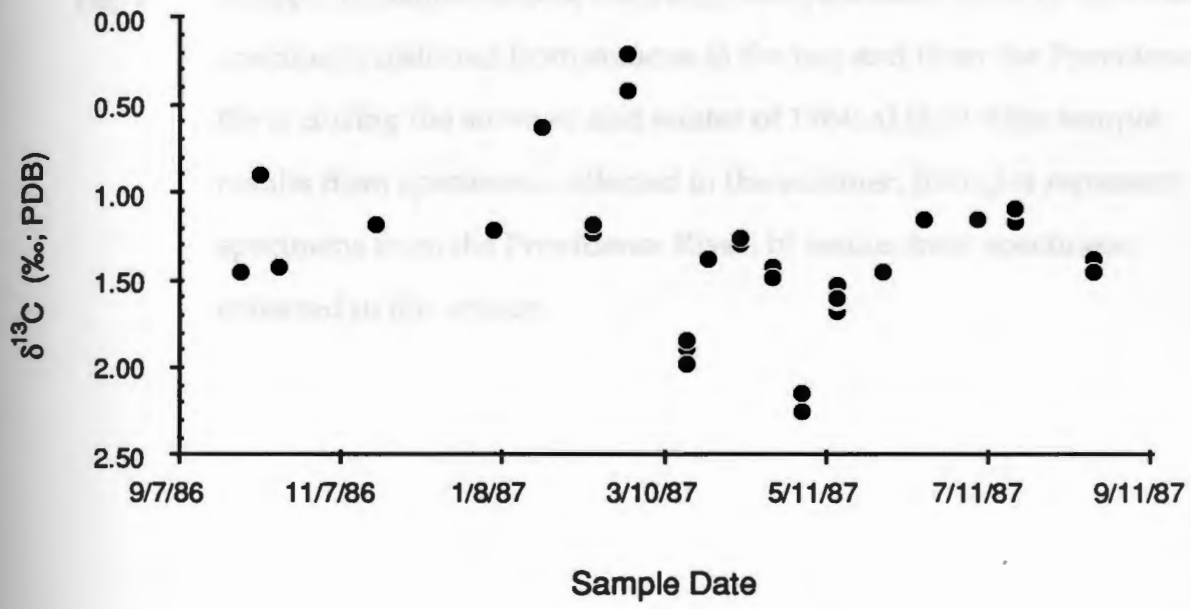
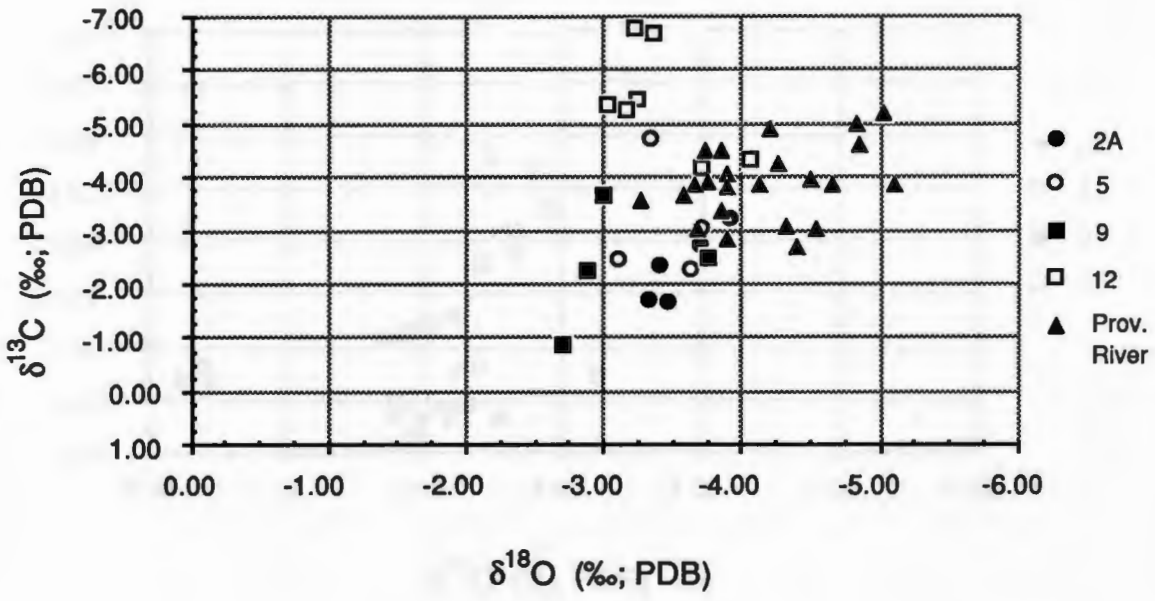
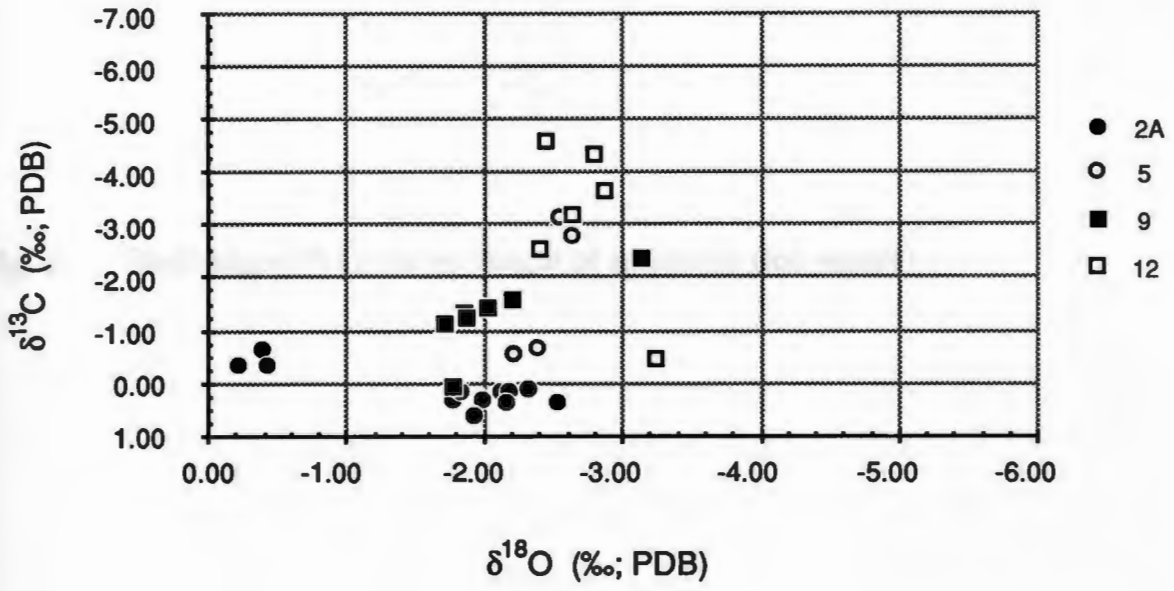

0.00
0.50
1.00
1.50
2.00
2.50
δ13C (‰; PDB)
9/7/86
11/7/86
1/8/87
3/10/87
5/11/87
7/11/87
9/11/87
Sample Date

Fig. 7. Isotopic measurements of shell edge samples taken from *M. mercenaria* specimens collected from stations in the bay and from the Providence River during the summer and winter of 1984; a) shell edge sample results from specimens collected in the summer, triangles represent specimens from the Providence River; b) results from specimens collected in the winter.


-7.00
-6.00
-5.00
-4.00
-3.00
-2.00
-1.00
0.00
1.00
0.00
-1.00
-2.00
-3.00
-4.00
-5.00
-6.00
δ13C (‰; PDB)
δ18O (‰; PDB)
2A
5
9
12
Prov. River


-7.00
-6.00
-5.00
-4.00
-3.00
-2.00
-1.00
0.00
1.00
0.00
-1.00
-2.00
-3.00
-4.00
-5.00
-6.00
δ13C (‰; PDB)
δ18O (‰; PDB)
2A
5
9
12

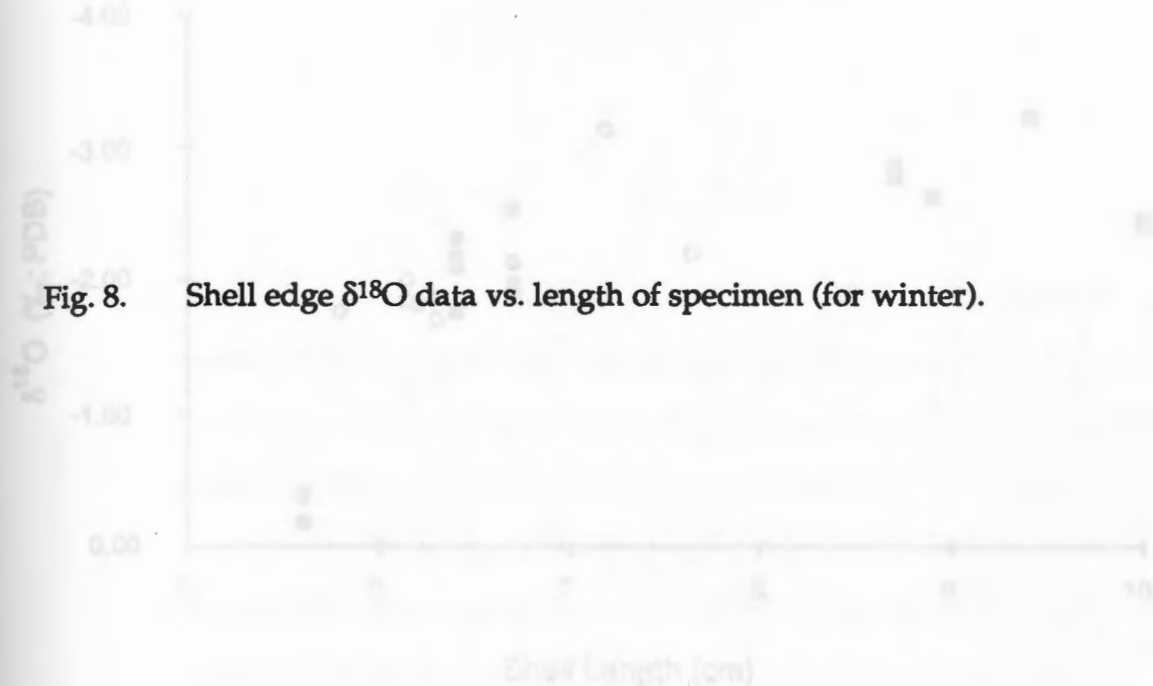


Fig. 8. Shell edge $\delta^{18}O$ data vs. length of specimen (for winter).

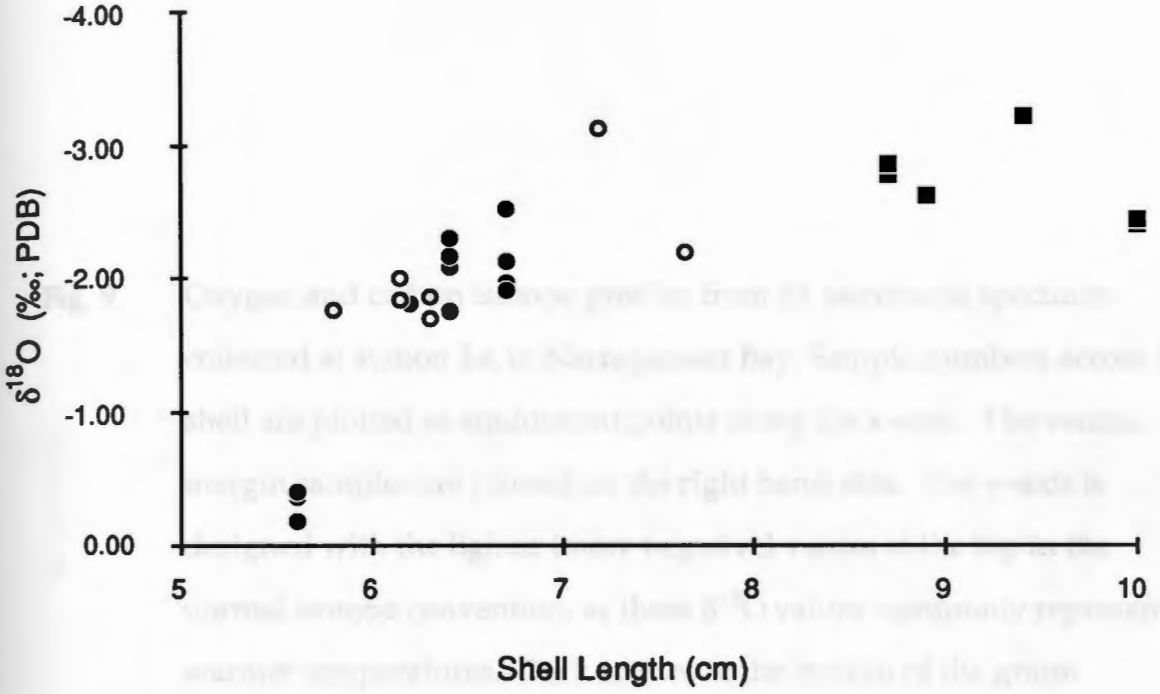

-4.00
-3.00
-2.00
-1.00
0.00
δ18O (‰; PDB)
5
6
7
8
9
10
Shell Length (cm)

Fig. 9. Oxygen and carbon isotope profiles from *M. mercenaria* specimen collected at station 2A in Narragansett Bay. Sample numbers across the shell are plotted as equidistant points along the x–axis. The ventral margin samples are plotted on the right hand side. The y–axis is designed with the lighter (more negative) values at the top in the normal isotope convention, as these $\delta^{18}O$ values commonly represent warmer temperatures. Dark arrows at the bottom of the graph represent the location of dark incremental growth bands as observed in cross section.

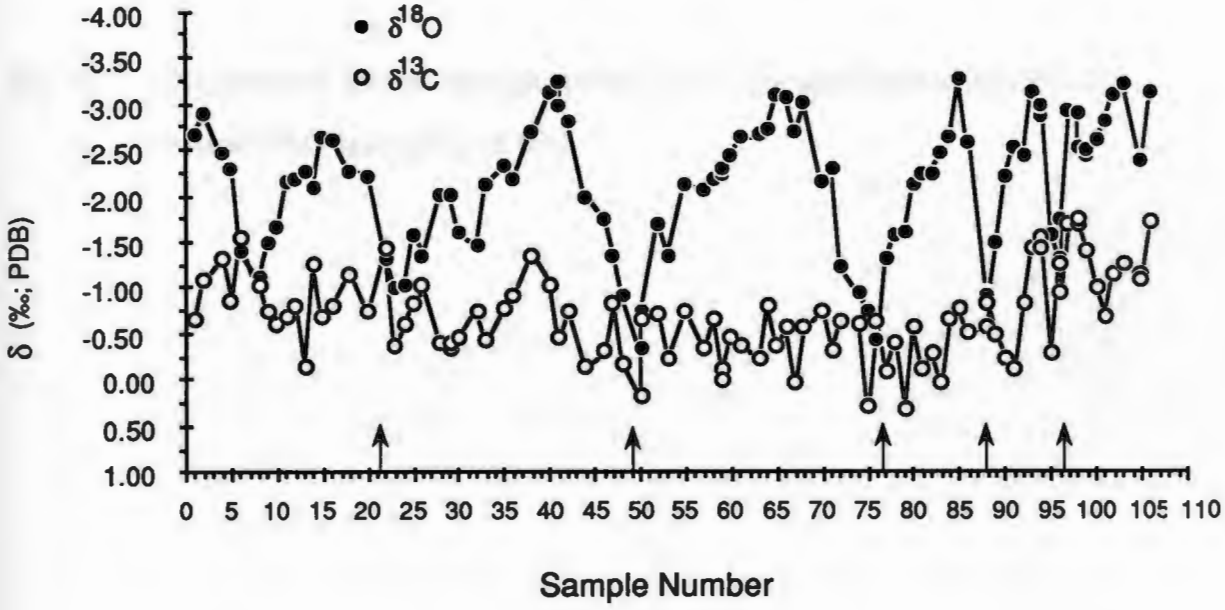
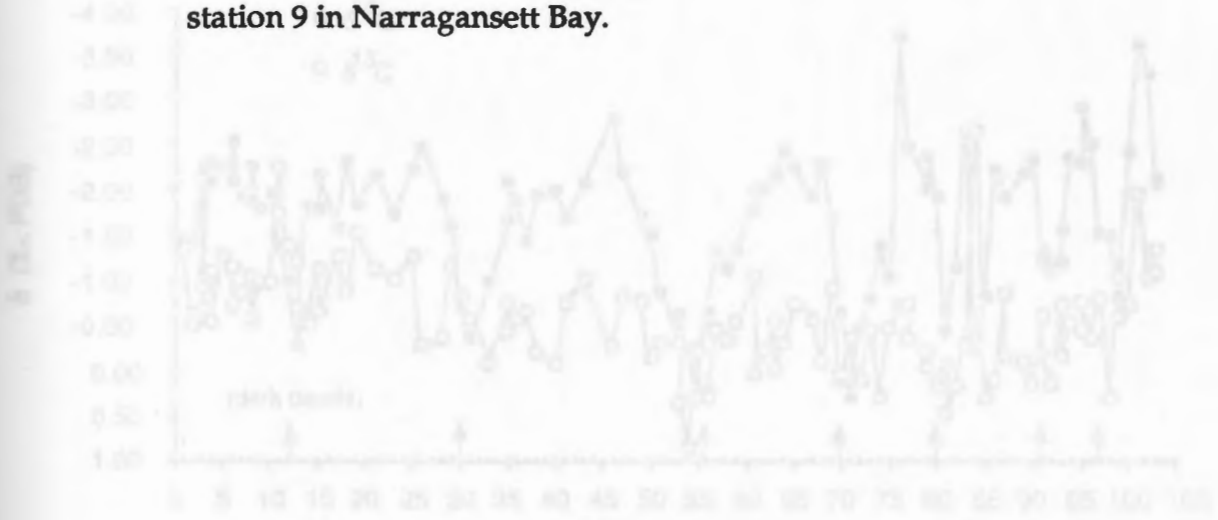

δ (‰; PDB)
-4.00
-3.50
-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
δ18O
δ13C
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110
Sample Number

Fig. 10. Oxygen and carbon isotopic profile from the specimen collected at station 9 in Narragansett Bay.



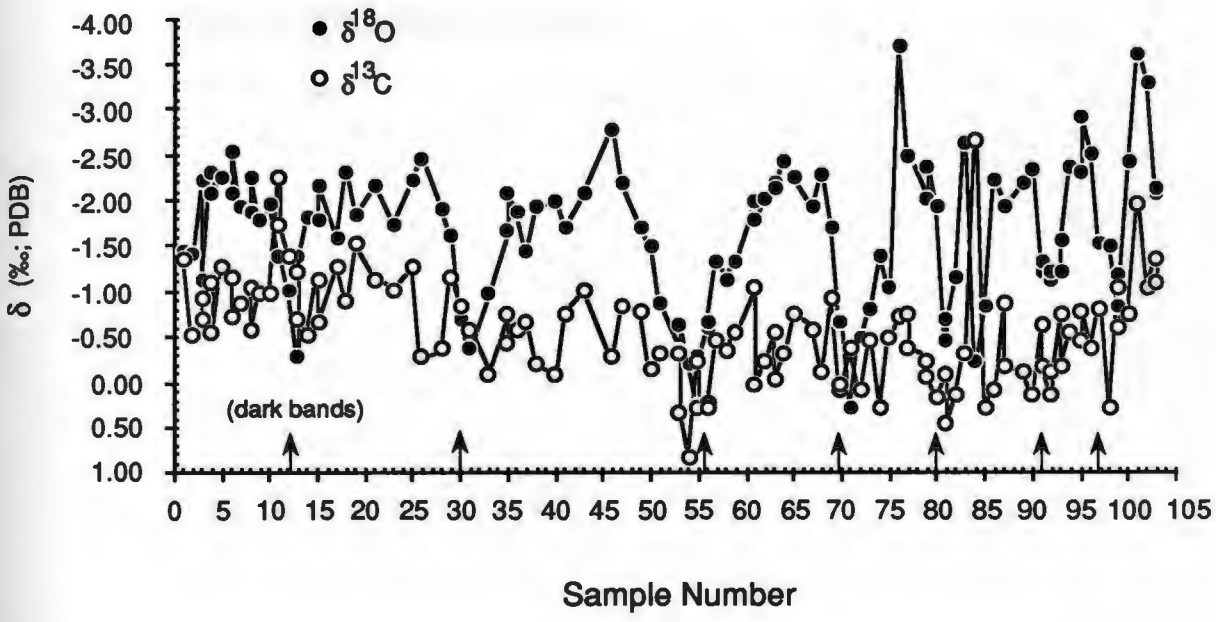

δ (‰; PDB)
-4.00
-3.50
-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
δ18O
δ13C
(dark bands)
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105
Sample Number

Fig. 11. Oxygen and carbon isotopic profile from the specimen collected at station 12 in Narragansett Bay.

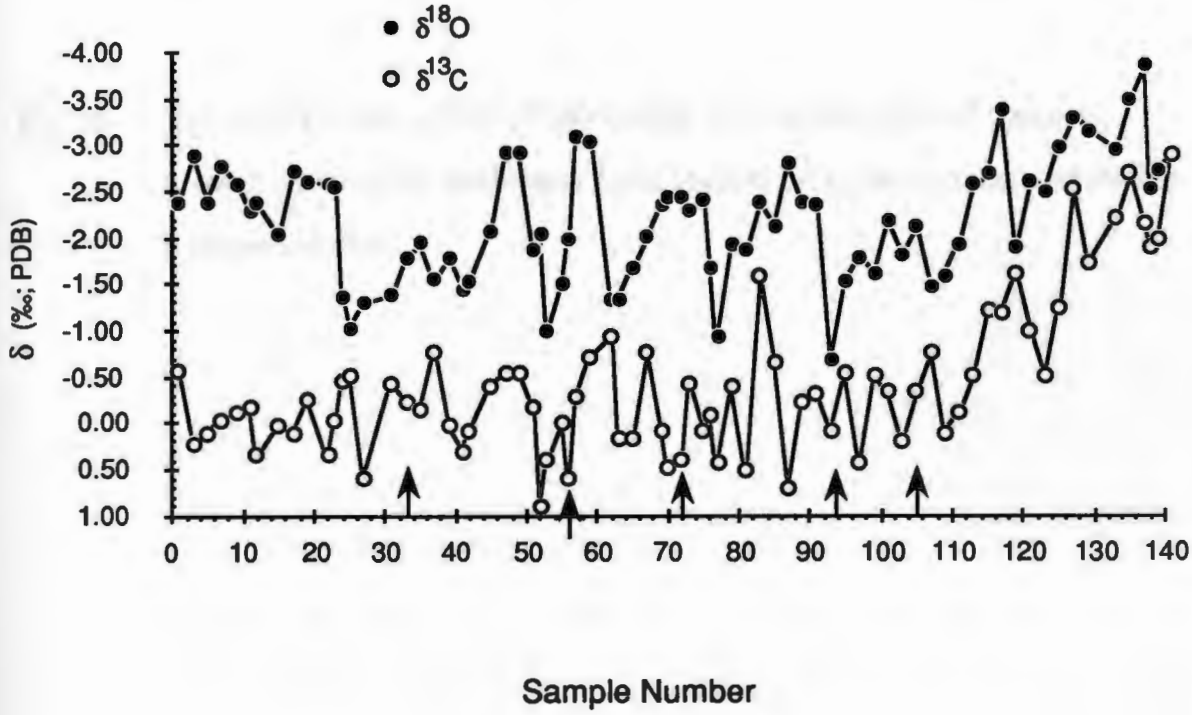
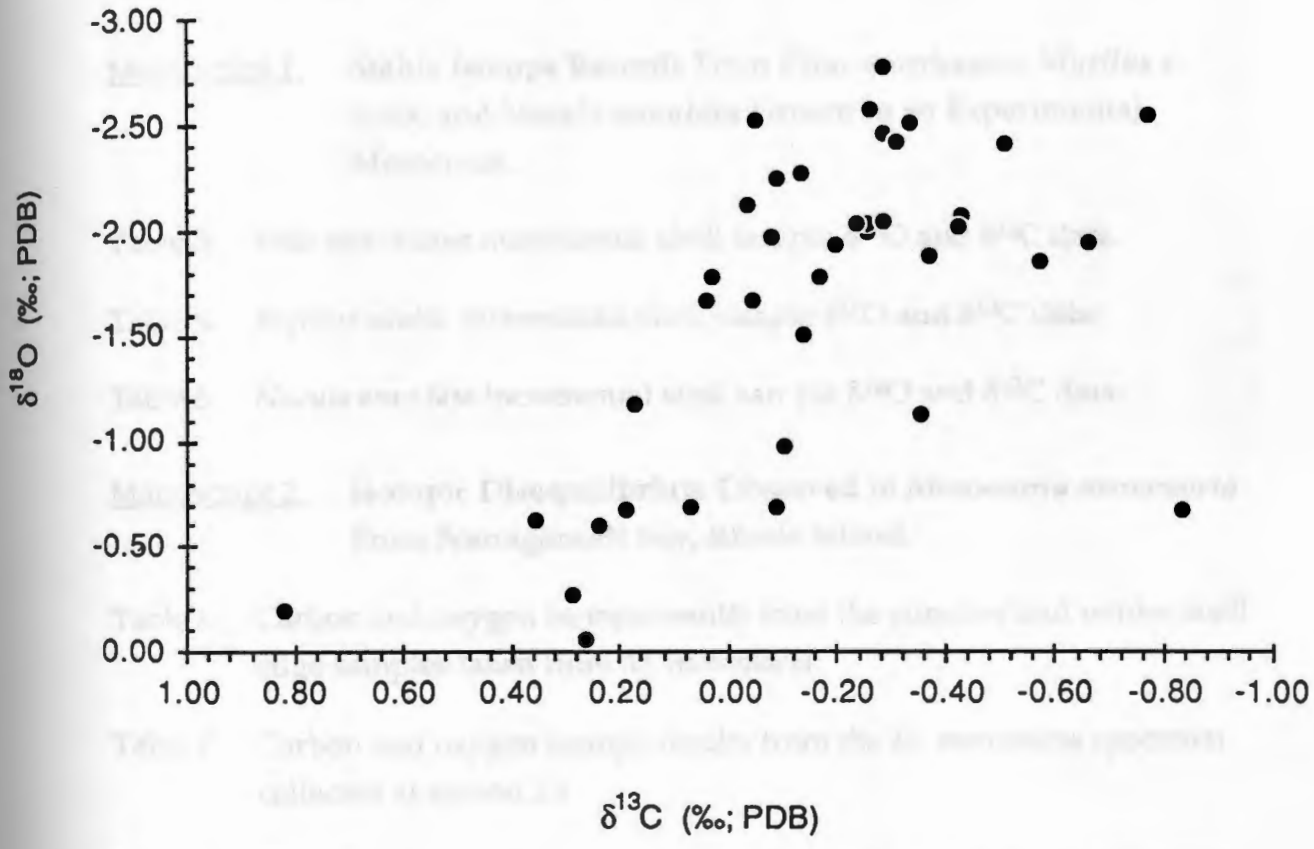

δ18O
δ13C
δ (‰; PDB)
-4.00
-3.50
-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Sample Number

Fig. 12. Plot of $\delta^{18}O$ versus $\delta^{13}C$ (PDB) values for the best defined (fastest) growth years of *M. mercenaria* from station 2A (open circles) and station 9 (closed circles).


-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
1.00
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.60
-0.80
-1.00
δ18O (‰; PDB)
δ13C (‰; PDB)

APPENDICES

APPENDIX I.: STABLE OXYGEN AND CARBON ISOTOPIC DATA

Table 1. $\delta^{18}O_{water}$ measurements, samples collected from the MERL header tank during 1986–1987.

Table 2. $\delta^{13}C_{DIC}$ of water samples collected from the header tank (T98) and a control tank (T12) at MERL.

Manuscript 1. **Stable Isotope Records From *Pitar morrhuana, Mytilus e dulis,* and *Nucula annulata* Grown in an Experimental Mesocosm.**

Table 3. *Pitar morrhuana* incremental shell sample $\delta^{18}O$ and $\delta^{13}C$ data.

Table 4. *Mytilus edulis* incremental shell sample $\delta^{18}O$ and $\delta^{13}C$ data.

Table 5. *Nucula annulata* incremental shell sample $\delta^{18}O$ and $\delta^{13}C$ data.

Manuscript 2. **Isotopic Disequilibrium Observed in *Mercenaria mercenaria* From Narragansett Bay, Rhode Island.**

Table 6. Carbon and oxygen isotope results from the summer and winter shell edge samples taken from *M. mercenaria*.

Table 7. Carbon and oxygen isotope results from the *M. mercenaria* specimen collected at station 2A.

Table 8. Carbon and oxygen isotope results from the *M. mercenaria* specimen collected at station 9. Note: Online samples were corrected by the addition of +0.499‰ for carbon and by –0.369‰ for oxygen based on sample duplicates from both laboratories.

Table 9. Carbon and oxygen isotope results from the specimen of *M. mercenaria* collected at station 12.

TABLE 1. $\delta^{18}O_{water}$ measurements (with respect to SMOW) of samples collected at the MERL header tank, 1986–1987.

Date Collected	Date Prepped	Weight (gm)	Date Run	$\delta^{18}O$ (meas.)	$\delta^{13}C$ (meas.)	$\delta^{18}O$ (SMOW)
7/10/86	10/13/87	0.984	10/25/87	-1.40	0.21	-0.91
7/10/86	10/13/87	0.966	10/25/87	-1.45	-0.19	-0.96
8/19/86	10/13/87	1.012	10/25/87	-1.52	-0.54	-1.04
9/23/86	10/13/87	1.122	10/25/87	-1.34	0.31	-0.85
9/23/86	10/13/87	0.857	10/25/87	-1.36	0.39	-0.87
10/11/86	10/12/87	0.96	11/1/87	-1.03	0.39	-0.53
10/11/86	10/12/87	0.892	11/1/87	-0.94	0.24	-0.45
11/20/86	10/12/87	1.073	11/1/87	-1.32	-0.22	-0.84
1/30/87	10/28/87	1.097	11/8/87	-1.55	-0.16	-1.06
2/24/87	11/20/87	1.107	11/22/87	-1.39	0.44	-0.90
2/24/87	11/20/87	0.892	11/22/87	-1.32	0.22	-0.83
3/4/87	10/14/87	0.79	10/25/87	-1.44	-0.13	-0.96
3/4/87	10/28/87	0.964	11/8/87	-1.53	-0.07	-1.04
3/4/87	10/28/87	0.984	11/8/87	-1.97	-0.15	-1.49
3/4/87	10/28/87	0.932	11/8/87	-1.98	0.12	-1.49
3/27/87	1/12/88	0.934	1/25/88	-1.70	0.37	-1.21
4/3/87	3/26/87	–	11/8/87	-1.13	-1.72	-0.65
4/3/87	3/26/87	–	11/8/87	-1.33	-1.03	-0.85
5/1/87	10/12/87	1.011	10/25/87	-1.17	-0.13	-0.68
7/6/87	1/12/88	0.969	1/25/88	-1.81	0.29	-1.32
7/14/87	11/20/87	1.02	11/22/87	-1.83	-0.39	-1.34
7/14/87	11/20/87	0.92	11/22/87	-1.98	-0.62	-1.50
7/21/87	1/12/88	1.109	1/25/88	-1.74	0.32	-1.25
8/20/87	1/12/88	0.694	1/25/88	-1.93	0.37	-1.44
					Average =	-1.02
					Std. Dev. =	0.30

TABLE 2. The $\delta^{13}C$ (PDB) of the total dissolved inorganic carbon (DIC) from water samples collected at MERL.

Collection Date	Prep. Date	Size (ml)	$\delta^{13}C$ (meas.)	Std.Dev. $\delta^{13}C_{meas.}$	$\delta^{18}O$ (meas.)	$\delta^{13}C$ (PDB)
9/30/86	7/7/87	12	0.545	0.010	-0.236	1.46
10/7/86	4/8/87	9	0.046	0.017	0.468	0.90
10/14/86	6/1/87	10	0.477	0.006	-1.212	1.42
11/20/86	11/18/86	20	0.300	–	0.000	1.19
1/5/87	2/11/87	6	0.354	0.009	1.027	1.21
1/22/87	1/22/87	3	-0.145	0.025	2.672	0.63
2/11/87	2/11/87	8	0.386	0.007	0.922	1.25
2/11/87	2/11/87	13	0.394	0.002	1.860	1.23
2/11/87	2/11/87	10	0.326	0.010	0.715	1.19
2/24/87	8/20/87	12	-0.451	0.008	-1.097	0.43
2/24/87	8/20/87	14	-0.646	0.009	-1.091	0.22
3/19/87	3/19/87	20	1.069	0.033	3.566	1.89
3/19/87	3/19/87	6	1.119	0.012	2.216	1.98
3/19/87	3/19/87	6	0.924	0.016	0.253	1.84
3/27/87	7/7/87	10	0.465	0.012	-0.429	1.38
4/8/87	4/8/87	8	0.428	0.007	0.817	1.30
4/8/87	4/8/87	8	0.401	0.011	1.227	1.25
4/20/87	4/20/87	6	0.551	0.012	0.787	1.43
4/20/87	4/20/87	5	0.583	0.013	0.038	1.49
5/1/87	5/1/87	6	1.365	0.012	1.980	2.25
5/1/87	5/1/87	6	1.223	0.008	0.716	2.15
5/15/87	5/16/87	11	0.796	0.012	3.520	1.60
5/15/87	5/16/87	12	0.722	0.003	3.221	1.53
5/15/87	5/16/87	10	0.735	0.013	-0.712	1.68
5/15/87	5/16/87	10	0.818	0.001	3.372	1.63
5/15/87	5/16/87	12	0.749	0.004	1.973	1.60
6/1/87	6/1/87	10	0.532	0.016	-0.460	1.45
6/16/87	6/16/87	6	0.217	0.023	-1.414	1.15
7/7/87	7/7/87	6	0.275	0.017	0.077	1.16
7/7/87	7/7/87	5	0.274	0.014	0.006	1.16
7/21/87	7/21/87	10	0.238	0.013	-1.592	1.18
7/21/87	7/21/87	12	0.188	0.006	-0.674	1.09
8/20/87	8/20/87	11	0.523	0.006	1.145	1.39
8/20/87	8/20/87	11	0.559	0.009	0.246	1.46
				Average =		1.36
				Std. Dev. =		0.42

TABLE 3. *Pitar morrhuana* incremental shell sample $\delta^{18}O$ and $\delta^{13}C$ data.

Pitar morrhuana specimen collected September 1983 (at the end of the MERL eutrophication experiment). Shell height of this specimen measured 42mm. Sample number 0 is from the (ventral) shell edge, and represents a sample of the last shell material formed before collection.

Sample No.	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)	Sample No.	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
0	-1.91	-0.11	26	-1.93	0.10
1	-1.49	-0.11	26	-1.99	-0.14
2	-1.32	0.02	26	-1.90	0.22
3	-0.58	-0.23	27	-1.73	0.18
4	-1.56	0.66	27	-1.59	0.24
5	-1.42	0.40	28	-1.55	0.31
6	-1.10	0.74	28	-1.56	0.31
6	-1.69	0.68	29	-1.22	0.28
7	-0.61	0.81	29	-1.15	0.96
7	-0.66	0.61	30	-0.84	0.29
8	0.81	-0.10	30	-0.81	0.34
9	-0.76	0.26	31	-0.74	0.46
10	-1.04	0.91	31	-0.54	0.42
10	-1.93	0.06	32	0.39	0.03
11	-1.67	0.14	32	0.47	0.10
11	-1.85	0.20	33	0.16	0.12
12	-1.08	0.25	33	-0.10	-0.02
12	-1.79	0.30	34	-0.80	-0.02
13	-1.55	0.67	34	-1.02	0.19
13	-1.97	0.36	35	-1.37	-0.36
14	-0.92	0.74	36	-1.52	-0.09
15	-0.87	0.57	36	-1.54	-0.22
16	-0.22	0.61	37	-1.67	-0.02
16	-0.31	0.58	38	-1.80	-0.15
16	-0.48	0.45	39	-1.76	-0.26
17	0.65	0.52	40	-1.78	0.03
17	-0.03	0.25	41	-1.90	0.35
18	-0.14	0.45	42	-1.38	-0.11
18	-0.01	0.46	43	-1.28	-0.12
19	-0.65	0.59	43	-1.30	-0.05
19	-0.50	0.40	44	-0.50	-0.25
20	-0.90	0.21	45	0.05	-0.43
21	-1.41	0.08	45	-0.42	-0.21
21	-1.31	0.24	46	-1.35	0.28
22	-1.69	0.08	46	-1.42	0.17
22	-1.71	0.17			
23	-1.87	0.00	Ave. =	-1.08	0.19
24	-1.95	-0.08			
25	-2.01	-0.18			
25	-1.96	0.02			

TABLE 3. cont., *Pitar morrhuana* incremental shell sample $\delta^{18}O$ and $\delta^{13}C$ data.

Isotopic fractionation of *Pitar morrhuana* shell samples due to sample preparation. Data for samples prepared off-line at the University of Florida and samples prepared on-line at the URI Graduate School of Oceanography.
Note: all *Mytilus edulis* and *Nucula annulata* samples were prepared at GSO.

Results of the same sample prepared at both locations (on-line prep. vs off-line prep.):

Location of prep.	Sample No.	Date Run	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
UF	6	11/2/84	-1.10	0.74
GSO	6	9/23/86	-1.69	0.68
UF	10	11/9/84	-1.04	0.91
GSO	10	9/23/86	-1.93	0.06
UF	12	11/2/84	-1.08	0.25
GSO	12	9/23/86	-1.79	0.30
UF	13	10/26/84	-1.55	0.67
GSO	13	9/23/86	-1.97	0.36
UF	17	11/6/84	0.65	0.52
GSO	17	9/23/86	-0.03	0.25
UF	29	12/19/84	-1.22	0.28
GSO	29	1/20/85	-1.15	0.96

The on-line $\delta^{18}O$ is approximately 0.66‰ ($\pm$0.15‰) lighter than the off-line $\delta^{18}O$ for a given (identical) sample prepared at the two locations.

TABLE 4. *Mytilus edulis* incremental shell sample $\delta^{18}O$ and $\delta^{13}C$ data.

Mytilus edulis sample number 0 is from the (ventral) shell edge, and represents a sample of the last shell material formed before collection. Only the outer calcitic layer of the shell was sampled. Shell height of this specimen measured 63mm

Sample No.	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)	Sample No.	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
0	-1.86	-0.40	26	-2.23	-0.33
1	-1.55	-0.26	27	-2.18	-0.74
1.5	-1.17	-0.73	28	-2.30	-0.79
2	-1.19	-0.83	29	-2.11	-0.67
2.5	-0.96	-0.96	30	-2.13	-0.80
3	-0.91	-0.92	31	-2.22	-0.74
4	-0.65	-0.95	32	-2.08	-0.61
5	-0.28	-1.05	33	-2.00	-0.61
6	-0.11	-0.83	34	-2.03	-0.61
7	-0.07	-1.01	35	-2.09	-0.64
8	0.55	-1.28	36	-1.77	-0.58
9	0.60	-1.04	37	-1.59	-0.53
10	0.68	-0.97	38	-1.70	-0.32
11	1.45	-0.97	40	-1.69	0.05
12	1.53	-0.43	40	-1.62	-0.10
13	0.99	-0.36	42	-0.88	-0.15
14	0.77	-0.52	42	-1.26	-0.10
16	0.24	-0.44	44	-1.45	0.11
17	0.26	-0.30	46	-1.00	0.37
18	-0.28	-0.48	46	-0.92	0.31
19.5	-0.88	-0.39	48	-0.18	0.39
20	-1.31	-0.44	48	0.01	0.49
21	-1.64	-0.58	50	1.32	1.00
21.5	-2.11	-0.96	50	1.21	1.07
22	-2.10	-1.12	52	1.06	1.64
23	-2.32	-0.43	52	0.90	1.47
24	-2.14	-0.67			
25	-2.25	-0.35	Ave.=	-0.88	-0.39

TABLE 5. *Nucula annulata* (whole) shell sample $\delta^{18}O$ and $\delta^{13}C$ data.

Specimens collected from the MERL mesocosms at the end of the MERL eutrophication experiment, September 1983.

MERL Tank	Shell Height	Nutrient Addition	Date Run	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)	Sample Comments
T-0	4.5	Control	7/27/84	-0.59	1.58	w/o periost.
T-0	4.5	Control	7/27/84	-0.14	2.12	w/o periost.
T-0m	4.5	Control	7/27/84	-0.84	1.54	w/o periost.
T-0	3.9	Control	7/27/84	0.34	1.99	w/o periost.
T-0	5.8	Control	7/27/84	-0.37	1.91	w/o periost.
T-0	-	Control	8/11/86	-0.28	1.96	w/o periost.
T-0	-	Control	8/11/86	-0.28	2.00	w/o periost.
T-0	-	Control	9/19/86	-0.13	1.99	w/o periost.
T-0	-	Control	8/11/86	-0.47	1.70	w/o periost.
T-0	-	Control	8/11/86	-0.52	1.62	w/o periost.
T-0	-	Control	10/6/86	-0.28	1.90	w/o periost.
T-0	-	Control	10/6/86	-0.35	2.00	w/o periost.
T-0	-	Control	9/19/86	-0.42	1.59	w/o periost.
T-1m	6.5	8x	7/27/84	-1.04	2.47	w/o periost.
T-1m*	6.5	8x	7/27/84	-0.25	2.88	w/o periost.
T-1	6.1	8x	7/27/84	-0.25	2.76	w/o periost.
T-1	6.0	8x	7/27/84	-0.37	2.64	w/o periost.
T-1	-	8x	7/8/86	-0.60	2.62	w/o periost.
T-1	-	8x	8/11/86	-0.78	2.21	w/o periost.
T-1	-	8x	9/19/86	-0.61	2.18	w/o periost.
T-1	-	8x	8/11/86	-0.88	2.62	w/o periost.
T-1	-	8x	8/11/86	-0.84	2.66	w/o periost.
T-1	-	8x	9/19/86	-0.57	2.65	w/o periost.
T-1	-	8x	10/6/86	-1.13	1.87	w/o periost.
T-2	4.8	16x	7/27/84	-0.89	2.25	w/o periost.
T-2*	4.8	16x	7/27/84	-0.81	2.23	w/o periost.
T-2m	6.3	16x	7/27/84	-0.72	2.55	w/o periost.
T-2	6.2	16x	7/27/84	-0.80	2.47	w/o periost.
T-2	-	16x	7/20/86	-0.96	2.15	w/periost.
T-2	-	16x	7/20/86	-1.17	2.35	w/o periost.
T-2	-	16x	8/4/86	-0.76	2.32	w/o periost.
T-2	-	16x	8/4/86	-1.07	2.25	w/o periost.
T-2	-	16x	9/19/86	-1.37	2.22	w/o periost.
T-2	-	16x	7/20/86	-0.79	2.65	w/o periost.
T-2	-	16x	10/6/86	-0.91	2.15	w/o periost.
T-2	-	16x	10/6/86	-0.48	2.34	w/o periost.
T-7	5.2	32x	7/27/84	-0.81	4.78	w/o periost.
T-7m	7.1	32x	7/27/84	-0.57	5.83	w/o periost.
T-7	6.5	32x	7/27/84	-0.36	4.29	w/o periost.
T-7	-	32x	7/20/86	-0.62	4.54	w/periost.
T-7	-	32x	8/11/86	-0.61	4.50	w/periost.
T-7	-	32x	7/20/86	-0.99	4.05	w/o periost.
T-7	-	32x	8/11/86	-1.16	4.03	w/o periost.
T-7	-	32x	9/19/86	-1.08	4.08	w/o periost.
T-7	-	32x	10/6/86	-1.10	4.07	w/o periost.
T-7	-	32x	10/6/86	-1.13	4.20	w/o periost.

* = duplicate, m = shell margin sample.

TABLE 6. $\delta^{18}O$ and $\delta^{13}C$ data from the *M. mercenaria* specimen collected at station 2A (Conimicut Point, Providence River mouth)

Sample No.	Prep. Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)	Sample No.	Prep. Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
1	7/22	-2.65	-0.65	59	on line	-2.24	-0.10
2	7/21	-2.89	-1.07	59	on line	-2.28	0.00
4	7/23	-2.45	-1.32	60	on line	-2.44	-0.44
5	on line	-2.29	-0.86	61	on line	-2.63	-0.37
6	7/22	-1.40	-1.54	63	on line	-2.66	-0.21
8	7/22	-1.12	-1.02	64	7/25	-2.71	-0.80
9	on line	-1.49	-0.75	65	on line	-3.08	-0.36
10	7/22	-1.66	-0.58	66	7/26	-3.07	-0.57
11	on line	-2.13	-0.68	67	on line	-2.70	0.03
12	7/22	-2.18	-0.79	68	7/26	-2.99	-0.56
13	on line	-2.27	-0.13	70	7/24	-2.14	-0.73
14	7/23	-2.07	-1.25	71	on line	-2.28	-0.32
15	on line	-2.62	-0.68	72	7/26	-1.22	-0.62
16	7/27	-2.61	-0.79	74	7/24	-0.95	-0.61
18	7/22	-2.26	-1.15	75	on line	-0.73	0.31
20	7/22	-2.19	-0.75	76	7/24	-0.42	-0.62
22	7/23	-1.31	-1.41	77	on line	-1.30	-0.09
23	on line	-1.00	-0.35	78	7/25	-1.58	-0.38
24	7/23	-1.04	-0.60	79	on line	-1.61	0.33
25	on line	-1.58	-0.82	80	7/25	-2.12	-0.56
26	7/22	-1.35	-1.02	81	on line	-2.22	-0.12
28	7/22	-1.99	-0.40	82	7/26	-2.24	-0.28
29	on line	-1.99	-0.34	83	on line	-2.46	0.03
29	on line	-2.00	-0.40	84	7/27	-2.64	-0.65
30	7/22	-1.60	-0.45	85	on line	-3.25	-0.77
32	7/22	-1.47	-0.74	86	7/25	-2.58	-0.50
33	on line	-2.12	-0.41	88	on line	-0.93	-0.57
35	on line	-2.30	-0.76	88	7/26	-0.90	-0.82
36	7/25	-2.18	-0.91	89	on line	-1.50	-0.49
38	7/24	-2.68	-1.35	90	on line	-2.19	-0.23
40	7/23	-3.13	-1.03	91	on line	-2.51	-0.10
41	on line	-3.23	-0.46	92	7/27	-2.43	-0.83
41	on line	-2.98	-0.45	93	on line	-3.13	-1.43
42	7/25	-2.79	-0.75	94	7/27	-2.85	-1.55
44	7/26	-1.98	-0.14	94	on line	-2.99	-1.44
46	7/26	-1.73	-0.30	95	on line	-1.58	-0.28
47	on line	-1.33	-0.82	96	7/26	-1.30	-1.27
48	7/25	-0.90	-0.17	96	on line	-1.75	-0.94
50	on line	-0.35	0.18	97	on line	-2.92	-1.69
50	7/24	-0.73	-0.66	98	on line	-2.88	-1.69
52	7/25	-1.68	-0.70	98	7/26	-2.51	-1.75
53	on line	-1.35	-0.22	99	on line	-2.43	-1.41
55	on line	-2.11	-0.73	99	on line	-2.48	-1.39
57	on line	-2.07	-0.35				
58	7/25	-2.16	-0.66				

TABLE 6. cont., Isotope results of *M. mercenaria*, from station 2A

Sample No.	Prep. Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
100	7/27	-2.59	-1.00
101	on line	-2.79	-0.69
102	7/27	-3.09	-1.13
103	on line	-3.21	-1.24
105	on line	-2.40	-1.15
105	on line	-2.36	-1.07
106	7/27	-3.11	-1.70
	Average =	-2.11	-0.70
	Std. Dev. =	0.71	0.47

Standards run with station 2A *M. mercenaria* shell samples.

Standards Date	Prep Run	Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
NBS-20	7/21	8/1/85	-4.17	-1.09
NBS-20	7/19	9/18/85	-4.15	-1.02
NBS-20	7/27	9/18/85	-4.24	-0.96
NBS-20	7/22	10/20/85	-4.17	-0.91
NBS-20	8/11	10/25/85	-4.18	-1.08
NBS-20	7/26	10/25/85	-4.34	-1.06
NBS-20	7/26	11/6/85	-4.50	-1.18
NBS-20	on line	11/6/85	-4.30	-1.11
NBS-20	7/25	11/16/85	-4.03	-1.13
NBS-20	7/24	11/16/85	-4.18	-1.19
NBS-20	on line	12/18/85	-4.33	-1.07
NBS-20	on line	12/18/85	-4.18	-1.04
NBS-20	on line	5/20/86	-4.04	-0.89
NBS-20	on line	5/20/86	-4.03	-0.88
NBS-20	on line	5/27/86	-4.20	-1.00
NBS-20	on line	6/9/86	-4.18	-0.96
NBS-20	on line	6/9/86	-4.14	-0.97
NBS-20	on line	8/18/86	-4.16	-1.01
NBS-20	on line	8/18/86	-4.24	-1.05
NBS-20	on line	9/7/86	-4.17	-1.27
NBS-20	on line	9/7/86	-4.32	-1.21
NBS-20	on line	10/31/86	-4.21	-1.15
NBS-20	on line	11/4/86	-4.11	-1.02
NBS-20	on line	11/4/86	-4.11	-1.05
		Average =	-4.19	-1.06
		Std. Dev. =	0.11	0.10

TABLE 7. Carbon and oxygen isotope results from the station 9*M. mercenaria* specimen. (Note: corrections – see below).

Sample No.	Prep Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)	Sample No.	Prep Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
1	7/16/85	-1.45	-1.37	53	7/19/85	-0.34	-0.31
2	7/16/85	-1.41	-0.53	53	on line	-0.63	0.36
3	7/16/85	-2.22	-0.68	54	on line	-0.19	0.82
3	7/20/85	-1.12	-0.93	55	7/18/85	0.27	-0.23
4	7/16/85	-2.31	-1.10	55	on line	-0.28	0.29
4	on line	-2.08	-0.55	56	on line	-0.60	0.24
5	7/16/85	-2.24	-1.28	56	on line	-0.67	0.28
6	7/21/85	-2.06	-1.16	57	7/21/85	-1.34	-0.46
6	on line	-2.54	-0.73	58	on line	-1.13	-0.35
7	7/16/85	-1.93	-0.87	59	7/18/85	-1.34	-0.54
8	7/16/85	-1.88	-1.02	61	7/17/85	-1.99	-1.05
8	on line	-2.26	-0.57	61	on line	-1.78	0.03
9	7/16/85	-1.78	-0.99	62	on line	-2.03	-0.24
10	7/16/85	-1.97	-0.99	63	7/17/85	-2.19	-0.54
11	7/21/85	-1.37	-2.25	63	on line	-2.12	-0.03
11	on line	-1.38	-1.71	64	on line	-2.42	-0.31
12	7/16/85	-1.00	-1.39	65	7/18/85	-2.24	-0.76
13	7/20/85	-0.30	-1.20	67	7/20/85	-1.92	-0.59
13	on line	-1.39	-0.69	68	on line	-2.28	-0.13
14	on line	-1.81	-0.53	69	7/27/85	-1.69	-0.92
15	7/21/85	-1.79	-1.11	70	on line	-0.69	0.07
15	on line	-2.17	-0.66	70	on line	-0.67	0.04
17	7/20/85	-1.59	-1.28	71	7/20/85	0.28	-0.36
18	on line	-2.29	-0.89	72	on line	-0.49	0.09
19	7/20/85	-1.84	-1.51	73	7/19/85	-0.81	-0.47
21	7/19/85	-2.17	-1.13	74	on line	-1.39	0.29
23	7/18/85	-1.73	-1.02	75	7/18/85	-1.04	-0.48
25	7/19/85	-2.22	-1.27	76	on line	-3.68	-0.73
26	on line	-2.46	-0.28	77	7/17/85	-2.45	-0.76
28	on line	-1.89	-0.37	77	on line	-2.49	-0.38
29	7/19/85	-1.61	-1.16	79	7/19/85	-2.03	-0.24
30	on line	-0.68	-0.83	79	on line	-2.37	-0.05
31	7/17/85	-0.36	-0.58	80	on line	-1.92	0.18
33	on line	-0.97	-0.10	81	7/19/85	-0.47	-0.08
35	7/19/85	-1.66	-0.75	81	on line	-0.69	0.45
35	on line	-2.07	-0.43	82	on line	-1.16	0.14
36	on line	-1.86	-0.57	83	on line	-2.63	-0.32
37	7/21/85	-1.45	-0.67	84	on line	-0.22	-2.66
38	on line	-1.94	-0.20	85	7/17/85	-0.85	0.28
40	on line	-1.97	-0.08	86	on line	-2.20	0.08
41	7/20/85	-1.70	-0.75	87	7/18/85	-1.95	-0.87
43	7/18/85	-2.08	-1.01	87	on line	-1.93	-0.16
46	on line	-2.77	-0.28	89	7/17/85	-2.19	-0.11
47	7/17/85	-2.18	-0.83	90	on line	-2.34	0.14
49	7/19/85	-1.71	-0.78	91	7/17/85	-1.22	-0.64
50	on line	-1.50	-0.14				
51	7/21/85	-0.85	-0.32				

TABLE 7. cont., Isotope results from station 9 *M. Mercenaria* specimen.

Sample No.	Prep Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
91	on line	-1.33	-0.18
92	on line	-1.13	0.15
92	on line	-1.21	-0.11
93	7/21/85	-1.21	-0.75
93	on line	-1.54	-0.18
94	on line	-2.35	-0.54
95	7/1885	-2.29	-0.45
95	on line	-2.90	-0.78
96	on line	-2.51	-0.38
97	7/18/85	-1.53	-0.81
98	on line	-1.51	0.30
99	7/18/85	-0.84	-1.04
99	on line	-1.19	-0.61
100	on line	-2.41	-0.75
101	on line	-3.60	-1.96
102	on line	-3.28	-1.04
103	7/17/85	-2.08	-1.37
103	on line	-2.13	-1.08
	Average =	-1.65	-0.56
	Std. Dev. =	0.76	0.57

Note: On-line samples were corrected by +0.499‰ for carbon and by –0.369‰ for oxygen based on sample duplicates from both laboratories (see below). Correction for fractionation between the on-line and off-line preparation techniques.

OXYGEN:
Average difference [on line - off line] of all 21 oxygen duplicates:
x = -0.219; std dev = 0.305
Average difference [on line - off line] of 11 oxygen duplicates:
x = -0.391; std dev = 0.0969 (9 duplicates used:6,15,35,53,55,79,81,93,99) Most on line oxygen values are lighter than the off line values (11 out of 16)

CARBON:
Average difference [on line - off line] of all 18 carbon duplicates:
x = 0.5244; std dev = 0.157
Average difference [on line - off line] of 14 carbon duplicates :
x = 0.472; std dev = 0.087 (11 duplicates used : 6,11,15,35,53,55,63,81,91,14,99) All on line carbon values are heavier than the off line values

TABLE 7. cont., Isotope results from station 9 *M. Mercenaria* specimen.

Isotope standards run with Station 9 specimen.

Standard	Prep. Date	Date Run	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
NBS-20	7/21/85	8/1/85	-4.17	-1.09
NBS-20	7/17/85	8/2/85	-4.24	-1.10
NBS-20	7/17/85	8/8/85	-4.15	-1.06
NBS-20	7/20/85	8/8/85	-4.11	-1.13
NBS-20	7/20/85	8/15/85	-4.19	-1.22
NBS-20	7/18/85	8/15/85	-4.17	-1.33
NBS-20	7/16/85	8/15/85	-4.28	-1.30
NBS-20	7/16/85	8/22/85	-4.12	-1.08
NBS-20	7/19/85	8/22/85	-4.54	-1.20
NBS-20	7/19/85	9/18/85	-4.15	-1.02
NBS-20	7/27/85	9/18/85	-4.24	-0.96
NBS-20	on line	5/3/86	-4.12	-0.98
NBS-20	on line	5/5/86	-4.13	-0.97
NBS-20	on line	5/5/86	-4.11	-0.99
NBS-20	on line	5/12/86	-4.10	-0.84
NBS-20	on line	5/12/86	-4.05	-0.89
NBS-20	on line	6/2/86	-4.11	-1.02
NBS-20	on line	6/2/86	-4.10	-0.94
NBS-20	on line	6/9/86	-4.18	-0.96
NBS-20	on line	6/9/86	-4.14	-0.97
NBS-20	on line	8/4/86	-4.13	-0.92
NBS-20	on line	8/4/86	-3.99	-0.89
NBS-20	on line	8/18/86	-4.16	-1.01
NBS-20	on line	8/18/86	-4.24	-1.05
NBS-20	on line	9/23/86	-4.04	-0.73
NBS-20	on line	10/6/86	-4.11	-0.97
NBS-20	on line	10/31/86	-4.21	-1.15
NBS-20	on line	11/4/86	-4.11	-1.02
NBS-20	on line	11/4/86	-4.11	-1.05
NBS-20	on line	11/11/86	-4.18	-1.02
NBS-20	on line	11/20/86	-4.16	-1.06
NBS-20	on line	11/20/86	-4.17	-1.08
NBS-20	on line	11/11/86	-4.16	-1.06
		Average =	-4.15	-1.03
		Std. Dev. =	0.09	0.12
		Off line Ave.=	-4.21	-1.14
		Std. Dev. =	0.12	0.11

TABLE 8. Carbon and oxygen isotope results from the specimen of *M. mercenaria* collected at station 12.

Sample No.	Prep Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)	Sample No.	Prep Date	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
1	off line	-2.38	-0.56	75	on line	-2.40	0.10
3	off line	-2.88	0.22	76	on line	-1.67	-0.08
5	off line	-2.38	0.12	77	on line	-0.93	0.44
7	off line	-2.76	-0.03	79	off line	-1.92	-0.38
9	off line	-2.59	-0.10	81	on line	-1.85	0.52
11	on line	-2.29	-0.16	83	off line	-2.37	-1.58
12	on line	-2.37	0.35	85	off line	-2.12	-0.65
15	off line	-2.03	0.02	87	off line	-2.79	0.72
17	off line	-2.71	0.11	89	off line	-2.37	-0.22
19	off line	-2.60	-0.26	91	off line	-2.35	-0.31
22	on line	-2.57	0.36	93	off line	-0.67	0.10
23	off line	-2.55	-0.03	95	off line	-1.52	-0.54
24	on line	-1.35	-0.46	97	off line	-1.79	0.42
25	off line	-1.02	-0.49	99	off line	-1.61	-0.50
27	on line	-1.29	0.61	101	off line	-2.18	-0.32
31	off line	-1.38	-0.41	103	off line	-1.81	0.20
33	off line	-1.78	-0.22	105	off line	-2.11	-0.33
35	off line	-1.95	-0.13	107	off line	-1.47	-0.75
37	off line	-1.54	-0.77	109	off line	-1.58	0.12
39	off line	-1.78	0.04	111	off line	-1.92	-0.10
41	on line	-1.44	0.31	113	off line	-2.57	-0.50
42	on line	-1.53	0.08	115	off line	-2.68	-1.20
45	off line	-2.07	-0.39	117	off line	-3.36	-1.19
47	off line	-2.91	-0.55	119	off line	-1.90	-1.61
49	off line	-2.91	-0.54	121	off line	-2.60	-0.99
51	off line	-1.86	-0.16	123	off line	-2.50	-0.49
52	on line	-2.04	0.92	125	off line	-2.96	-1.25
53	on line	-0.99	0.41	127	off line	-3.29	-2.52
55	off line	-1.50	0.00	129	off line	-3.15	-1.71
56	on line	-1.98	0.61	133	off line	-2.94	-2.20
57	off line	-3.07	-0.27	135	off line	-3.47	-2.67
59	off line	-3.03	-0.71	137	off line	-3.84	-2.16
62	on line	-1.33	-0.93	138	on line	-2.50	-1.88
63	off line	-1.33	0.19	139	off line	-2.70	-1.96
65	off line	-1.67	0.17	141	off line	-2.90	-2.89
67	off line	-2.01	-0.75				
69	on line	-2.35	0.10		Average =	-2.19	-0.42
70	on line	-2.43	0.49		Std. Dev. =	0.65	0.82
72	on line	-2.43	0.40				
73	off line	-2.28	-0.41				

TABLE 9. Carbon and oxygen isotope results from the summer and winter shell edge samples taken from *M. mercenaria*.

Narrgansett Bay Locations: **SUMMER**

Location	Date Collected	Date Run	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
Greenwich Bay				
2A-2	7/23/84	4/16/86	-3.39	-2.38
2A-3	7/23/84	3/31/86	-3.69	-2.76
2A-4	7/23/84	5/5/86	-3.91	-3.2
2A-5	7/23/84	3/31/86	-3.45	-1.69
2A-5	7/23/84	5/5/86	-3.31	-1.72
Longmeadow				
4-2	7/23/84	4/7/86	-3.69	-2.38
4-2	7/23/84	3/9/86	-3.52	-2.60
4-3	7/23/84	4/7/86	-3.90	-4.07
4-4	7/23/84	3/9/86	-3.50	-2.72
4-5	7/23/84	4/16/86	-3.41	-4.59
Warren River				
5-2	7/23/84	3/31/86	-3.11	-2.47
5-3	7/23/84	3/9/86	-3.64	-2.28
5-4	7/23/84	3/31/86	-3.71	-3.07
5-5	7/23/84	3/9/86	-3.34	-4.73
Mountview				
9-2	7/23/84	4/16/86	-2.68	-0.91
9-3	7/23/84	3/9/86	-2.88	-2.26
9-4	7/23/84	3/9/86	-2.98	-3.68
9-5	7/23/84	4/16/86	-3.74	-2.51
Wickford Bkw				
12-1	7/23/84	4/16/86	-4.06	-4.30
12-1	7/23/84	5/1/86	-3.70	-4.16
12-3	7/23/84	4/16/86	-3.24	-5.47
12-3	7/23/84	3/31/86	-3.16	-5.23
12-3	7/23/84	5/5/86	-3.03	-5.33
12-5	7/23/84	3/9/86	-3.36	-6.66
12-5	7/23/84	5/5/86	-3.22	-6.76
		Average =	-3.43	-3.52
		Std. Dev.=	0.34	1.55

TABLE 9. cont., Isotopic results of *M. mercenaria* Shell Edge Samples

Providence River Locations: **SUMMER**

Sample No.	Date Collected	Date Run	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
1-1	7/2/84	3/9/86	-4.54	-3.06
1-2	7/2/84	4/16/86	-3.74	-3.94
1-2	7/2/86	5/1/86	-3.65	-3.86
1-4	7/2/84	4/16/86	-4.20	-4.88
1-5	7/2/84	3/9/86	-4.81	-5.00
1-6	7/2/86	5/1/86	-4.26	-4.28
2-1	7/2/84	3/9/86	-4.65	-3.87
2-2	7/2/84	3/31/86	-5.09	-3.90
2-3	7/2/84	4/25/86	-4.48	-3.97
2-5	7/2/84	3/31/86	-4.39	-2.69
3-1	7/2/84	4/16/86	-4.31	-3.09
3-2	7/2/84	3/9/86	-4.84	-4.64
3-3	7/2/84	3/9/86	-5.03	-5.22
10-1	7/2/84	4/16/86	-3.89	-4.09
10-2	7/2/84	3/9/86	-3.85	-3.40
10-2	7/2/84	5/1/86	-3.66	-3.04
10-3	7/2/84	5/1/86	-3.74	-4.50
10-4	7/2/84	4/25/86	-3.89	-2.87
10-5	7/2/84	5/1/86	-3.27	-3.56
10-6	7/2/84	5/1/86	-3.84	-4.51
10-7	7/2/84	5/1/86	-3.57	-3.67
10-9	7/2/86	5/1/86	-4.12	-3.89
1010	7/2/84	3/9/86	-3.89	-3.85
		Average =	-4.16	-3.90
		Std. Dev. =	0.50	0.69

TABLE 9. cont., Isotopic results of *M. mercenaria* Shell Edge Samples

Narragansett Bay Locations: WINTER

Location	Date Run	Date Run	$\delta^{18}O$ (PDB	$\delta^{13}C$ (PDB)	Height (cm)
Greenwich Bay					
2A-1	12/17/84	6/9/86	-2.31	0.07	6.4
2A-1	12/17/84	6/9/86	-2.17	0.32	6.4
2A-1	12/17/84	7/3/86	-1.75	0.28	6.4
2A-1	12/17/84	11/11/86	-2.10	0.13	6.4
2A-1	12/17/84	11/20/86	-2.17	0.14	6.4
2A-2	12/17/84	6/9/86	-2.14	0.32	6.7
2A-2	12/17/84	11/14/86	-1.97	0.28	6.7
2A-3	12/17/84	6/9/86	-2.52	0.35	6.7
2A-3	12/17/84	1/14/86	-1.91	0.61	6.7
2A-4	12/17/84	6/9/86	-0.39	-0.63	5.6
2A-4	12/17/84	11/11/86	-0.20	-0.34	5.6
2A-4	12/17/84	11/20/86	-0.42	-0.33	5.6
2A-5	12/17/84	11/14/86	-1.81	0.15	6.2
(no Longmeadow specimens available for winter)					
Warren River					
5-2	12/17/84	11/11/84	-2.20	-0.54	
5-2	12/17/84	11/14/86	-2.38	-0.63	
5-3	12/17/84	11/14/86	-2.63	-2.81	
5-5	12/17/84	11/20/86	-2.53	-3.12	
Mountview					
9-1	12/17/84	11/14/86	-2.20	-1.587.65	
9-2	12/17/84	11/11/86	-1.76	0.035.8	
9-3	12/17/84	11/11/86	-1.85	-1.356.15	
9-3	12/17/84	11/14/86	-2.01	-1.436.15	
9-4	12/17/84	11/20/86	-3.12	-2.407.2	
9-5	12/17/84	11/11/86	-1.69	-1.176.3	
9-5	12/17/84	11/14/86	-1.85	-1.246.3	
Wickford Bkw					
12-1	12/17/84	6/9/86	-3.23	-0.469.4	
12-2	12/17/84	11/14/86	-2.63	-3.208.9	
12-3	12/17/84	6/9/86	-2.41	-2.5510.0	
12-3	12/17/84	7/3/86	-2.44	-4.6010.0	
12-4	12/17/84	11/14/86	-2.79	-4.318.7	
12-5	12/17/84	11/14/86	-2.88	-3.648.7	
		Average =	-2.08	-1.12	
		Std. Dev. =	0.71	1.52	

APPENDIX II.

TABLE A. Aragonite fractionation due sample preparation techniques.

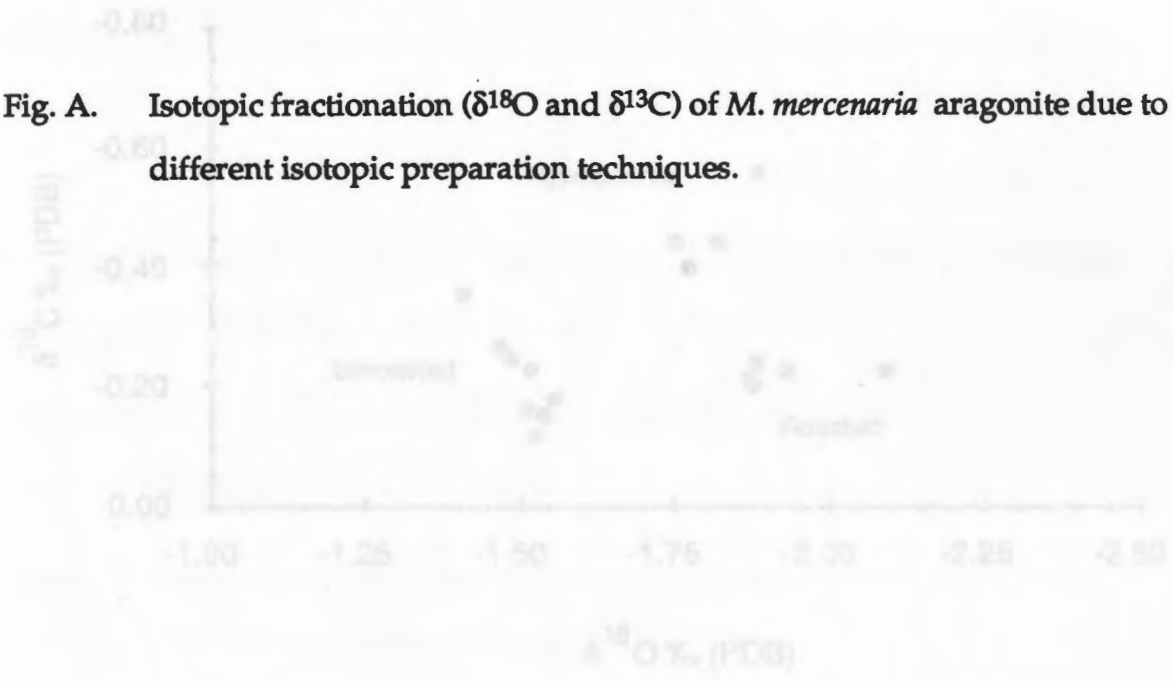
A section of *M. mercenaria* shell was ground and seived (through a 163 micron seive) for this experiment. The samples labelled unroasted (untreated) were run after the grinding; the samples labelled roasted were heated in vacu for 1 hour at 390°C (our standard carbonate preparation technique); the samples labelled hypochlorite were soaked in a 5% hypochlorite solution for 24 hours, air dried at 40°C then run on the mass spectrometer.

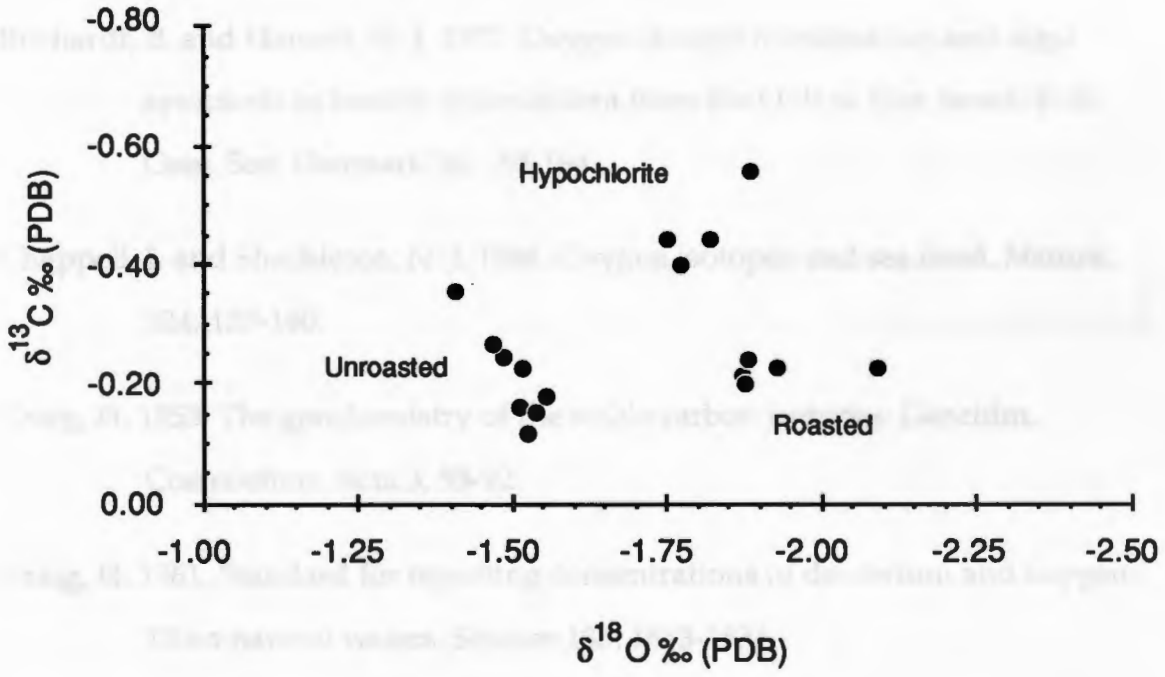
The $\delta^{18}O$ values of the samples that were roasted were typically 0.43‰ lighter (more depleted) than the samples that were not roasted. The samples treated with hypochlorite solution were 0.31‰ lighter than the samples that were not roasted, but 0.12‰ heavier than the samples that were roasted.

The $\delta^{13}C$ values were approximately the same between the roasted and unroasted samples, however the samples treated with hypochlorite were depleted by approx. 0.24‰ relative to the other methods.

SAMPLE PREP.	$\delta^{18}O$ (PDB)	$\delta^{13}C$ (PDB)
Roasted	-2.09	-0.23
	-1.93	-0.23
	-1.87	-0.21
	-1.88	-0.24
	-1.88	-0.20
Average =	-1.93	-0.22
Std. Dev. =	0.09	0.02
Unroasted	-1.48	-0.24
	-1.51	-0.16
	-1.54	-0.15
	-1.53	-0.11
	-1.51	-0.23
	-1.55	-0.18
	-1.47	-0.27
	-1.41	-0.35
Average =	-1.50	-0.21
Std. Dev. =	0.05	0.08
Hypochlorite	-1.77	-0.40
	-1.82	-0.44
	-1.88	-0.56
	-1.75	-0.44
Average =	-1.81	-0.46
Std. Dev. =	0.06	0.07

Fig. A. Isotopic fractionation ($\delta^{18}O$ and $\delta^{13}C$) of *M. mercenaria* aragonite due to different isotopic preparation techniques.




-0.80
-0.60
-0.40
-0.20
0.00
$\delta^{13}C$ ‰ (PDB)
Hypochlorite
Unroasted
Roasted
-1.00
-1.25
-1.50
-1.75
-2.00
-2.25
-2.50
$\delta^{18}O$ ‰ (PDB)

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