

**Quantitative Ecological and Taphonomic Patterns in Late Cenozoic
Mollusk-Dominated Marine Fossil Assemblages**

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Abstract

Applications in paleontological research are far from being limited to taxonomic collection and identification. Nor is such research limited to working solely on fossil data. Actualistic paleontology is the study of modern or recent organisms and processes to better understand those of the past. The bulk of this body of research falls under the category of actualistic paleontology, and examines geochronological methods and error biases in dating biological specimens ranging in age from modern to thousands of years old. Although such methods are arguably not perfect, error rates of \pm a few hundred to few thousand years can be extremely important when considering ecological relationships among both Holocene taxa and time-averaged paleocommunities, but quite diminished when considering implications on more traditional dating techniques for ancient strata. Regardless, understanding implications of time resolution is important in analyses of and comparisons between any biological dataset. The following chapters are united by quantitative and statistical management of data with varying levels of temporal resolution, and represent four manuscripts that either are in press or soon to be submitted for publication.

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The best way to make your dreams come true is to wake up – Paul Valery

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Chapter 4.

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Introduction

Understanding the resolution of the fossil record is key to interpreting patterns in paleontological data. In order to research big picture ideas (e.g., changes in paleoecology over time, climate change, evolution, etc.), we must first develop a geochronological toolset that will allow us to say something more definite about patterns we discover. Commonly, indirect methods, such as biostratigraphic relationships or inference based on modern processes, must be used for dating. In some cases, a researcher may be able to directly date strata of interest (e.g., glauconite and Strontium dates, Chapter 4). High resolution dating techniques are also available to paleontologists to date individual fossil or subfossil specimens. Recent developments in the geochemical method of amino acid racemization has allowed an abundance of modern to Pleistocene biological specimens to be dated at a relatively low cost. As Quaternary fauna and flora are well understood, studying the modern sea floor is an excellent way to gain a greater understanding about ancient fossil horizons, if we can accept modern settings as analogues to the past.

Biogeochemical techniques such as amino acid racemization have allowed researchers to compare different taxa, environments and sedimentary layers to assess quantitatively the potential limits of the resolution of the fossil record (Chapter 2). Cumulative research efforts over the past two decades by various researchers suggest that time averaging, or temporal mixing of skeletal remains of organisms found in the same sedimentary layers or at present-day sediment-water interfaces can be quite high. Even thin or surficial sedimentary horizons are time-rich, commonly representing specimens that vary in age over 10^2 to 10^4 years time scales. Implications for the paleontological record, including ecological relationships among taxa, morphological and evolutionary

change over time are immediately obvious. What may be less obvious is the amount of artificial “time averaging” produced by error rates in the methodologies we use to quantify specimen ages.

Chapter 1 discusses error introduced in calibrating raw amino acid values to radiometric dates. Here I use D/L Aspartic values calibrated against reservoir-corrected radiocarbon dates to produce age calculation algorithms that can be used to calculate ages of specimens not directly dated using radiocarbon methods. The age calibration algorithm chosen may drastically affect the accuracy of calibrations. Generally, heating experiments on live-collected specimens can be used to model racemization kinetics for research data. However, live-collected taxa were not available in the case of this study, so age calibrations must be based solely on goodness of fit statistics. Error rates are modeled for how different calibration algorithms affect age estimates of radiocarbon dated late Holocene specimens within a single data set. The amount of offset in calculated (D/L amino acid age algorithm transformed) versus calibrated (radiometrically dated, or known) ages of specimens gives us insight into calculation error, or how closely available D/L age transformations are able to reproduce calibrated specimen ages. Error rates between calculated and calibrated ages provide insight into the amount of artificial temporal mixing in age afflicted on a specimen purely due to age transformation mathematics, which ultimately affects the reliability of any data set.

In Chapter 2, an age calculation algorithm determined appropriate from Chapter 1 is used to calibrate D/L Aspartic acid values to radiocarbon dates for two taxa (brachiopod *Bouchardia rosea* and molluscan bivalve *Semele casali*) collected simultaneously from surficial sediments at two depths in Ubatuba Bay, Brazil. Marine

invertebrates are an important target for high-resolution geochronological studies in the late Quaternary, because shells collected from modern seafloors and coastlines tend to represent time-averaged assemblages that may potentially provide nearly complete multi-centennial to multi-millennial time series for the Holocene, and in some cases the Pleistocene. Data presented in this chapter show that D/L Asp ratios plotted against radiocarbon ages over the time span of multiple millennia can be used to develop geochronologies not only for aragonitic mollusks (previously widely used for dating), but also for calcitic brachiopods. Concurrent time series of aragonitic and calcitic shells can be assembled using Asp racemization dating, and parallel multi-centennial to multi-millennial records can be developed simultaneously for both biomineral systems. Such records are useful for analyses of isotopic records, time averaging, and shell survival or taphonomy over time.

Chapter 2 illustrates that Asp D/L values show an excellent correlation with reservoir-corrected AMS radiocarbon ages. Marine samples must be corrected for reservoir age, which is the lag time for ^{14}C mixing between the atmosphere and ocean, when radiocarbon dating. Reservoir ages vary from region to region and over time, so collected shells representing multiple millennia may actually record different reservoir signatures. Previously published marine reservoir estimates for the region have been quite variable, ranging from 204 ± 44 to 720 ± 40 years BP (Stuiver et al., 1998; Nadal de Masi, 1999; Eastoe et al., 2002; Angulo et al., 2005 – see references in Chapter 2), possibly reflecting temporal variability in regional ocean upwelling. The value of 408 ± 18 years used to calibrate data in Chapter 2 was derived by Angulo et al. (2005) as representative of the majority of the shells dated in the region. However, the sensitivity

of our age estimates to changes in the postulated reservoir age is worth examining because of the variability of published reservoir ages. Sensitivity analyses are conducted to estimate the affect of changing reservoir age on specimen age calculations, as changing the assumed reservoir age would affect the numerical age estimates of Asp dated shells. Altering reservoir ages can create a shift in shell age from hundreds to thousands of years – again potential *artificial* temporal mixing of specimen ages due to mathematical uncertainties in age calibration models.

In Chapter 3, age calibrations developed in previous chapters are used to date 58 individual brachiopod shells and 69 bivalve shells from Ubatuba Bay, Brazil to analyze the informative value of taphonomic signatures on pre-burial history of marine benthic shells. Studies of burial history of modern sea floors have become increasingly important for understanding rates of time averaging and taphonomic processes. Availability of these numerous individually dated specimens allows for a rigorous test of how taphonomic signatures vary over time, among taxa with differing life habits and skeletal mineralogy, as well as between sites of varying collection depth. Correlations between specimen age, color and taphonomic grade are investigated for the presence of a taphonomic clock, or the ability to use taphonomic grade (degree of shell degradation) as a proxy for shell age.

Chapter 4 deviates from the previous three chapters to investigate faunal changes across the Miocene-Pliocene boundary, which is marked by a regionally traceable erosional disconformity. Although the two depositional members studied (Cobham Bay Member of the upper Miocene Eastover Formation and Sunken Meadow Member of the lower Pliocene Yorktown Formation) have been dated via radiometric methods on

glauconite grains or biostratigraphic relationships, the duration of the unconformity at the contact can be estimated, but is unknown. Specimens were collected from shell beds, which are known to typically be time-averaged deposits. Here fine-scale bulk sampling efforts were conducted from the shell beds proximal to the boundary to provide direct quantitative insights into how faunal composition and environmental and ecological parameters may have changed in the region across the Miocene-Pliocene boundary.

Chapter 1 –Impacts of D/L Aspartic calibration transformations on shell age reproducibility

Abstract

Racemization/epimerization has proven a useful tool for age dating Quaternary, and even older, biological specimens. Here we use D/L Aspartic values calibrated against reservoir-corrected radiocarbon dates to produce age calculation algorithms that can be used to calculate ages of specimens not directly dated using radiocarbon methods. As the age calibration algorithm chosen can greatly affect the accuracy of calibrations, heating experiments on live-collected specimens should ultimately be used to model racemization kinetics for research data. For the purpose of paleontological data, live-collected organisms may not always be available, and age transformations must be made based on what data are available. Here we model error rates in how different calibration algorithms affect age estimates of radiocarbon dated late Holocene specimens within a single data set. Error rates between calculated and calibrated ages of specimens provide insight into the amount of artificial temporal mixing in age afflicted on a specimen due purely to age transformation mathematics, which ultimately affects the reliability of any data set.

Introduction

Racemization/epimerization kinetics have been widely studied as a dating method for a number of amino acids (see Goodfriend et al. 2000; and Wehmiller and Miller 2000 for recent reviews). The extent of racemization, or ratio of D (dextro) to L (laevo) isomers of an amino acid, is used to date biological samples. Living organisms are composed of nearly 100% (D/L =

0) of the L chiral configuration of amino acids. Racemization occurs when the L isomers are transformed to D isomers after the organism is deceased. Raw D/L amino acid values plotted against time maintain a similar non-linear concave-down profile if racemization is allowed to proceed to equilibrium. Racemization occurs quickly in the initial time after death producing a steep slope when D/L values are plotted against time. The slope shallows with time as D/L equilibrium is reached due to an increase in the rate of the reverse reaction relative to the increase in the D form of the amino acid. Amino acids racemize at different rates (e.g., Wehmiller et al. 1995 Table 2a; Kaufman and Manley 1998 Table 2), making some more useful than others for geologic dating depending on the environmental history of the sample in question. The rate of racemization is also dependent on temperature as well as type of organic material and taxonomic classification (Lajoie et al. 1980; Miller and Hare 1980; Andrews et al. 1985; Goodfriend et al. 1997; Wehmiller and Miller 2000).

The rate and kinetics of racemization can be modeled using heating experiments where D/L values are calculated for specimens at given intervals in time. Absolute ages can then be calibrated using fossil or sub-fossil specimens of known age (e.g., radiocarbon dated). Calibrations can be conducted in multiple ways (see below), but essentially rely on linearization and characterization (e.g., regression) of the racemization curve for projection and extrapolation of calibrated specimen(s) of known age to those of unknown age. The age calibration algorithm chosen may drastically affect the accuracy of calibrations. The purpose of this study is to model error rates in how different calibration algorithms affect age estimates of radiocarbon dated late Holocene specimens within a single data set. The amount of offset in calculated (D/L Asp age algorithm transformed) versus calibrated (radiometrically dated, or known) age of specimens from a range of ages will give insight into calculation error, or how closely available D/L age

transformations are able to reproduce calibrated specimen age. Error rates between calculated and calibrated ages provide insight into the amount of artificial temporal mixing in age afflicted on a specimen purely due to age transformation mathematics.

Apparent Parabolic Kinetics

The apparent parabolic kinetics method (Mitterer and Kriausakul 1989) linearizes data by taking the square root of the time axis. Age is calculated using the equation:

$$\text{Equation 1 - 1} \quad t = [(aa)_s / m_c]^2$$

where t is the age of the sample (x in the line equation $y = mx+b$), and aa is the D/L value of the amino acid in the sample (modeled by Mitterer and Kriausakul (1989) using A/I or D-alloisoleucine/L-isoleucine). The value m is the slope of the line generated by a calibration sample of known age regressed through the origin (time = 0), which assumes the D/L value of a live-collected specimen with no racemization/epimerization. This approach is methodologically simple, but assumes that the undated specimens maintain a parabolic relationship with time, or in other words remain linear when the time axis is root transformed, and that the regression line through the data crosses the y-axis at the origin. Samples of known age from Hearty et al. (1986) were modeled by Mitterer and Kriausakul (1989) using this transformation based on the calibration of one of the youngest samples (127 ka) among a suite from different aminogroups collected from the Mediterranean basin. The age calibration produced calculated ages with a remarkably close match to the known ages of specimens (see their Table 1). Ortiz et al (2004) noted that the applicability of the transformation is questionable at very low and high D-alloisoleucine/L-isoleucine (A/I) values. The latter assumption of the regression line crossing

through the origin is also frequently violated, as processing samples for amino acids produces a small amount of racemization.

The intention of this transformation is to be able to calculate ages for samples beyond the initial rapid racemization stage, which is in itself nearly linear (i.e. Figure 1 in Mitterer and Kriausakul 1989). However, the choice of a calibration sample remains critical, as a calibration sample constituting the initial rapid increase in racemization/ epimerization as opposed to one taken from the transitional or slower portions of a plot of values will ultimately determine the effectiveness and accuracy of this transformation as equated by Mitterer and Kriausakul (1989).

Power Transformation

In a power transformation, the D/L value of the amino acid is raised to some power to linearize it with respect to time. The amino acid values are calibrated by regressing power transformed D/L values against time for multiple specimens of known age. The equation for the regression line can be used to calculate ages of specimens that were not directly dated:

$$\text{Equation 1 - 2} \quad t = \frac{(aa^p) - b}{m}$$

where t (x in the line equation $y = mx + b$) is the age of a sample, aa is the D/L value of the amino acid raised to some power p , b is the y-intercept of the regression line and m is the slope of that line. This method requires three or more dated specimens to produce a calibration, and is most effective when a wide range of sample D/L values are directly dated, especially those with very high or the highest D/L value found to most accurately characterize the nature of the calibrated regression line. This method is less cost effective, but has the potential to more accurately delineate the change in racemization/epimerization rates over a large range in time if

appropriate calibration models are produced. Some taxa cannot be adequately linearized using Equation 1.2 above and show systematic trends away from linear for some age-transformed D/L values (e.g. Goodfriend et al. 1996). Manley et al. (2000) modified the simple power transformation to create better linearization for these taxa by replacing the D/L value (aa in Equation 1.2 with $(1 + aa)/(1 - aa)$).

Methods

Specimens used in this study were collected in conjunction with an ongoing project of the marine ecology group of the São Paulo State University from two collection sites (10 m and 30 m depth) in Ubatuba Bay, a small embayment off the coast of the state of São Paulo, Brazil (Fig. 1.1). A total of 18 specimens from both sites and two taxa (brachiopod *Bouchardia rosea* and bivalve *Semele casali*) were prepared for radiocarbon and amino acid (D/L aspartic) analyses using a uniform, standard methodology. Details regarding sampling and dating methodology, as well as sampling site parameters is found in Barbour Wood et al. (2006). A summary of sample Asp D/L values and calibrated ^{14}C ages is found in Table 1. In an effort to model the effect of possible age transformations on a data set, ages of carbon dated specimens were calculated using each age transformation, and deviations between the calculated (age-transformed) age and calibrated (reservoir corrected, calibrated) ^{14}C age were measured.

Apparent Parabolic Transformation Methods

The parabolic kinetics method (Mitterer and Kriausakul 1989) was used to calculate ages of dated specimens in two ways. First, as described in Mitterer and Kriausakul (1989), single specimens from each taxon (Table 1.1) were iteratively used for independent age calibrations for

the sampling site at which the specimen was collected. Equation 1.1 was applied using the D/L Asp value and slope of the line between each individual specimen and the origin (D/L Asp = 0, or 0 years BP), and used to calculate an estimated age for the remaining specimens of that taxon for that collection site. For example, using brachiopod specimen 13022 would yield a calibration of $\text{age} = (\text{D/L Asp} / 0.0125)^2$, which could then be used to calculate ages for remaining brachiopod specimens from Site 1 (30 m) using their respective D/L Asp values (Fig. 1.2). This procedure was repeated for all specimens of a particular taxon separately for each sampling site. Slopes calculated for each specimen are provided in Table 1.2.

Second, the age calibration equation presented in Mitterer and Kriausakul (1989) was modified as in Kaufman (2003), Ortiz et al. (2004) and Sloss et al. (2004) by plotting raw D/L values of multiple specimens against respective root-transformed ages (Fig. 1.2) yielding an age equation of:

Equation 1 - 3
$$t = \left[\frac{aa - b}{m} \right]^2$$

where t (x in the line equation $y = mx + b$) is the age of a sample, aa is the D/L value of the amino acid, b is the y-intercept of the regression line and m is the slope of that line. This transformation results in linearization of the data, and the equation of the regression line through the root-transformed data can then be used to calculate ages of specimens from each taxonomic group, independently for each sampling site. The regression line statistics are tabulated in Table 1.4, and differences between calibrated and calculated ages of specimens were measured and tabulated in Table 1.5.

Power Transformation Methods

Power transformations were modeled by plotting D/L Asp values raised to a power, p , and regressed against reservoir corrected, calibrated ^{14}C age. Powers were chosen in multiple ways, and included the following. First, an “*a-priori*” power transformation was applied, where the power of D/L Asp² was arbitrarily chosen to linearize the data. Second, power transformations were iteratively applied to the data between powers of 2.0 and 4.0, and r^2 values for each collection site and both taxa were recorded. The power yielding the highest r^2 value while maintaining a zero or positive y-intercept was selected as the “per-site/per-taxon” best fit power transformation. Four calibration equations were thus produced: one for each taxon at each collection site. Third, mean iterative r^2 values were calculated for each taxon by pooling data from both collection sites. Two age calibrations were produced (one for each taxon, or “taxonomic best fit”) by identifying the power that yielded the highest mean r^2 values while maintaining a zero or positive y-intercept. Finally, the highest mean r^2 values were identified for all taxa and collection sites combined yielding a single “best fit for all samples” age calibration. This transformation is similar to the “*a priori*” transformation, but based on pooled regression statistics. Resulting slopes, intercepts and regression line statistics, including the r^2 value, p-value, F-statistic and root mean square error are recorded in Table 1.4. The slope and y-intercept of each regression line were used to calculate ages of specimens from each taxonomic group and compared to calibrated specimen age (Table 1.5, Figure 1.3a,b).

Results

Apparent Parabolic Transformation

The apparent parabolic kinetic method was developed to linearize D/L A/I values with respect to time with the intent of being a reliable method to linearize and date D/L values above the initial rapid epimerization stage. Parabolic kinetics transformations as originally proposed in Equation 3 by Mitterer and Kriausakul (1989) produce poor accuracy results with this dataset, regardless of specimen used for calibration. Calculated deviations, or differences between the calibrated and calculated age of a specimen, range between hundreds to thousands of years (e.g., Table 1.3; Fig. 1.2) depending on the specimen chosen for the single specimen calibration transformation. As noted by Ortiz et al. (2004), the transformation may have less utility at low D/L values, and the amount of deviation decreases when older specimens are used for calibration (Table 1.3).

However, the apparent parabolic kinetics method has proven successful for transformation of D/L Asp values (e.g., Ortiz et al. 2004; Sloss et al. 2004) when applied to a suite of calibration samples. This modified parabolic transformation method, which uses the equation of a regression line produced by a suite of calibration samples plotted against root-transformed ages, produces much lower deviations from known sample age. Regression line statistics showed high, significant correlations between D/L Asp values and root-transformed specimen ages (Table 1.4). Deviations for individual samples range from 0.2 to 541 years, with an average deviation for all specimens of 146 years. Brachiopods and bivalves also show similar average deviations (148 and 144 years respectively, Table 1.5).

Power Transformation

Specimen age reproducibility was similar in range of age deviations using power transformations. Brachiopod *B. rosea* was tested over the range D/L Asp² to D/L Asp³, and bivalve *S. casali* over the range D/L Asp² to D/L Asp⁴. Taxa from both sites maintained r^2 values greater than 0.9 for all iterative power transformations tested (Table 1.4). Likewise, all maintain significant p-values over the tested range, except for *S. casali* at Site 9 (10 m), which becomes significant at power transformations of D/L Asp^{2,3} and above. Results for each category of power transformation are discussed below.

A-priori transformation. The a-priori transformation (D/L Asp², Table 1.4) was applied to all specimens in the data set. An average deviation of 193 years between calibrated and calculated specimen age was found (Table 1.5). Lower deviations were apparent for *B. rosea* (148 years) than *S. casali* (238 years). This is likely due to a higher similarity between the a-priori transformation and that most appropriate for *B. rosea* as opposed to *S. casali* (the brachiopod r^2 values peaked between 2.1 and 2.8, whereas bivalves peaked above 3.0).

Best fit for all samples. This transformation pooled both taxa and collection sites and was intended to be similar to the a-priori transformation where all data are treated similarly. The transformation D/L Asp^{2,9} (Table 1.4) applied to all specimens provided the highest mean r^2 values when considering the complete data set. However, this transformation produced very poor results, with an average deviation between calibrated and calculated specimen age of 252 years (157 years for brachiopods and 372 years for bivalves, Table 1.5, Figure 1.3).

Per-site/per-taxon best fit. This transformation applies a separate power function to each taxon separately per collection site to yield the tightest r^2 values for the correlation of transformed Asp values and specimen ages. Best fit transformations for brachiopods were D/L

Asp^{2.8} at Site 9 and D/L Asp^{2.1} at Site 1. Transformations for bivalves were D/L Asp^{3.1} at Site 9 and D/L Asp^{3.7} at Site 1 (Table 1.4). This transformation created the lowest observed deviations between calibrated and calculated specimen age: 126 years for brachiopods and 93 years for bivalves with an average of 110 years for all specimens (Table 1.5, Figure 1.3).

Taxonomic best fit. The taxonomic best fit transformation found the most appropriate power transformation for all specimens pooled for each taxon individually, yielding D/L Asp^{2.8} for brachiopods and D/L Asp^{3.1} for bivalves (Table 1.4). This transformation produced similar results to the per-site/per-taxon best fit transformation, though with slightly less accuracy in predicting specimen age (120 vs. 109 years average deviation Table 1.5) with deviations of 145 years for brachiopods and 108 years for bivalves.

Figure 1.3 shows that both the taxonomic best fit and per-site/per-taxon best fit transformations offer the lowest amounts of deviation between known and calculated sample age (see also Table 1.5). Additionally, both these transformations create the least amount of variance in age between brachiopods and bivalves. Finally, Figure 1.3 suggests that brachiopods are largely unaffected by the power transformation chosen as compared to bivalves, with deviations typically ranging between 140 to 150 years.

Power transformations consistently provided low to moderate estimates of calculated specimen age. Interestingly, the entire range of power transformations tested for each taxon provided tight and mostly significant correlations between D/L Asp values and calibrated specimen age. Thus, any of the modeled transformation values would seemingly be suitable to linearize the data for a first approximation of sample age (e.g., the *a-priori* or *best fit for all samples* transformations) as shown below. A single transformation value applied to all taxa will likely produce large deviations between calculated and calibrated specimen ages, even when

based on statistical “best fit” scenarios, (e.g. *best fit for all samples* provide larger deviations than *a-priori* transformations, Fig. 1.3). Single transformation values may also potentially create unexpected biases against one or more taxa in a study (e.g. larger age deviations in bivalves, Fig. 1.3), essentially mathematically increasing the time-averaging (decreasing age resolution) of samples.

Discussion

Heating experiments on live-collected specimens should ultimately be used to model racemization kinetics for research data. In cases where live-collected specimens are not available, as in this study, the chosen transformation should ideally be representative of what would be expected in heating experiments. For example, although per-site/per-taxon best fit transformations produced the least amount of deviation between calculated and calibrated specimen ages, there is no biological reason for choosing more than one transformation value per taxon (Goodfriend et al. 1996; Wehmiller and Miller 2000). Thus, the taxonomic best fit transformation should be used to calculate specimen ages based on Asp D/L values.

Conclusions

This study suggests that taxonomic best fit power transformations may produce a more reliable and accurate linearization of data, based on D/L Asp values for specimens from the last several millennia. Transforming amino acid data for the purpose of linearization with respect to time can be an intensive process, especially where live-collected specimens are not available or heating experiments unpractical. Calculating appropriate transformation values solely from a death assemblage will likely add error to specimen age estimates. There is uncertainty

surrounding diagenetic temperature change over time, which will affect racemization D/L values differently between young and old specimens. In addition, slight differences in rates of racemization between collection sites, as in the modeled data, will also add to uncertainties in age calibration, but is ultimately unavoidable. The method of data transformation may greatly influence the accuracy of specimen age estimates, and on a specimen-by-specimen basis may introduce hundreds to thousands of years, potentially more, in shell age error. Studies based on age-calibrated specimens must ultimately consider and address error constraints on age resolution for appropriate interpretation of results.

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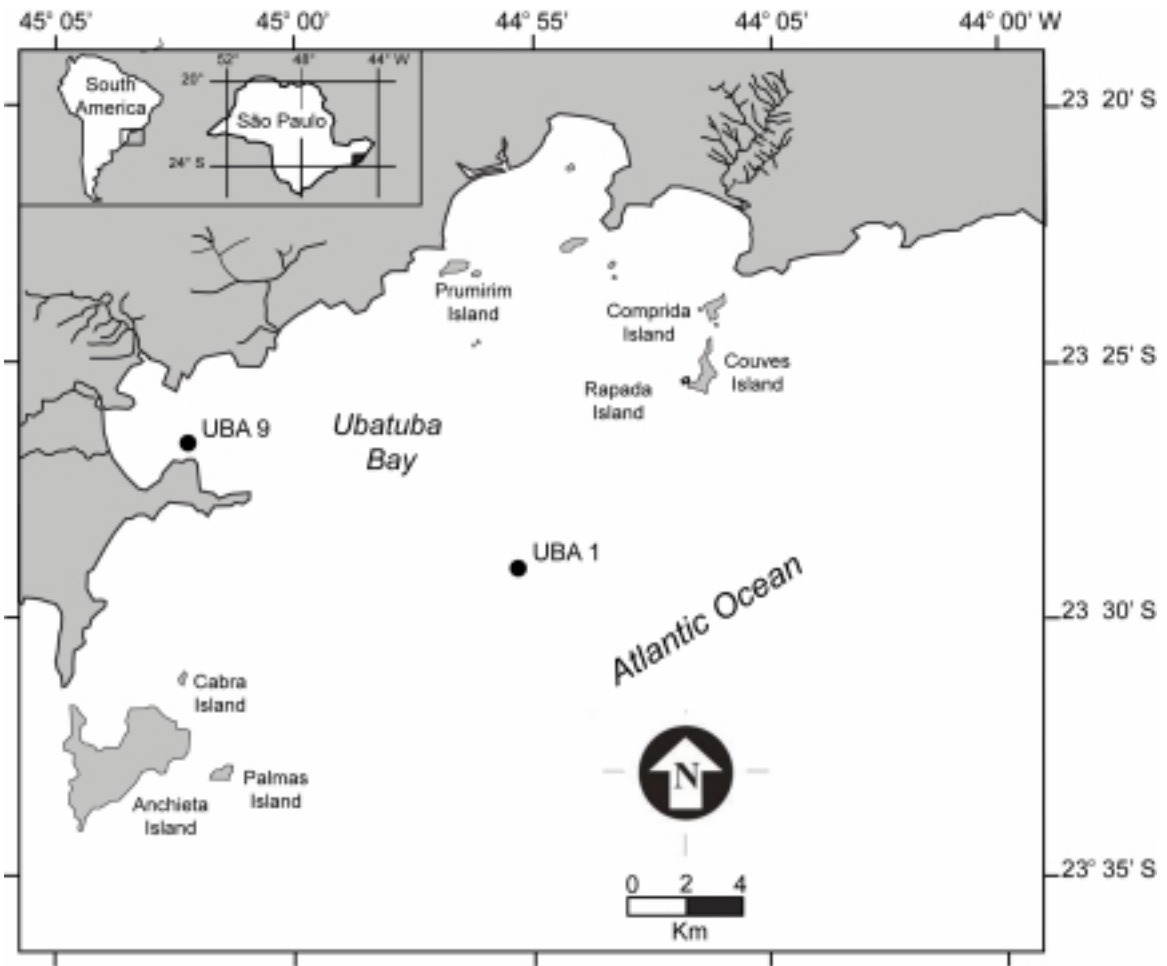


Figure 1 - 1. Map of the study area and collection sites.

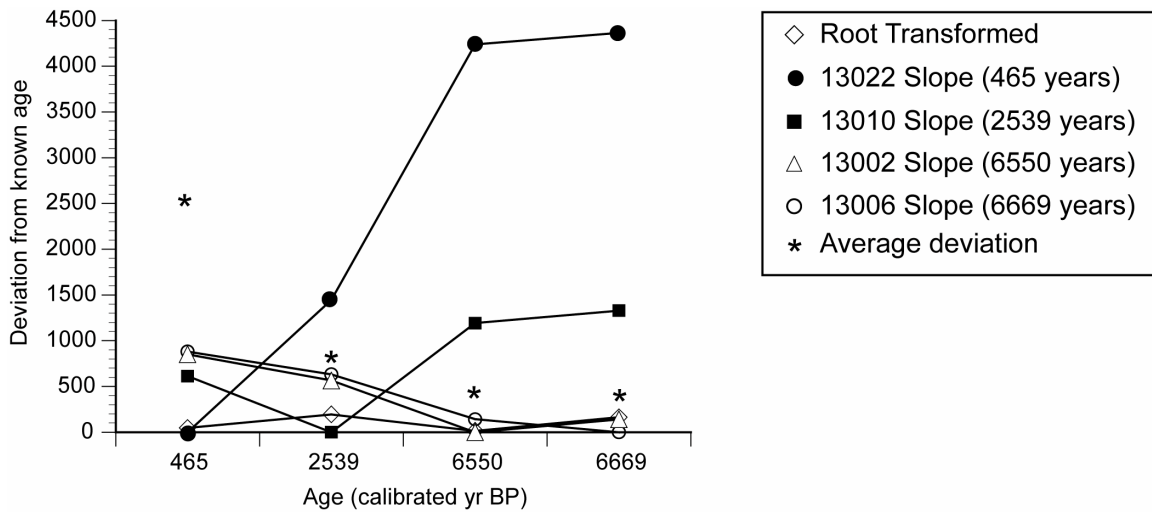


Figure 1 - 2. Changes in deviation through time between calibrated and calculated ages of specimens based on apparent parabolic kinetics when calibrated using a single sample (13022, closed circles; 13010, closed squares; 13002, triangles; and 13006, open circles) and a suite of samples (root transformed, diamonds). Average deviations for each calibration sample are plotted as asterisks. Root-transformed age calibrations produce consistently low deviations in age.

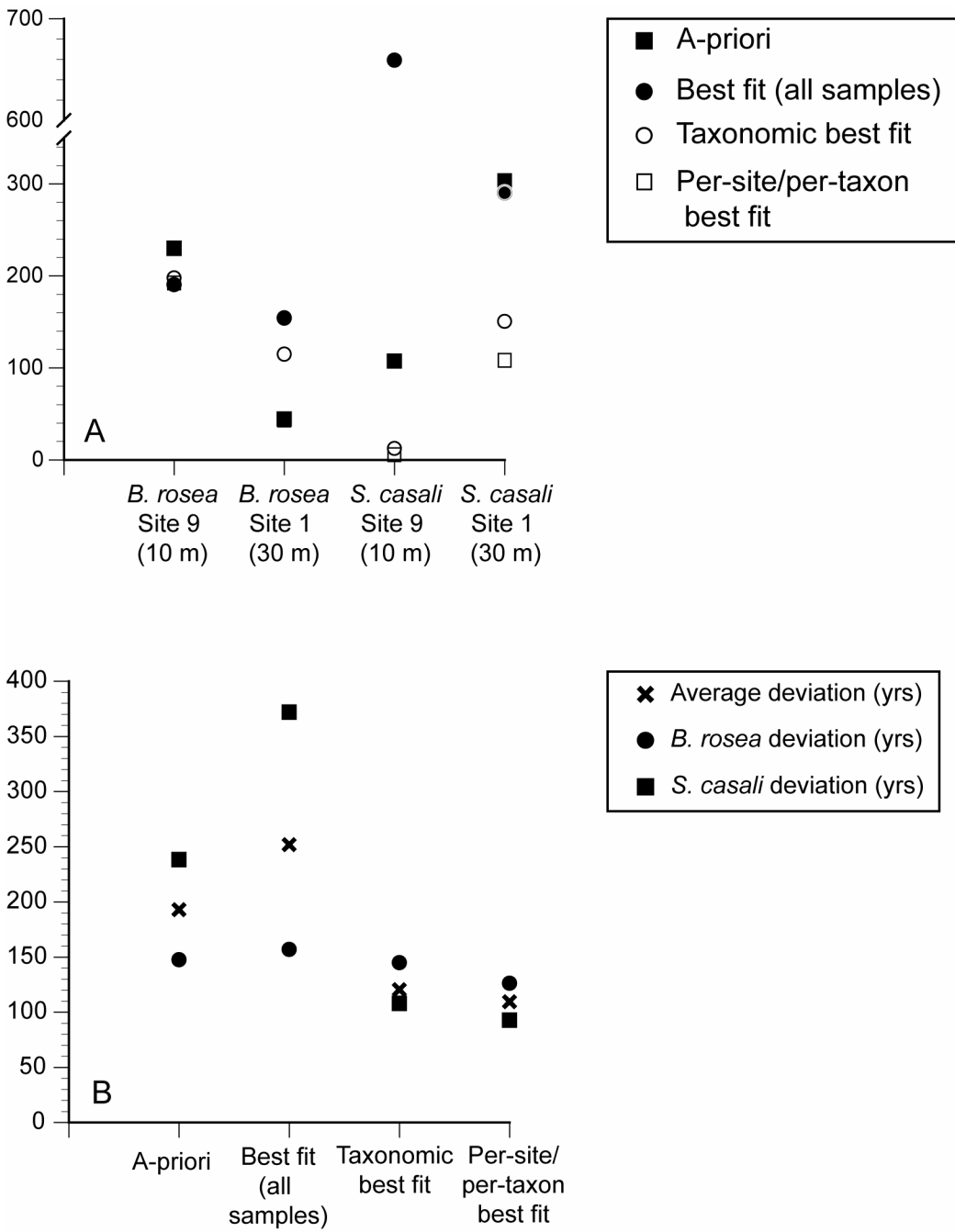


Figure 1 - 3. Average deviations using power transformation age calculation algorithms. A. Deviations are plotted for each taxon. B. Deviations are plotted by type of transformation.

Table 1-1 Sample calibration data. Calibrated ages were calculated using Calib 5.0 (Stuiver et al. 2005) using the SHCal04 and marine04.14c databases (Hughen et al. 2004; McCormac et al. 2004), assuming a mean marine reservoir age of 408 ± 18 years ($\Delta R 8 \pm 17$). Median age and 1-sigma age ranges are shown for calibrated specimen ages.

Sample	Delaware aspartic lab no.	Asp D/L	No. injections	NOSAM S ¹⁴ C Lab no.	$\delta^{13}\text{C}$	¹⁴ C age (yr BP)	Calibrated age (yr BP)
<i>B. rosea</i>, Site 9 (10 m)							
91018	2003020	0.098	2	OS-42387	1.08	(1.103556 F Modern)	0
91006	2003034	0.230	1	OS-42386	1.44	480 \pm 30	80 (43 – 119)
BB15	CH126, 241	0.340	2	OS-26545	1.92	1250 \pm 30	784 (726 – 829)
BB14	CH125, 304	0.438	2	OS-26544	1.68	2790 \pm 45	2522 (2433 – 2612)
91032	2003026	0.534	1	OS-42388	1.31	3870 \pm 35	3825 (3759 – 3888)
<i>B. rosea</i>, Site 1 (30 m)							
13022	2003210	0.269	1	OS-42383	2.15	835 \pm 30	465 (439 – 494)
13010	2003199	0.413	1	OS-42378	2.40	2800 \pm 35	2539 (2461 – 2613)
13006	2004035	0.600	3	OS-43395	1.85	6130 \pm 90	6550 (6441 – 6654)
13002	2003024	0.599	1	OS-42377	1.11	6230 \pm 45	6669 (6611 – 6734)
<i>S. casali</i>, Site 9 (10 m)							
91071	2003106	0.071	1	OS-42389	1.47	(1.111611 F Modern)	0
91062	2003104	0.172	1	OS-39672	2.14	745 \pm 35	378 (324 – 425)
91075	2003141	0.317	2	OS-42453	2.21	2770 \pm 30	2484 (2389 – 2562)
<i>S. casali</i>, Site 1 (30 m)							
13077	2003086	0.075	2	OS-39670	2.34	375 \pm 35	0
13081	2003088	0.083	2	OS-42384	2.20	555 \pm 30	183 (138 – 247)
13087	2003138	0.119	2	OS-42385	2.12	590 \pm 25	222 (147 – 163)
13088	2003139	0.184	2	OS-39671	2.76	1130 \pm 30	676 (645 – 703)
13075	2003131	0.222	2	OS-43396	2.47	1350 \pm 50	883 (818 – 941)
13071	2003082	0.273	2	OS-39673	2.07	3050 \pm 35	2808 (2754 – 2846)

Table 1-2. Calibration data used in the parabolic kinetics method models. Sample slopes were equated for each specimen from the equation of a line with a y-intercept of zero. Group slopes were equated from the equation of a line by regressing D/L aspartic values of a species from a sampling site against the square root of sample ages.

Sample	D/L Asp	¹⁴ C age (cal. yr BP)	Slope (sample)
<i>B. rosea</i>, Site 9 (10 m)			
91018	0.098	0	-
91006	0.230	80	0.0257
BB15	0.340	784	0.0122
BB14	0.438	2522	0.0087
91032	0.534	3825	0.0086
<i>B. rosea</i>, Site 1 (30 m)			
13022	0.269	465	0.0125
13010	0.413	2539	0.0082
13006	0.600	6550	0.0073
13002	0.599	6669	0.0074
<i>S. casali</i>, Site 9 (10 m)			
91071	0.071	0	-
91062	0.172	378	0.0088
91075	0.317	2484	0.0064
<i>S. casali</i>, Site 1 (30 m)			
13077	0.075	0	-
13081	0.083	183	0.0061
13087	0.119	222	0.0080
13088	0.184	676	0.0071
13075	0.222	883	0.0075
13071	0.273	2808	0.0051

Table 1-3. Deviation in years between the ^{14}C age (cal. yr BP) and calculated age using the group slope or slopes generated for individual specimens. Data are shown only for *B. rosea* collected from 30 m depth.

^{14}C age (cal. yr BP)	Root-transformed	13022	13010	13002	13006
465	46.26	0.00	612.13	879.97	851.57
2539	194.74	1442.90	0.00	631.35	564.41
6550	14.21	4363.30	1328.08	0.00	140.82
6669	162.54	4236.60	1191.23	141.29	0.00
<i>Average Deviation (yrs)</i>	104.44	2510.70	782.86	413.15	389.20

Table 1-4. Apparent parabolic kinetics (root-transformed data) and power transformation regression line information and statistics.

Sample	Parabolic Kinetics	A-priori	Best fit (all samples)	Taxonomic best fit	Per-site/per-taxon best fit
<i>B. rosea</i>, Site 9 (10 m)					
Power Function	-	Asp ^{2.0}	Asp ^{2.9}	Asp ^{2.6}	Asp ^{2.8}
Slope	6.40E-03	6.46E-05	3.88E-05	4.63E-05	4.12E-05
Intercept	0.14	3.80E-02	6.52E-03	1.27E-02	8.26E-03
r ²	0.957	0.950	0.975	0.975	0.976
P	0.003	3.00E-03	1.10E-03	1.10E-03	1.00E-03
F	89.92	82.20	158.84	156.24	162.05
RMSE	5.46	362.80	263.22	265.35	260.64
<i>B. rosea</i>, Site 1 (30 m)					
Power Function	-	Asp ^{2.0}	Asp ^{2.9}	Asp ^{2.6}	Asp ^{2.1}
Slope	5.58E-03	4.66E-05	3.41E-05	3.82E-05	4.53E-05
Intercept	0.14	5.10E-02	7.71E-05	1.04E-02	4.19E-02
r ²	0.996	0.999	0.993	0.997	0.999
P	0.001	2.00E-04	2.70E-03	1.10E-03	2.00E-04
F	827.51	5130.50	362.84	889.39	5134.83
RMSE	1.73	74.20	278.24	178.01	74.15
<i>S. casali</i>, Site 9 (10 m)					
Power Function	-	Asp ^{2.0}	Asp ^{2.9}	Asp ^{3.1}	Asp ^{3.0}
Slope	4.92E-03	3.68E-05	1.42E-05	1.14E-05	1.27E-05
Intercept	0.07	1.00E-02	5.84E-04	1.35E-04	3.29E-04
r ²	0.999	0.980	1.000	1.000	1.000
P	0.0149	7.00E-02	4.20E-03	6.40E-03	2.00E-03
F	1836.33	84.30	22776.80	9751.76	249475.00
RMSE	0.83	205.00	12.54	19.17	3.79
<i>S. casali</i>, Site 1 (30 m)					
Power Function	-	Asp ^{2.0}	Asp ^{2.9}	Asp ^{3.1}	Asp ^{3.7}
Slope	4.21E-03	2.50E-05	8.28E-06	6.44E-06	3.01E-06
Intercept	0.06	1.10E-02	1.10E-03	6.55E-04	1.82E-05
r ²	0.883	0.850	0.921	0.933	0.958
P	0.003	6.00E-03	1.50E-03	1.10E-03	4.00E-04
F	38.58	29.14	59.45	70.15	114.65
RMSE	6.20	403.97	291.96	270.09	213.51

Table 1-5. Apparent parabolic kinetics (root-transformed data) and power transformation age deviations between calculated and calibrated specimen age.

Sample	D/L Asp	¹⁴ C age (cal. yr BP)	Parabolic Kinetics		A-priori		Best fit (all samples)		Taxonomic best fit		Per-site/per-taxon best fit	
			Calc. age	Deviation	Calc. age	Deviation	Calc. age	Deviation	Calc. age	Deviation	Calc. age	Deviation
<i>B. rosea</i>, Site 9 (10 m)					Asp^{2.0}		Asp^{2.9}		Asp^{2.6}		Asp^{2.8}	
91018	0.098	0	37.75	37.75	-439.57	439.57	-137.41	137.41	-221.81	221.81	-164.17	164.17
91006	0.230	80	209.71	129.71	230.65	150.65	195.14	115.14	199.49	119.49	195.79	115.79
BB15	0.340	784	1005.23	221.23	1203.71	419.71	962.36	178.36	1035.21	251.21	985.75	201.75
BB14	0.438	2522	2208.47	313.53	2382.63	139.37	2184.74	337.26	2251.31	270.69	2206.98	315.02
91032	0.534	3825	3611.11	213.89	3825.94	0.94	4009.59	184.59	3950.95	125.95	3990.52	165.52
<i>B. rosea</i>, Site 1 (30 m)					Asp^{2.0}		Asp^{2.9}		Asp^{2.6}		Asp^{2.1}	
13022	0.269	465	511.26	46.26	458.39	6.61	649.61	184.61	587.92	122.92	475.21	10.21
13010	0.413	2539	2344.26	194.74	2565.86	26.86	2257.89	281.11	2351.18	187.82	2521.04	17.96
13006	0.600	6550	6683.21	14.21	6605.17	63.83	6641.60	27.40	6626.34	42.66	6599.25	69.75
13002	0.599	6669	6712.54	162.54	6630.90	80.90	6673.82	123.82	6656.33	106.33	6625.65	75.65
<i>S. casali</i>, Site 9 (10 m)					Asp^{2.0}		Asp^{2.9}		Asp^{3.1}		Asp^{3.0}	
91071	0.071	0	0.17	0.17	-134.76	134.76	-76.54	76.54	12.29	12.29	2.27	2.27
91062	0.172	378	404.73	26.73	532.17	154.17	599.98	221.98	363.42	14.58	375.05	2.95
91075	0.317	2484	2449.04	34.96	2450.33	33.67	4163.04	1679.04	2473.53	10.47	2472.45	11.55
<i>S. casali</i>, Site 1 (30 m)					Asp^{2.0}		Asp^{2.9}		Asp^{3.1}		Asp^{3.7}	
13077	0.075	0	7.28	7.28	-217.99	217.99	-3.39	3.39	-52.17	52.17	16.28	16.28
13081	0.083	183	22.25	160.75	-164.44	347.44	10.54	172.46	-32.46	215.46	27.24	155.76
13087	0.119	222	172.91	49.09	121.69	100.31	104.20	117.80	107.07	114.93	118.19	103.81
13088	0.184	676	817.34	141.34	906.89	230.89	475.74	200.26	708.13	32.13	620.42	55.58
13075	0.222	883	1423.85	540.85	1531.36	648.36	856.93	26.07	1359.84	476.84	1261.45	378.45
13071	0.273	2808	2472.99	335.01	2530.25	277.75	1586.17	1221.83	2657.30	150.70	2699.73	108.27
Average deviation (yrs)				146.11		192.99		251.86		120.40		109.49
Brachiopod deviation (yrs)				148.21		147.60		156.97		144.89		126.20
Bivalve deviation (yrs)				144.02		238.37		371.94		107.96		92.77

**Chapter 2 – Aspartic Acid Racemization Dating of Holocene
Brachiopods and Bivalves from the Southern Brazilian Shelf, South
Atlantic**

Preface

This chapter was accepted for publication by Quaternary Research in March 2006 under the current title by the following authors: Susan L. Barbour Wood, Richard A. Krause, Jr., and Michał Kowalewski (Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA), John Wehmiller (Department of Geology, University of Delaware, Newark, DE 19716, USA, jwehm@udel.edu), and Marcello G. Simões (Instituto de Biociências, Universidade Estadual Paulista, Distrito de Rubião Junior, CP. 510, 18.610-000, Botucatu, SP, Brazil, btsimoes@ibb.unesp.br).

Susan Barbour Wood is the primary author with help in laboratory analyses by Richard Krause and John Wehmiller. Editorial comments were provided by all secondary authors. Specimens were collected by Michał Kowalewski, Marcello Simões and others, including Adilson Fransozo (UNESP, Botucatu campus). This project builds directly on our joint research with Glenn Goodfriend who passed away in 2002.

Abstract

The extent of racemization of aspartic acid has been used to estimate the ages of 9 shells of the epifaunal calcitic brachiopod *Bouchardia rosea* and 9 shells of the infaunal aragonitic bivalve *Semele casali*. Both taxa were collected concurrently from the same sites at depths of 10 m and 30 m off the coast of Brazil. Asp D/L values show an excellent correlation with radiocarbon age at both sites and for both taxa ($r^2_{\text{Site 9 } B. \text{ rosea}} = 0.97$, $r^2_{\text{Site 1 } B. \text{ rosea}} = 0.997$, $r^2_{\text{Site 9 } S. \text{ casali}} = 0.9998$, $r^2_{\text{Site 1 } S. \text{ casali}} = 0.93$). The Asp ratios plotted against reservoir-corrected AMS radiocarbon ages over the time span of multiple millennia can thus be used to develop reliable and precise geochronologies not only for aragonitic mollusks (widely used for dating previously), but also for calcitic brachiopods. At each collection site, *Bouchardia* specimens display consistently higher D/L values than specimens of *Semele*. Thermal differences between sites are also notable and in agreement with theoretical expectations, as extents of racemization for both taxa are greater at the warmer, shallower site than at the cooler, deeper one. In late Holocene marine settings, concurrent time series of aragonitic and calcitic shells can be assembled using Asp racemization dating, and parallel multi-centennial to multi-millennial records can be developed simultaneously for multiple biomineral systems.

Introduction

Amino-acid racemization/epimerization techniques are an exceptionally useful and versatile tool of Quaternary geochronology (e.g., Wehmiller and Miller, 2000). They are attractive because they can be applied to a wide range of biomineralized fossils, subfossils and modern material, including skeletal material of marine organisms (e.g., mollusks, corals, brachiopods), remains of terrestrial organisms (e.g., ostrich eggs, plants, bones, teeth), soils, and other biogenic materials (e.g., Goodfriend et al, 2000). In particular, marine invertebrates are an important target for high-resolution geochronological studies in the Late Quaternary, because shells collected from modern seafloors and coastlines tend to represent age mixed (time-averaged) assemblages that may potentially provide nearly complete multi-centennial to multi-millennial time series for the Holocene, and in some cases the Pleistocene (e.g., Flessa and Kowalewski, 1994; Wehmiller et al., 1995; Meldahl et al., 1997; Kowalewski et al., 1998; Carroll et al., 2003).

This project focuses on marine benthic shelly remains from open habitats of the southern Brazilian shelf and provides a comparative radiocarbon-based assessment of aspartic acid racemization dating methods for two very different shelled invertebrates (calcitic epifaunal brachiopods and aragonitic infaunal bivalves) collected concurrently at two sites that differ in depth and may have had different thermal histories. Using independent radiocarbon calibrations for each site and each shell type, several important aspects of the amino acid geochronology are explored quantitatively.

First, this study compares amino acid dating methods for two different biomineral systems (the aragonitic infaunal bivalve mollusk *Semele casali* versus the calcitic

epifaunal brachiopod *Bouchardia rosea*) collected simultaneously from the same sampling sites and same shelly assemblages. Bivalves and brachiopods have been important producers of marine shell beds since the early Paleozoic. Many previous researchers have noted that differences may exist in apparent rates of racemization across genera, families, and higher taxonomic groups (Lajoie et al, 1980; Miller and Hare, 1980; Andrews et al., 1985; Goodfriend et al, 1997; Wehmiller and Miller, 2000). This analysis is an explicit attempt to quantitatively contrast racemization rates between sympatric organisms representing different biomineral systems. Such direct comparisons allow insight into the diagenetic histories of two major groups (bivalves and brachiopods) that are among the most important taxa represented in the fossil record.

Second, multiple studies showed that marine aragonitic bivalves can be dated reliably using amino acid racemization methods (e.g., Wehmiller et al., 1995; Goodfriend et al., 1997; Kowalewski et al., 1998). However, calcitic brachiopods have remained virtually untested, with an exception of one recent study (Carroll et al., 2003), which demonstrated that A/I (D-alloisoleucine/L-isoleucine) ratios can be used to date shells of the brachiopod *Bouchardia rosea* from the Brazilian Atlantic Coast. Here, we attempt to test the applicability of Asp D/L values for dating brachiopods, thereby providing comparisons of results for two amino acid ratios determined on the same two species of interest (*B. rosea* and *S. casali*) from the same collection sites (Sites 1 and 9, Fig. 1.1).

Last, racemization rates are known to be temperature dependent, and thus amino acid geochronologies may vary notably across sites with different thermal histories. To test if this effect can be observed in environments with subtle thermal (bathymetric)

differences, samples of both species targeted in this analysis were collected from two sites that may have differed slightly in their late Holocene thermal history.

The independent per-site, per-species radiocarbon calibrations of Asp racemization carried out in this study should allow us to evaluate these issues rigorously and evaluate the practical applicability of the Asp racemization method for dating large numbers of marine invertebrate shells collected from modern seafloors. This study will permit the development of simultaneous time series for multiple biomineral systems from the same depositional systems, thus offering a high-resolution geochronological framework for future geochemical, paleoenvironmental, and paleoecological studies.

Methods

Specimens were collected from two sites situated at Ubatuba Bay, a small embayment off the coast of the state of São Paulo, Brazil (Fig. 2.1), located on the inner shelf in the Southeast Brazilian Bight Marine Province (Campos et al. 1995; Mahiques et al., 2004). The Bay is characterized by humid tropical climate, shallow depths (0 – 30 m within the sampled area), full marine salinity (34-35 ppm) and warm water masses (mean annual temperature ~24°C) (Mahiques, 1992, 1995; Mahiques et al., 1998; Mantelatto and Fransozo 1999). The area is fed by the South Brazil Current, a warm, western boundary current, and within the bay is dominated by Coastal Water (Campos et al. 1995). The eastward-opening bay is protected from the dominant S-SW winds and high-energy waves (Mahiques et al., 1998). The Bay's substrate is dominated by fine-grained (silt and very fine sand) terrigenous sediments, terrestrial organic matter (Burone 2002) and coarse biogenic constituents (brachiopods, mollusks, echinoids, bryozoans, and

foraminifers) (Mahiques et al., 1998; Mantelatto and Fransozo, 1999). Rhynchenelliform (terebratulid) brachiopods, overwhelmingly dominated by *Bouchardia rosea* are locally abundant (Simões et al., 2004), and a diverse molluscan fauna is also present. Further details on Ubatuba Bay hydrodynamics, sedimentation, sediment geochemistry and faunal content can be found in Emilson (1959), Matsuura (1986), Castro Filho et al. (1987), Mahiques (1992, 1995), Sanches (1992), Mantelatto and Fransozo (1999), Burone (2002) and Muniz (2003).

Samples were collected in conjunction with an ongoing project of the Marine Ecology Group of São Paulo State University. Specimens were collected at two sites (10 m and 30 m, Fig. 2.1) using a Van Veen grab sampler (1/40 m²), which collects unconsolidated surficial deposits (the uppermost several centimeters of the substrate) which represent a time-averaged, or temporally mixed assemblage (e.g., Walker and Bambach, 1971). Physical parameters at each sampling site (number of specimens analyzed, average temperature and salinity) were recorded (Table 2.1), and all brachiopod and mollusk specimens recovered from each grab were retained. Temperature measurements were conducted through the calendar year in 2000 and included three bottom water measurements per month at each sampling site, ranging over the year from 19.3° – 25.2° C at the shallow site and 18.0° – 21.7° C at the deep site, with an average temperature difference between the two sites of 2.6° C.

Each specimen was prepared for radiocarbon and amino acid analyses using a uniform, standard methodology. First, shell fragments (18.9 – 132.0 mg in weight) were taken from posterior portions of each shell, when possible, using wire snips. This controlled sampling location was used to minimize intra-shell variability in amino acid

ratios, known to occur in mollusks and brachiopods vertically across shell layers with different microstructure and/or spatially within a given shell layer (e.g., Goodfriend et al., 1997; Carroll et al., 2003). All shells were cleaned following routine procedural methods (e.g., Goodfriend, 1987), which consisted of a surficial cleaning performed on shell fragments using dental tips attached to a Dremel[®] rotary tool, followed by ultrasonication and etching with dilute HCl. In the case of brachiopods, mechanical cleaning of *B. rosea* specimens also served to remove the outer primary layer of the shell, so that all analyses were only performed on the thickest, secondary layer. Lab preparations were performed at George Washington University, Virginia Tech, and the University of Delaware.

Analysis of the extent of racemization of aspartic acid was conducted at the University of Delaware using an Agilent 6890 Gas Chromatograph equipped with a 25 m Chirasil-Val column and flame ionization detector. A representative chromatogram can be found in Wehmiller and Miller (2000). Sample pretreatment involved hydrolysis of the dissolved sample in 6N HCl for 20 hours at 100° C., desalting with HF, and preparation of the N-TFA isopropyl derivative of the amino acid mixture. Under normal operating conditions, D/L values for six or seven amino acids are obtained with this procedure. However, for this study only Asp D/L values are reported because the other amino acid D/L values are generally too low to calculate consistently from sample to sample due to the young age of the samples, and thus offer little age-resolution information. D/L values were calculated from the peak-area ratios obtained from at least two chromatograms of each sample derivative when possible. A small proportion of chromatograms were rejected due to low concentrations of amino acids in the derivative, resulting in small aspartic peaks. In such cases, the sample derivative was concentrated

and always successfully rerun. Integration of peak areas was accomplished using both HP3390 integrators and Chemstation integration software. The typical coefficient of variation for multiple measurements of Asp D/L values on a single derivative is < 3%. Analyses of interlaboratory comparison samples (Wehmüller 1984) during the period of the present study revealed no systematic drift of the overall laboratory results. During the interval 2001-2004, which includes the period in which the reported analyses were completed, mean and standard deviation D/L Asp values for ILC A and ILC C powders were 0.418 (0.024) and 0.903 (0.039) (n = 41 and 35, respectively).

A total of eighteen specimens from the two species including both sites and representing a broad range of Asp D/L values were selected for radiocarbon analysis at the NOSAMS Lab (Woods Hole) where ^{14}C was measured by Accelerator Mass Spectrometry (see <http://www.nosams.who.edu/nosams.html> for procedural details).

Shell ages were calibrated to calendar years using CALIB (Stuiver et al., 2005; version 5.0), and error estimates for radiocarbon were based on information provided by NOSAMS. Age values were determined by the SHCal04 (Southern Hemisphere) and marine04.14c databases (Hughen et al., 2004; McCormac et al., 2004), assuming a mean marine reservoir age of 408 ± 18 years ($\Delta R 8 \pm 17$) recently established through an extensive empirical analysis by Angulo et al. (2005). Calibrated ages are reported in Table 2.2 as median age with 1-sigma age ranges.

Results

Nine specimens of *B. rosea* and nine of *S. casali* have paired AMS-radiocarbon and Asp D/L results, as summarized in Table 2.2. Raw Asp D/L values plotted against

calibrated ^{14}C age show initially rapid increases in D/L Asp, followed by a slowing in the apparent rate in older samples. It has often proven convenient to identify a transformation that results in a linear plot of Asp racemization against time (e.g. Goodfriend et al., 1996; Goodfriend and Stanley, 1996; Manley et al., 2000). Many workers have employed the simple "parabolic kinetic" equation $\text{D/L} = k t^{0.5}$ ($k =$ constant, $t =$ time - Mitterer and Kriausakul, 1989) for the analyses of results like those presented here. However, a power transformation (e.g. Goodfriend et al., 1996) was chosen as the most appropriate transformation for Asp D/L values in this data set. As live-collected specimens were not available for heating experiments, the single most appropriate transformation for each taxon ($\text{D/L Asp}^{2.6}$ for *B. rosea* and $\text{D/L Asp}^{3.1}$ for *S. casali*) was identified by iteratively raising the power of D/L Asp until maximum r^2 values were obtained while maintaining a positive y-intercept (D/L ratio). Taxon-specific transformations are used consistently for all specimens as if deduced by heating experiments, and not adjusted on a per-site basis. Transformations show a high significant linear correlation ($r^2 > 0.93$ in all cases) with the calibrated ^{14}C age of the specimen (Table 2.3), suggesting that Asp is a good predictor of age within this system for each site and each species. It is noteworthy that regardless of the particular transformation chosen, results and conclusions that follow below were not significantly altered.

The CALIB-calibrated radiocarbon estimates and the resulting Asp D/L calibrations are summarized in Table 2.2 and Figure 2.2. For data pooled across sites (Fig. 2.2), Asp ratios of both brachiopods and bivalves show high and significant ($r^2_{B. rosea} = 0.98$, $p < 0.001$ and $r^2_{S. casali} = 0.86$, $p = 0.0002$) linear correlations. Note that regression

equations and statistics were computed using the program SAS (Version 9.1) with the dependent variable (D/L Asp values) on the Y-axis and calibrated shell age on the X-axis. Equations were transformed to provide a formula for calculating shell age from D/L Asp values (Equations 2.1 – 2.4). Statistics do not vary regardless of which variable is considered dependent or independent.

Calibration plots for *B. rosea* grouped by site (Figure 1.3a) yield the following regression equations:

$$\text{Equation 2 - 1} \quad \text{Age} \equiv \frac{\text{Asp}^{2.6} - 0.01266}{4.633\text{E} - 05} \quad (\text{Site 9})$$

$$\text{Equation 2 - 2} \quad \text{Age} \equiv \frac{\text{Asp}^{2.6} - 0.01043}{3.824\text{E} - 05} \quad (\text{Site 1})$$

Calibration plots for *S. casali* grouped by site (Figure 1.3b) yield the following regression equations:

$$\text{Equation 2 - 3} \quad \text{Age} \equiv \frac{\text{Asp}^{3.1} - 0.00013503}{1.137\text{E} - 05} \quad (\text{Site 9})$$

$$\text{Equation 2 - 4} \quad \text{Age} \equiv \frac{\text{Asp}^{3.1} - 0.00065487}{6.44\text{E} - 06} \quad (\text{Site 1})$$

The calibrations are valid for the studied taxa from each sampling site within the approximate age ranges of the radiocarbon dated specimens, or less than around 3,000 years in age for *S. casali* and 7,000 years for *B. rosea*.

A comparative plot of calibration curves for brachiopods and bivalves (Fig. 2.2) suggests that the two species differ notably in racemization rates. First, the intercept is significantly higher ($t = 14.81$, $p < 0.0001$) for brachiopods (0.011 vs. $2.68\text{E}-4$) suggesting that the initial Asp ratio (primarily reflecting artificial racemization induced

during sample processing – see Gillard et al., 1991) is greater for *B. rosea*. Moreover, the slope of the racemization curve is visibly steeper for brachiopods (the difference between the two slopes is statistically significant; $t = 7.32$, $p < 0.0001$). Consequently, regardless of the calibrated age, the Asp ratios are always higher (by a factor of 1.2 to 2.6) for *B. rosea* relative to *S. casali* of the same age.

Figure 2.3 also suggests that racemization rates differ between the two collection sites. This difference is consistently shown by both taxa: both brachiopod and bivalve shells from Site 9 (10 m) appear to have racemized at faster rates than samples from Site 1 (30 m). Differences between calibrated slopes ($t = 4.51$, $p = 0.006$) and intercepts ($t = 3.48$, $p = 0.02$) are statistically significant between collection sites for *S. casali*, but only significant for intercepts between collection sites for *B. rosea* (slopes: $t = 2.18$, $p = 0.08$; intercepts: $t = 7.41$, $p = .0007$).

Carroll et al. (2003) showed that D-alloisoleucine/L-isoleucine (A/I) epimerization ratios in the brachiopod *B. rosea* could be used successfully to estimate the numerical shell age via radiocarbon calibration. Here, specimens analyzed by Carroll et al. (2003) were re-analyzed for Asp ratios. The A/I and Asp ratios show a high and positive correlation with one another (Fig. 1.4), and A/I ratios display slower racemization rates than the Asp ratios.

Discussion

The tight positive correlation between D/L aspartic acid values and calibrated radiocarbon ages observed consistently for both species at each of the two targeted sites (Figs. 2.2 – 2.3) indicates that Asp racemization techniques provide reliable means for

dating late Holocene invertebrate shells collected from present-day seafloors, as noted in many previous studies, including for microfossils (Hearty et al., 2004). Particularly encouraging is the successful calibration of aspartic acid chronology in calcitic brachiopods, which, to our knowledge, have never been dated with Asp D/L values before. The good correlation of the racemization ratios between A/I (Carroll et al., 2003) and Asp ratios (Fig. 2.4) in conjunction with their independently derived ^{14}C calibrations indicate that both of these amino acids can be used reliably for amino acid racemization dating of *B. rosea* (see also below). Admittedly, the analysis by Carroll et al. (2003) and this study both target the same brachiopod species from a single region. It is desirable, therefore, to further test the utility of amino acid racemization dating for other brachiopod species in other depositional and climatic settings. The only other amino acid racemization study on brachiopods that we are aware of (Torres et al., 1997) dealt with fossils that span beyond the range of radiocarbon calibration, preventing those authors from rigorous testing of the dating reliability of amino acid racemization techniques. In addition, whereas Asp D/L values can clearly provide reliable dating means, the results of this study also provide useful quantitative insights into several problems that may weaken the utility and reliability of the amino acid racemization techniques.

1. Reservoir Age. First, it is worth exploring the assumption of the reservoir age (408 ± 18 years with a ΔR of 8 ± 17 years, see also above). Whereas the assumed reservoir age is supported by an extensive regional compilation of reservoir estimates (Angulo et al., 2005), previously published marine reservoir estimates for the region have been quite variable, ranging from 204 ± 44 to 720 ± 40 years BP (Stuiver et al., 1998; Nadal de Masi, 1999; Eastoe et al., 2002; Angulo et al., 2005), possibly reflecting

temporal variability in regional ocean upwelling (Eastoe et al., 2002). These reservoir ages appear to cluster into two groups: one yielding a mean reservoir correction of 220 ± 20 years and the other at 515 ± 10 years (Eastoe et al., 2002). The value of 408 ± 18 years used here was derived by Angulo et al. (2005) as representative of the majority of the shells dated in the region (see Angulo et al., 2005 for discussion). However, the sensitivity of our age estimates to changes in the postulated reservoir age is worth examining because of the variability in published reservoir ages. A sensitivity analysis (Fig. 2.5) indicates that changing the reservoir age shifts the intercept of the calibration curve, with no significant change in slope of the calibration trends (reservoir age 408 vs. 204: $t = 0.10$, $p = 0.93$; reservoir age 408 vs. 540: $t = 0.68$, $p = 0.52$; reservoir age 204 vs. 540: $t = 0.78$, $p = 0.46$) with numerical age estimates progressively becoming older as the assumed reservoir age is decreased. Thus, changing the assumed reservoir age would affect the numerical age estimates of Asp dated shells. However, such changes would *not* alter the estimated rates of racemization (both the shape and the slope of a given calibration curve remains virtually the same as the reservoir age is changed; Fig. 2.5). The stability of the calibration curve implies that neither age differences between shells, nor the relative position of dated shells when arrayed into a time series are affected by changes in the assumed reservoir age. The only effect of assuming the incorrect reservoir age is thus a shift in numerical age estimates. In the worst-case scenario, this shift could be as high as 200-300 years for more recent specimens, and even greater for specimens thousands of years old. It is therefore advisable to monitor regional estimates of reservoir age and update the calibration equations whenever significant errors in regional estimates of reservoir effect are conclusively demonstrated. Pre-bomb collected shells from our

sampling sites were not available for analysis. However, the extent of racemization of *B. rosea* specimens plotted against uncalibrated radiocarbon ages were used to estimate a reservoir age of 560 years in Carroll et al. (2003). This estimate is well within the range of published regional reservoir ages (Angulo et al., 2005).

Variability due to age estimation of modern shells is also problematic. Shells too young for radiocarbon calibration may actually be variable in age, from recently dead (collected in 2000, or -50 yr BP) to collected in 1950 (0 yr BP) for this dataset. The fraction modern (F14C) value (Table 2.2) was used on the CALIBomb web site (<http://calib.qub.ac.uk/CALIBomb/frameset.html>) in attempt to calibrate modern shells (Reimer et al., 2004). Modern *B. rosea* specimen 91018 from Site 9 (10 m) yielded a one-sigma age range of either 1958.68 (September) to 1959.01 (January) or 1996.67 (September) to 1996.94 (December). Modern *S. casali* specimen 91071 from Site 9 (10 m) yielded a one-sigma age range of either 1958.74 (September) to 1959.04 (January) or 1995.68 (September) to 1996.94 (December). *S. casali* specimen 13077 from Site 1 (30 m) with uncalibrated radiocarbon age 375 yrs BP was too young for calibration after reservoir corrections were made and too old for use with the CALIBomb program, so is thus likely closer in age to the year 1950 than 2000. In the calibration of amino acids against calibrated shell age, a 50 year offset in modern shell ages yields an offset in calibrated age between 179 years (D/L Asp = 0.98) and 195 years (D/L Asp = 0.44) for modern specimens of *B. rosea* from Site 9 (10 m). This error is equivalent to or less than the error produced by minor shifts in reservoir age. Negative shells ages are also graphically and conceptually difficult to handle, and thus the standard age of 0 cal yr BP was chosen to represent all modern specimens.

2. Taxonomic Effects. The notable differences in overall rates or extents of racemization between the two species provide compelling evidence that it is critical to calibrate amino acid D/L values separately for each taxon that is being studied. As in many previous studies of both Holocene and Pleistocene racemization geochronology (e.g., Wehmiller, 1982; Andrews et al., 1985; Wehmiller and Miller, 2000; and Hearty et al., 2004) this study provides direct evidence that the variation in apparent racemization rates can be very significant for different taxa collected from the same site. Not only does *B. rosea* racemize significantly faster than *S. casali*, but, in fact, the difference in racemization is quite dramatic (e.g. a 3615 year old *S. casali* shell (D/L Asp = 0.3) from Site 1 would appear 870 years old if the *B. rosea* calibration curve from the same site were applied). The data acquired in this study do not allow us to rigorously evaluate the causative factors responsible for such dramatic differences in racemization rates – most likely though, these are due to differences in shell mineralogy and protein structures between aragonitic bivalves and calcitic brachiopods. Note that the mode of life is unlikely to be the cause here, considering that it would be more likely that it were infaunal bivalves that experienced slightly cooler thermal history, and racemized more slowly, than epifaunal brachiopods, especially at the shallow site which is more likely to be affected by solar insolation.

3. Bathymetric Effects. This study suggests that even minor bathymetric differences, including sites representing the same regional and environmental settings, may result in significant disparities in racemization rates. For both taxa, samples from Site 9 (10 m) show greater racemization rates than samples from the deeper Site 1 (30 m), significantly so for *S. casali*; despite the fact that the two sites are located in the same bay

and differ in depth by 20 m only (Fig. 2.1). These consistent offsets suggest differences in the late Holocene thermal histories between the two sites, with the more nearshore site being slightly warmer than the more offshore one. This is to be expected: as reported above, currently the average annual temperature difference between the two sites is $\sim 3^\circ\text{C}$ (2.6°C ; data for the year 2000). The direction of the offset is predictable theoretically. First the proximal, shallower Site 9 should be warmer on average because of the relatively stronger effects of solar insolation at shallower depths. Second, the cooling effect of water masses brought in by the shelf-break upwelling, which operates intermittently in the region (e.g., Campos et al., 1995; Kowalewski et al., 2002), should be more manifested in the deeper, more offshore Site 1. Most importantly, neither of the sites is believed to have been subaerially exposed (or notably variable in depth) during the late Holocene, as the sea level is believed to have been relatively stable in the region ($\sim 1\text{m}$ fluctuations) during the last 3000 years (Angulo et al., 1999; Lessa et al., 2000; Baker et al., 2001). If the bathymetric temperature difference observed today for the two sites persisted into the past, it would be substantial enough to produce the observed difference in racemization rates between collection sites. Finally, in the case of this specific study, the effect of thermal differences are much less pronounced than taxonomic effects. Indeed, data pooled within each species across the two collection sites (Fig. 1.2) provide calibration curves with respectable r^2 values for both taxa ($r^2_{B. rosea} = 0.98$, $p < 0.0001$; $r^2_{S. casali} = 0.86$, $p = 0.0002$). However, the calibration curves carried out separately for each collection site offer a better fit (for both species r -square values are equal or higher for per-site calibrations than for pooled data; see Table 2.3), and thus, a more precise and accurate calibration.

4. Shell Transport. Given observed thermal differences between nearby sites, the tight D/L Asp vs. calibrated age correlation within each site has an interesting corollary. Although episodic winter storms may generate some shell transport, such processes are unlikely to have been substantial enough to homogenize the distribution of shells across the bay. The high per-species correlations within each site and the drop in those correlations when data are pooled across sites both indicate that no substantial post-mortem shell transport affected the surficial shell assemblages throughout the late Holocene. In other words, subtle thermal differences across nearby sites can only have been detected if the majority of shells were preserved in place, and not mixed spatially by offshore-onshore or lateral transport. This interpretation is further supported by a highly patchy distribution of shells (likely reflecting original patchiness in biological populations). This is also consistent with many taphonomic studies which suggest that out-of-habitat post-mortem shell transport is rarely a factor even in higher-energy environments (e.g., Kidwell and Flessa 1995; Flessa 1998; Martin 1999; Behrensmeyer et al. 2000).

5. Comparison of Racemization Rates Between Amino Acids. Finally, the comparison of Asp ratios against the A/I ratios of Carroll et al. (2003) (Fig. 2.4) shows that in the case of *B. rosea* (no A/I data are available for *S. casali*) aspartic acid racemizes at a much faster overall rate than isoleucine, thus potentially providing better time resolution for late Holocene brachiopod shells. This is consistent with other studies for other organisms that all demonstrate the very rapid initial racemization of aspartic acid compared with other amino acids (e.g. Goodfriend, 1992). Once high values of Asp D/L are achieved, the overall rate of Asp racemization falls and is often comparable to that of

other amino acids generally considered as "slow racemizers" (e.g., Manley et al., 2000; Wehmiller and Miller, 2000). As importantly, the consistency of these two techniques suggests that they can be used jointly to enhance their calibrations, cross-check their performance against one another, and maximize their dating range (see also Goodfriend, 1992).

Conclusion

In summary, whereas various complicating factors may limit the utility of amino acid racemization techniques, the per-site, per-species ^{14}C calibrations employed here provided a successful strategy for developing reliable geochronological calibrations for both species and both sites. Consequently, the calibrated Asp D/L values provided an effective and inexpensive way to assemble extensive time series of both brachiopods and bivalves. This study illustrates the powerful opportunity provided by Holocene marine shell assemblages for developing multi-centennial to multi-millennial geochronological frameworks concurrently for calcitic and aragonitic biomineral systems. Future use of sensitive reverse-phase (RPLC) analytical methods (e.g., Kaufman and Manley, 1998; Hearty et al., 2004) for high resolution analysis of small samples should additionally enhance the utility of amino acid dating for detailed chronological analysis of many different types of shell assemblages.

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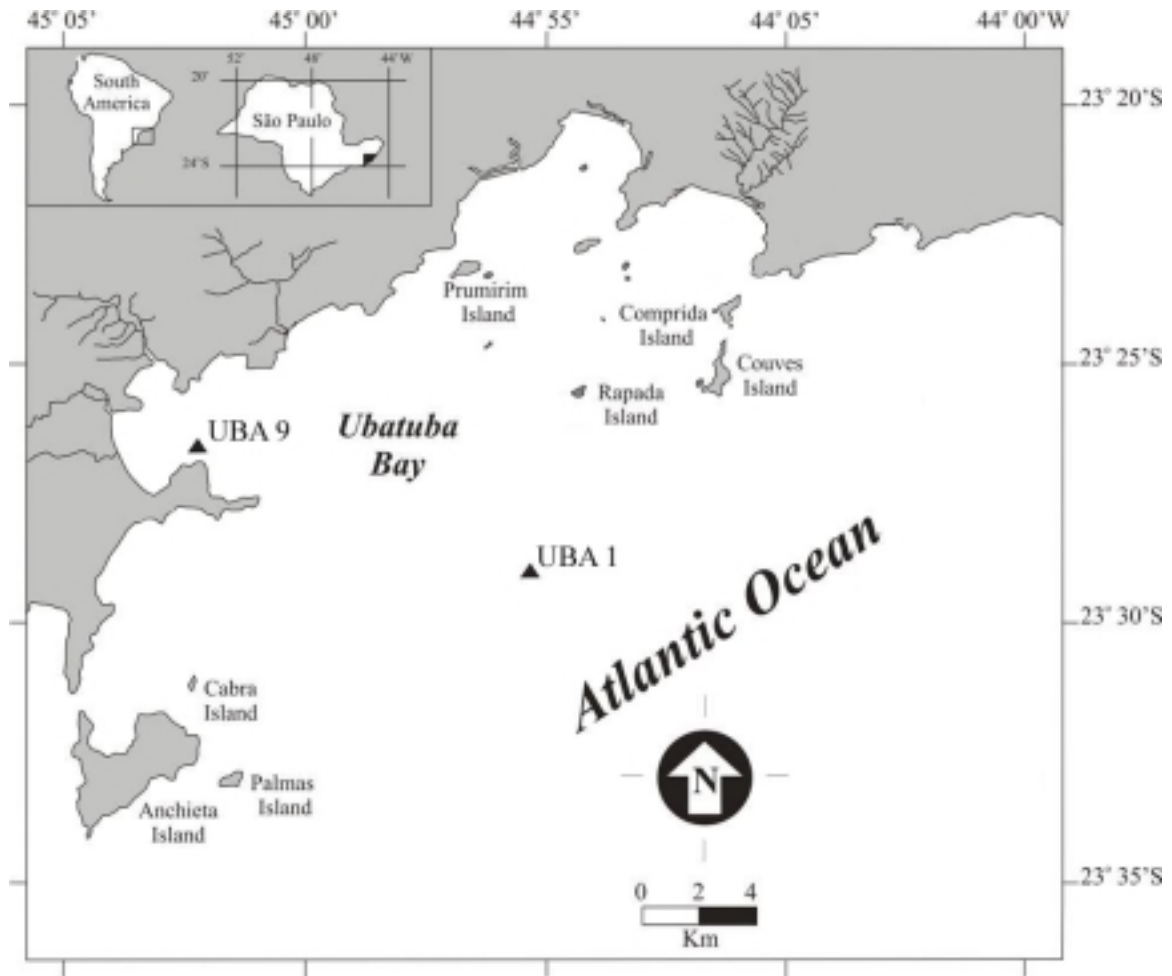


Figure 2 - 1. Map of the study area and collection sites.

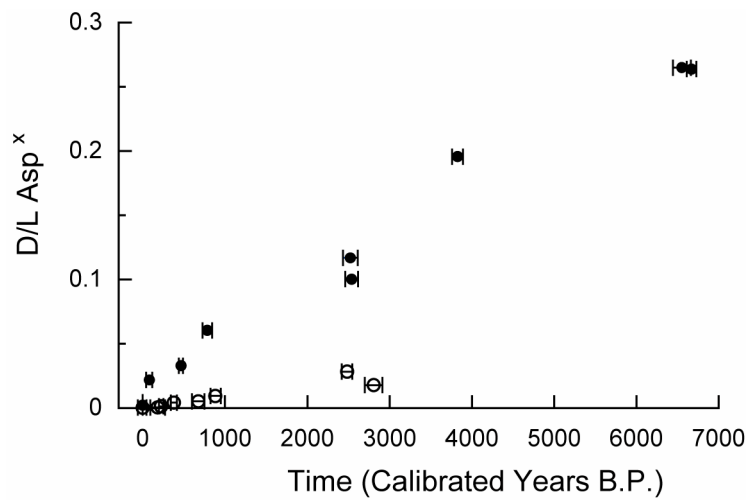


Figure 2 - 2. Plot of aspartic acid ratios for *B. rosea* (D/L Asp^{2.6}, closed circles) and *S. casali* (D/L Asp^{3.1}, open circles) graphed against (median) calibrated radiocarbon age (years B.P.) and 1-sigma age ranges. Racemization rates are significantly higher for *B. rosea* as compared to *S. casali* (see text for more details).

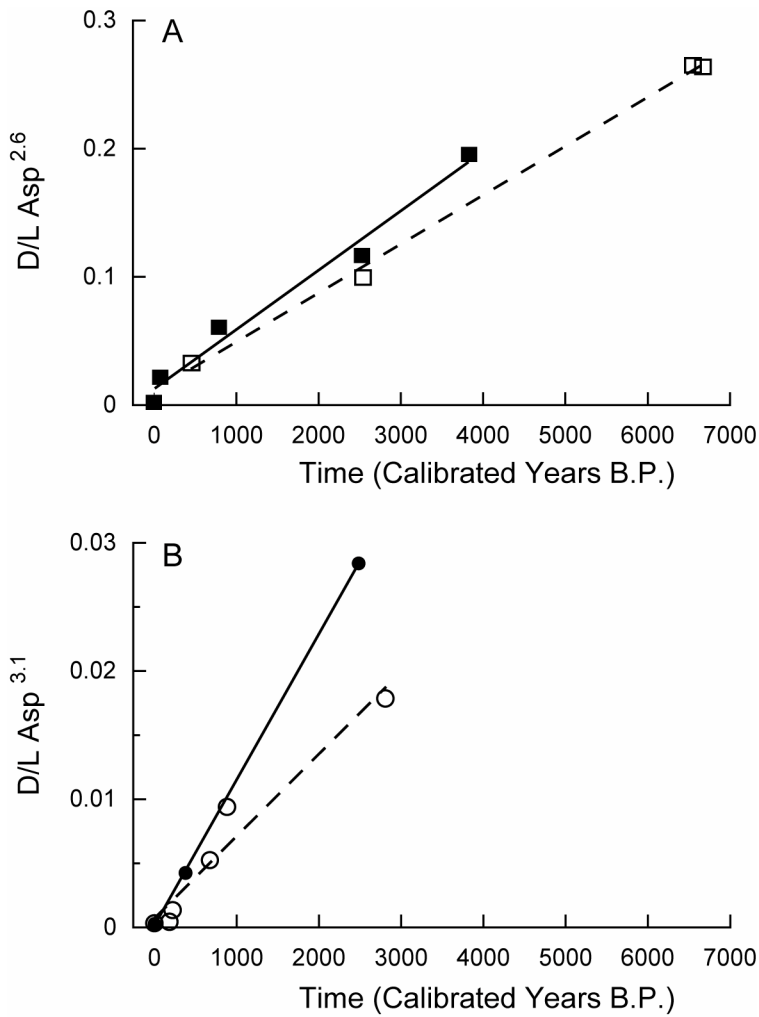


Figure 2 - 3. Plot of aspartic acid ratios for A) *B. rosea* and B) *S. casali* graphed against calibrated radiocarbon age (years B.P.). For both plots, sampling Site 9 (10 m, bold line) and Site 1 (30 m, dashed line) are plotted separately. Site-specific calibrations show that samples from Site 9 racemize at a faster rate than samples from Site 1.

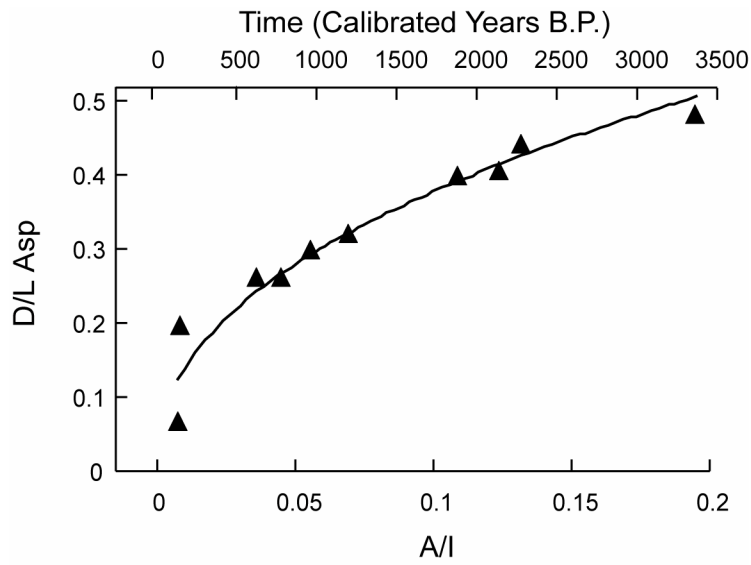


Figure 2 - 4. Cross-validation data using D/L Asp values plotted against A/I values obtained for the same set of *B. rosea* specimens (A/I data analyzed using High Performance Liquid Chromatography (HPLC) after Carroll et al., 2003).

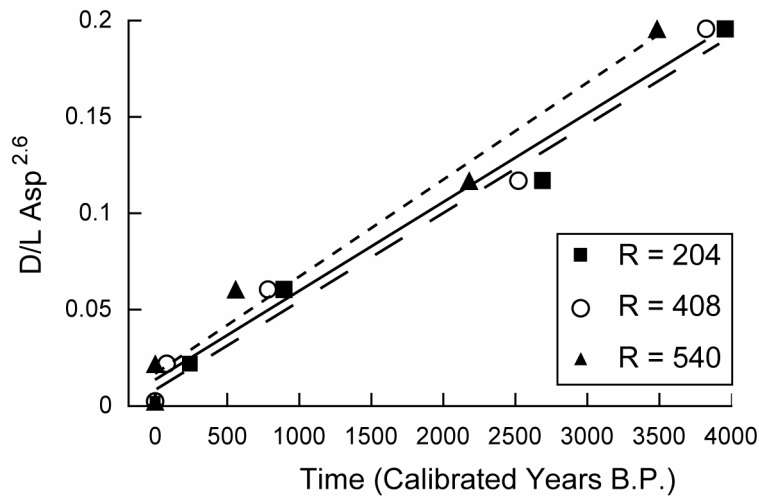


Figure 2 - 5. Radiocarbon calibration plots for *B. rosea* samples (Site 1) simulating the minimum (squares, Eastoe et al., 2002), average (circles, Angulo et al., 2005) and maximum (triangles, Eastoe et al., 2002) published reservoir ages for the collection area. Recalibration shifts the ages of specimens to older values with a decrease in the estimated reservoir age.

Table 2 - 1. Sampling site data. Temperatures are averages of monthly bottom water measurements from 2000.

Site	9	1
Depth	10 m	30 m
Latitude	23° 26' 41"	23° 28' 53"
Longitude	45° 02' 07"	44° 55' 21"
Temp C°	22.0	19.4
Salinity ‰	34.0	35.0
No. analyzed shells: <i>Bouchardia</i>	5	4
No. analyzed shells: <i>Semele</i>	3	6

Table 2 - 2. Sample calibration data. Samples marked with an asterisk were analyzed at George Washington University. Calibrated ages were calculated using Calib 5.0 (Stuiver et al., 2005) using the SHCal04 and marine04.14c databases (Hughen et al., 2004; McCormac et al., 2004), assuming a mean marine reservoir age of 408 ± 18 years ($\Delta R 8 \pm 17$). Median age and 1-sigma age ranges are shown for calibrated specimen ages. Asterisked ages are represented by F Modern values.

Sample	Delaware lab no.	Asp D/L	No. injections	NOSAMS ¹⁴ C Lab no.	$\delta^{13}\text{C}$	¹⁴ C age (yr BP)	Calibrated age (yr BP)
<i>B. rosea</i>, Site 9 (10 m)							
91018	2003020	0.098	2	OS-42387	1.08	1.103556*	0
91006	2003034	0.230	1	OS-42386	1.44	480 ± 30	80 (43 – 119)
BB15*	CH126, 241	0.340	2	OS-26545	1.92	1250 ± 30	784 (726 – 829)
BB14*	CH125, 304	0.438	2	OS-26544	1.68	2790 ± 45	2522 (2433 – 2612)
91032	2003026	0.534	1	OS-42388	1.31	3870 ± 35	3825 (3759 – 3888)
<i>B. rosea</i>, Site 1 (30 m)							
13022	2003210	0.269	1	OS-42383	2.15	835 ± 30	465 (439 – 494)
13010	2003199	0.413	1	OS-42378	2.40	2800 ± 35	2539 (2461 – 2613)
13006	2004035	0.600	3	OS-43395	1.85	6130 ± 90	6550 (6441 – 6654)
13002	2003024	0.599	1	OS-42377	1.11	6230 ± 45	6669 (6611 – 6734)
<i>S. casali</i>, Site 9 (10 m)							
91071	2003106	0.071	1	OS-42389	1.47	1.111611*	0
91062	2003104	0.172	1	OS-39672	2.14	745 ± 35	378 (324 – 425)
91075	2003141	0.317	2	OS-42453	2.21	2770 ± 30	2484 (2389 – 2562)
<i>S. casali</i>, Site 1 (30 m)							
13077	2003086	0.075	2	OS-39670	2.34	375 ± 35	0
13081	2003088	0.083	2	OS-42384	2.20	555 ± 30	183 (138 – 247)
13087	2003138	0.119	2	OS-42385	2.12	590 ± 25	222 (147 – 163)
13088	2003139	0.184	2	OS-39671	2.76	1130 ± 30	676 (645 – 703)
13075	2003131	0.222	2	OS-43396	2.47	1350 ± 50	883 (818 – 941)
13071	2003082	0.273	2	OS-39673	2.07	3050 ± 35	2808 (2754 – 2846)

Table 2 - 3. Calibration information for all sites and taxa, including the calibration equation number (from text), slope and intercept of the calibration regression line. Calibration statistics, including adjusted r^2 , p-value, f-statistic and root mean square error for the regression of D/L aspartic values against shell age are also noted for all sites and taxa.

Site	Species	Equation	Slope	Intercept	Adjusted r^2	p	f	RMSE
9	<i>B. rosea</i>	1	6.46E-05	0.038	0.97	0.001	156.2	265.4
1	<i>B. rosea</i>	2	4.66E-05	0.051	0.997	0.001	889.4	178.0
9	<i>S. casali</i>	3	3.68E-05	0.010	0.9998	0.006	9751.8	19.2
1	<i>S. casali</i>	4	2.50E-05	0.011	0.93	0.001	70.2	270.1

Chapter 3: The search for a taphonomic clock: A comparison of rates of time averaging and taphonomic decay between brachiopods and bivalves

Abstract

Studies of burial history of modern sea floors have become increasingly important for understanding rates of time averaging and taphonomic processes. Sixty-nine specimens of the aragonitic tellinid bivalve *Semele casali* and fifty-eight of the calcitic terebratulid brachiopod *Bouchardia rosea* were used to analyze the informative value of taphonomic signatures on pre-burial history of marine benthic shells. Specimens were collected from the surface at two depths (10 m and 30 m) in Ubatuba Bay, a mixed carbonate-siliciclastic embayment off the coast of the state of São Paulo, Brazil. Individual specimens were dated using amino acid (D/L aspartic acid) racemization techniques calibrated against AMS-radiocarbon dates. Availability of these numerous individually dated specimens allows for a rigorous test of how taphonomic signatures vary over time, among taxa and between collection sites.

Overall similarities in physical attributes suggest that preservation potential may be comparable between collection sites. However, substantial differences do exist between the two taxa. Brachiopods and bivalves in this data set tend to have differential amounts of time averaging and taphonomic destruction, which are believed to be due to differences in life habit. Specimen age, color and taphonomic grade are significantly correlated for both total and conservative (post death) taphonomic scoring methods, but the presence of a taphonomic clock, or ability to use taphonomic grade as a proxy for shell age, is not straightforward. Although older and darker colored shells tend to only be found in a more heavily degraded state, young shells may be present with any degree of taphonomic alteration or coloration. Infaunal *S. casali*

tends to be both older and better preserved than epifaunal *B. rosea*, but site by site differences may also be impacted by additional factors such as patchiness and migratory history over time.

Introduction

Centuries of research have been devoted to studying taphonomy, the science concerning the process of fossilization and preservation (Cadée 1991; Martin 1999). Recently the quantification of taphonomic processes, from scoring shell decay to comparative analyses of fossilization processes across environments, among different ecological niches, and between different types of organisms, has become prominent in the literature (e.g. Flessa et al. 1993; Best and Kidwell 2000; Kidwell et al. 2001; Behrensmeyer et al. 2005; Kidwell 2005; Kidwell et al. 2005). Kidwell et al. (2001) noted that sample size, specimen size (the sieve affect), and the system used to score taphonomic grade impact the outcomes of taphonomic analyses.

Taphonomic literature suggests that we should expect to see differences in the taphonomic grade, or level of decay of shells, between shelly specimens buried in different environments, with specimens in siliciclastic sediments being better preserved than those in carbonate or mixed-carbonate settings (Best and Kidwell 2000; Kidwell et al. 2005). Specimens with hard parts constructed of different mineralogies and microstructures may also be subject to bias due to differential amounts of postmortem dissolution and diagenesis (Cherns and Wright 2000; Wriight et al. 2003; Bush and Bambach 2004). Epifaunal taxa are also expected to be prone to more surface alteration and/or quicker deterioration than infauna (Kidwell et al. 2001), as they are more likely to suffer exterior surface damage by encrustation, drilling and breakage by other life forms prior to death, whereas infaunal organisms typically must be exhumed before being altered. Water depth, energy, bioturbation and sedimentation rates affecting exhumation and burial also play an important role in taphonomic processes.

Taphonomic grade has been used in paleontological research as a proxy for time averaging and the duration of pre-burial taphonomic history (age-since-death) with varying

results. Time averaging of fossil assemblages can be described as temporal mixing of shells that lived at different times so that they appear to have occurred at the same time in the fossil record (Walker and Bambach 1971). Studies of rates of time averaging in present-day settings are important for understanding the temporal resolution of the fossil record. Studies on dated benthic mollusks suggest time averaging on the level of 10^2 to 10^4 years (Flessa et al. 1993; Wehmiller et al. 1995; Goodfriend and Stanley 1996; Martin et al. 1996; Anderson et al. 1997; Meldahl et al. 1997; Flessa 1998; Kowalewski et al. 1998; Behrensmeier et al. 2000; Kidwell and Best 2001; Carroll et al. 2003; Kowalewski and Bambach 2003). Although most time averaging research thus far has been on mollusks, Carroll et al. (2003) documented that recent brachiopod assemblages can also be affected by temporal mixing on the order of hundreds to thousands of years. That study was expanded recently to include the first comparison of time averaging rates for bivalves and brachiopods from the same sampling sites (Krause 2006).

Here, we use directly dated specimens of the tellinid bivalve *Semele casali* and the terebratulid brachiopod *Bouchardia rosea* to analyze the informative value of taphonomic signatures on pre-burial history on time-averaged shelly assemblages. The two targeted species are approximately the same in terms of size, but differ in many respects. *S. casali* has an aragonitic shell and a shallow infaunal life habit, whereas *B. rosea* is a calcitic, epifaunal free-lying suspension feeder. Individual dated shells can be inspected for various taphonomic signatures (e.g. fragmentation, abrasion, etc.) to analyze the presence or absence of a taphonomic clock, or burial history of an assemblage.

Materials and Methods

Samples were collected in conjunction with an ongoing project of the marine ecology group of the São Paulo State University. Specimens were collected using a Van Veen grab sampler (1/40 m²), which collects unconsolidated surficial deposits (the uppermost several centimeters of the substrate), from two sites (10 m and 30 m, Fig. 3.1) situated at Ubatuba Bay, a mixed carbonate-siliciclastic embayment off the coast of the state of São Paulo, Brazil (Fig. 3.1). Fine-grained (silt and very fine sand) terrigenous sediments, terrestrial organic matter (Burone 2002) and coarse biogenic constituents, primarily consisting of brachiopods, mollusks, echinoids, bryozoans, and foraminifers (Mahiques et al. 1998; Mantelatto and Fransozo 1999), dominate the Bay's substrate. Both rhynchonelliform (terebratulid) brachiopods, dominated by *Bouchardia rosea* (Simões et al. 2004), and a diverse molluscan fauna are present. Physical parameters at each sampling site (temperature, salinity, and organic content of the bottom water) were recorded (Table 3.1). Further details on Ubatuba Bay physical characteristics, hydrodynamics, sedimentation, sediment geochemistry and faunal content can be found in Emilson (1959), Matsuura (1986), Castro Filho et al. (1987), Mahiques (1992; 1995), Sanches (1992), Mantelatto and Fransozo (1999), Burone (2003), and Muniz (2003).

A total of 58 individual brachiopod shells and 69 bivalve shells were included in the dataset (Table 3.2). Specimens were dated using amino acid (D/L aspartic acid) racemization techniques calibrated against AMS-radiocarbon dates based on calibration curves reported in Barbour Wood et al. (2006). To produce calibration curves, nineteen specimens from the two species including both sites and representing a broad range of Asp D/L values were selected for radiocarbon analysis at the NOSAMS Lab (Woods Hole) where ¹⁴C was measured by Accelerator Mass Spectrometry (see <http://www.nosams.who.edu/nosams.html> for procedural

details). Each specimen was prepared for radiocarbon and amino acid analyses using a uniform, standard methodology described in Barbour Wood et al. (2006).

Shell ages were calibrated to calendar years using CALIB version 5.0 (Stuiver et al. 2005) and error estimates for radiocarbon were based on information provided by NOSAMS. Age values were determined by the SHCal04 (Southern Hemisphere) and marine04.14c databases (Hughen et al. 2004; McCormac et al. 2004), assuming a mean marine reservoir age of 408 ± 18 years ($\Delta R 8 \pm 17$) recently established through an extensive empirical analysis by Angulo et al. (2005). Calibration equations can be found in Table 3.2. Details regarding the amino acid dating procedures, radiocarbon calibrations, and the precision and accuracy of resulting age estimates are provided in Barbour Wood et al. (2006).

Specimens were digitally photographed and measured for length, width and height. Specimens were scored for several taphonomic variables (Table 3.3), using additive presence-absence scores (e.g., 0=absent, 1=present), where higher taphonomic scores indicate a more degraded shell. Individual taphonomic variables included disarticulation, fragmentation, edge completeness, glossiness, interior and exterior surface alteration, visibility of muscle scars and shell color. These additive variables were then combined to estimate (1) Total Taphonomic Score, which included all variables; and (2) Conservative Taphonomic Score, restricted to variables recording post-mortem taphonomic damage only (Carroll et al. 2003), which reflect effects that can only happen after death of the organism (e.g. interior shell alteration). Shell color rank was also calculated for each species separately using a categorical scale where a score of one denotes shells with original pigmentation and light overall color, a score of two an intermediate color indicating some alteration, and a score of three darkly colored, highly altered

shells. Observed Total and Conservative Taphonomic Scores for each specimens are summarized in Table 3.2.

Various statistical techniques were used to analyze taphonomic scores, changes in color and age distributions both between taxa and between collection sites at a significance level alpha value of 0.05. Mean, median and range data were computed using the program SAS (Version 9.1.3, SAS Institute, 2003). The Wilcoxon Rank Sum test was used to test for differences in median ages, taphonomic scores and conservative taphonomic scores at each sampling site and for both taxa. Distributions of specimen ages, taphonomic scores and conservative taphonomic scores were evaluated using the Kolmogorov-Smirnov Test. Spearman correlation coefficients were also calculated between variables for each specimen, and a contingency table analysis using Fisher's Exact Test was conducted on observed versus expected specimen colors for each species and sampling site.

Results

Specimen ages, taphonomic scores, conservative taphonomic scores and specimen colors are all significantly correlated ($p < 0.0001$, Table 3.5). Comparisons of taphonomic scoring methods and shell color between and among collection sites and taxa are discussed below.

Distribution of Shell Ages. Rates of time averaging appear to be similar at each site, and are approximately 10^2 to 10^3 years (Fig. 3.2). However, bivalve *S. casali* experiences longer durations of time averaging than brachiopod *B. rosea*. At Site 9 (10 m), brachiopods range in age from modern to ~4600 yrs BP and bivalves from modern to ~12,000 yrs BP. Brachiopod shells from Site 1 (30 m) range in age from modern to ~8700 yrs BP and bivalves from modern

to ~11,000 yrs BP. Means, medians and ranges of ages for each taxon and sampling site can be found in Table 3.4.

Age distributions for both sites and taxa are illustrated in Figure 3.2. Median ages between brachiopods and bivalves are not significantly different from shallow Site 9 (10 m) ($Z = 1.16$, $p = 0.3$) or if specimens from both collection sites are pooled ($z = 1.76$, $p = 0.08$), but are significantly different at deep Site 1 (30 m) ($Z = 4.06$, $p < 0.0001$; Table 3.6). Distributions of ages are also significantly different for bivalves and brachiopods at the deep site ($D = 0.5$, $p = 0.001$), but not from the shallow site, or if specimens are pooled from both collection sites (Kolmogorov-Smirnov Test, Table 3.6). Taxa are also different between the two collection sites. Median ages and age distributions for brachiopod *B. rosea* are significantly different between Sites 1 and 9 (Wilcoxon $Z = 4.40$, $p < 0.0001$; Kolmogorov-Smirnov $D = 0.53$, $p = 0.0007$; Table 3.7), where specimens tend to be older at deeper Site 1. Ages and age distributions can not be statistically distinguished for bivalve *S. casali* between the collection sites (Table 3.7).

Taphonomic Comparisons by Taxon. Brachiopods and bivalves are statistically different from one another in terms of total taphonomic score and conservative taphonomic score when data are pooled from both collection sites, as well as when observed from the shallow and deep collection sites separately with p-values consistently < 0.0001 (Wilcoxon Test, Table 3.6). Figure 3.3 suggests that brachiopod *B. rosea* tends to have worse preservation (generally higher total and conservative taphonomic scores) than bivalve *S. casali* regardless of collection site. Significant differences between taxa are also found in terms of distribution of taphonomic scores and conservative taphonomic scores at collection sites independently, and for both sites pooled (Kolmogorov-Smirnov Test, Table 3.6).

Taphonomic Comparisons by Collection Site. Neither Total Taphonomic Scores nor Conservative Taphonomic Scores allow us to distinguish statistically the brachiopod *B. rosea* between the two sampling sites (Table 3.7; Fig. 3.4 a, c). Although total taphonomic scores could not be distinguished between bivalve *S. casali* at the two collection sites (Fig. 3.4b), conservative taphonomic scores of bivalves was found to be significantly different between Site 9 and Site 1 (Wilcoxon $Z = 2.17$, $p = 0.03$). Figure 3.4d suggests that specimens from shallow Site 9 (10 m) have slightly better preservation, and are thus more heavily weighted toward lower taphonomic scores. However, no evidence exists to suggest that there exists a significant difference the two collection sites in the shape of distributions of either Total or Conservative Taphonomic Scores for either of the two taxa (Table 3.7).

Shell Color. Specimens of each taxon were noted to vary greatly in color with age. *B. rosea* varied from white or pale pink with pink stripes to dark brown. *S. casali* showed more subtle color variations from white to light gray. An association between the color of shells and specimen age has been noted by Wehmiller et al. (1995). Shell color may qualitatively indicate degrees of alteration. Lightly colored shells are more commonly associated with lower taphonomic grades than darkly colored shells, but may represent specimens of any age or taphonomic state, whereas darkly colored shells only represent specimens with high taphonomic grades (Fig. 3.6). Fisher's Exact Test suggests that proportion of dark-colored shells is significantly lower at the shallower sampling site ($p = 8.68E-5$) than expected. Median color values and distributions are significantly different between brachiopods and bivalves at both collection sites and for pooled taxonomic data ($p \leq 0.003$ for all comparisons, Table 3.6). Median color values and distributions are significantly different between collection sites for *B. rosea* ($Z = 3.42$, $p = 0.0006$, $D = 0.58$, $p = 0.0001$) with darkly colored shells being much more

abundant at Site 1 (30 m, Fig. 3.5c) (Table 3.7). The shells of *S. casali* do not display any significant differences in color between the sites and is predominately represented by light-colored specimens. Only *B. rosea* has darkly colored shells at shallow Site 9, and includes the vast majority of dark shells at deep Site 1 (Fig 3.5a-b).

Discussion and Conclusions

Taphonomic Clock. Analysis of individually dated specimens allows a rigorous test of how taphonomic signatures vary over time, among taxa and between collection sites. The utility of taphonomic grade and shell color as indicators of time since death (i.e. taphonomic clocks) for a specimen has had mixed reviews in literature. As discussed in Flessa et al. (1993), several studies (e.g. Nelson and Bornhold 1983; Panin et al. 1983) found relationships between taphonomic grade and shell age. Kidwell et al. (2005) found significant relationships between shell damage and shell age when specimens were grouped into “young” and “old” categories. However, many others (Powell and Davies 1990; Flessa et al. 1993; Meldahl et al. 1997; Carroll et al. 2003) found little or no link between taphonomic grade and shell age, with suspected causes being variable burial history, differences in time of surface exposure and depositional environment. The current dataset suggests a significant correlation between taphonomic grade and shell age ($p = <0.0001$, Table 5), but the utility of a taphonomic clock is not simple. Although older shells tend to only be found in a more heavily degraded state, young shells may present with any degree of taphonomic alteration. This trend is especially visible at collection Site 1 and for brachiopod *B. rosea*. Thus, taphonomic alteration cannot be used as a proxy for age estimation in this data set.

Over long time scales, shell color and other taphonomic characteristics may be indicative of relative shell age. Flessa et al. (1993) note that Pleistocene shells in Bahia la Choya are notable due to lack of color and chalky surface. Wehmiller et al. (1995) noted that reworked Pleistocene shells tended to be very dark in color. Similarly, here we also note that shell color significantly correlates with shell age ($p = <0.0001$, Table 5), but as with taphonomic grade, color cannot be used solely as a taphonomic clock.

Between-Site Comparisons. As previously noted, physical characteristics of depositional settings (e.g. water depth, energy, bioturbation and sedimentation rates and sediment type) may impact preservation potential and exhumation history of fossil shells. However, the two collection sites are both located on the inner shelf, and thus are very similar in terms of substrate with both containing similar carbonate and organic matter content. Grain size, sorting and average bottom water temperatures constitute the primary differences between the shallow and deep deposits (Table 3.1), but do not appear to have systematically influenced specimen preservation. Thus, overall similarities in physical attributes between the two sampling sites suggest that between-site preservation potential may be comparable, which ideally allows for direct comparisons between taxa. Age distributions for the studied taxa suggest that time averaging is substantial at both sites. Brachiopods and bivalves in this data set do tend to have differential amounts of time averaging and taphonomic destruction, and differences are likely due to life habit. Infaunal bivalve *S. casali* tends to be both older and better preserved than epifaunal *B. rosea*. Only *S. casali* shows significant variation in taphonomy between collection sites, and then only in the conservative (post death) taphonomic score (Table 3.7). As suggested by Figure 3.4d, bivalve specimens from the deeper site (1, 30 m) may be slightly better preserved than those from the shallow site in terms of postmortem processes. Although no data are

available regarding either bottom water energy, which would be expected to be greater at the shallow site, or rates of bioturbation between sites, an intuitive hypothesis would suggest that shallow water specimens would indeed show greater amounts of exhumation leading to higher taphonomic scores and shell degradation.

Taxonomic Comparisons. Analyses comparing *B. rosea* to *S. casali* at individual collection sites and for pooled data suggest that either shell mineralogy or life habit may pose the greatest preservation bias, with both taphonomic scores and conservative scores being statistically significant between the two taxa regardless of collection method. For both taphonomic scoring methods, epifaunal, calcitic brachiopod *B. rosea* appears to have greater taphonomic alteration than infaunal, aragonitic bivalve *S. casali* (Fig. 3.3). It is not possible to discern definitively which factor, mineralogy or life habit, has the greatest influence on shell degradation using only the two taxa in the present study. However, life habit may be the more likely culprit based on recent research by Kidwell et al. (2001), which illustrates lower amounts of damage for infauna than epifaunal, even when specimens of similar mineralogy (e.g. aragonite) are compared. Although calcite biases have been noted in the fossil record (Cherns and Wright 2000; Wright et al. 2003; Bush and Bambach 2004), taphonomic studies concerning shell mineralogy and durability suggest little, no or inconclusive correlations between expected trends of greater preservation among “more durable” calcitic or low organic shells and preservation potential (Best and Kidwell 2000; Behrensmeyer et al. 2005; Kidwell 2005).

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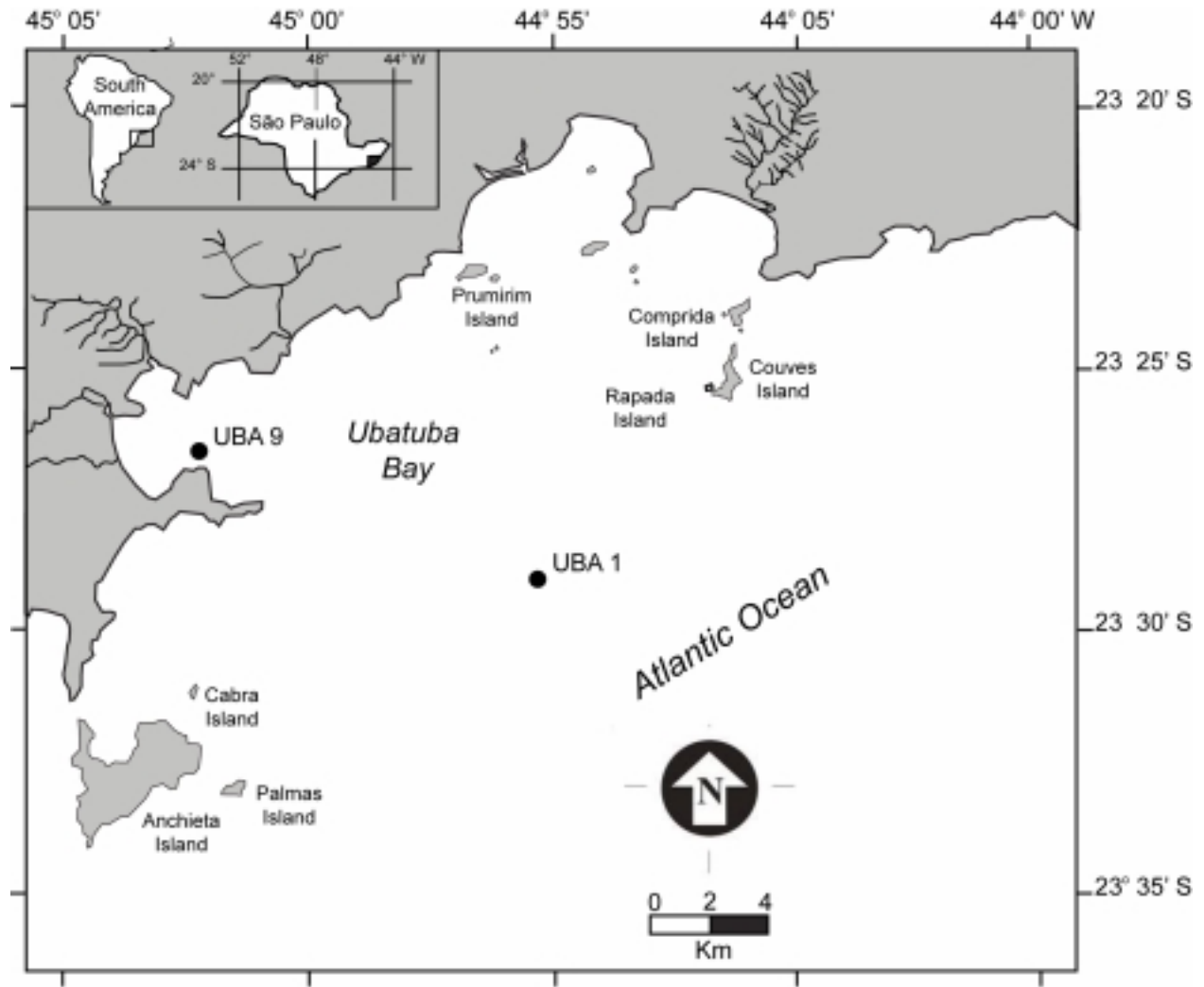


Figure 3 - 1. Map of the study area and collection sites.

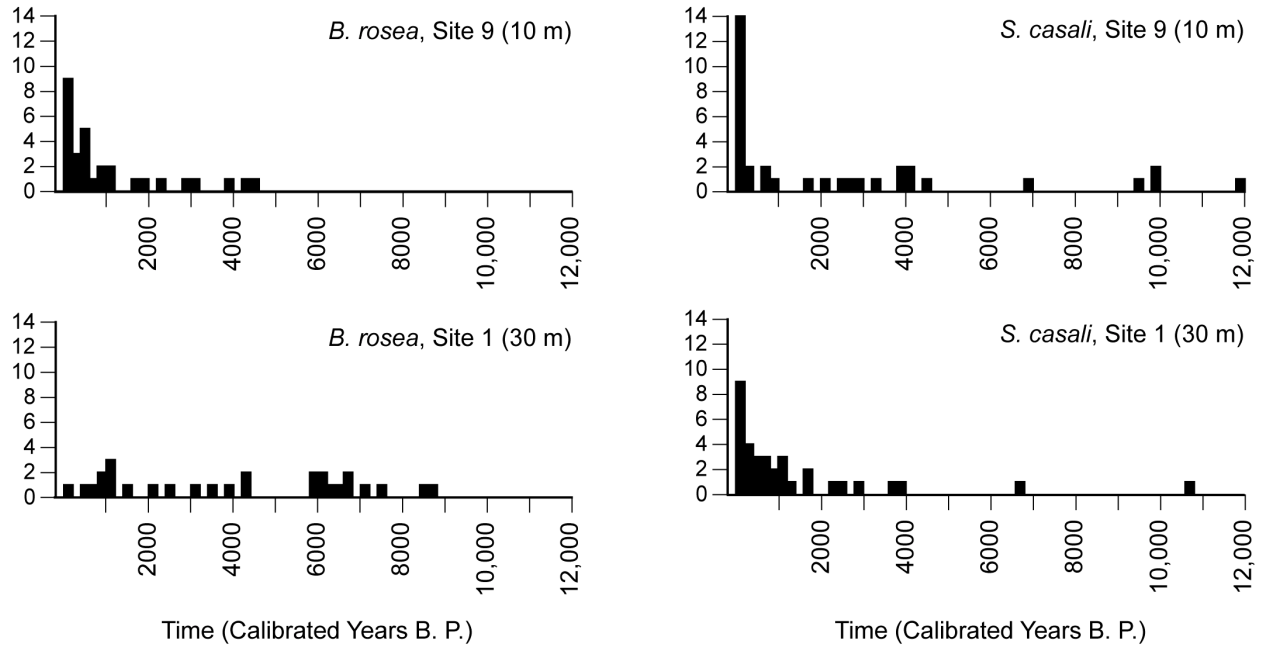


Figure 3 - 2. Age distribution histograms are plotted for taxa plotted by collection site. Age bins are 200 years in duration, and ages are calibrated in years before present.

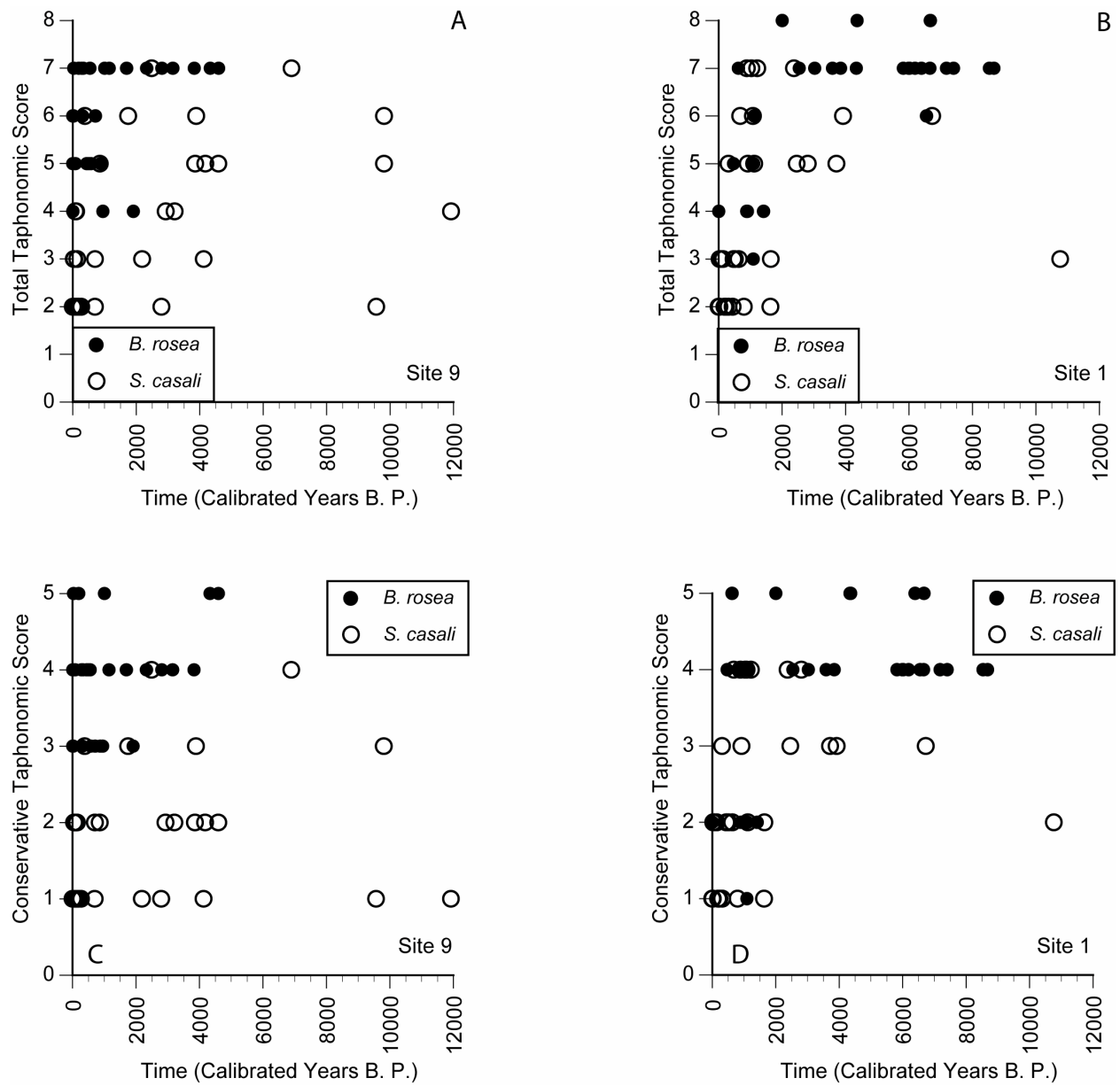


Figure 3 - 3. Taphonomic distribution diagrams comparing *B. rosea* (closed circles) to *S. casali* (open circles). A-B: Total taphonomic scores for Sites 9 (10 m) and 1 (30 m), respectively. C-D: Conservative taphonomic scores for Sites 9 (10 m) and 1 (30 m), respectively.

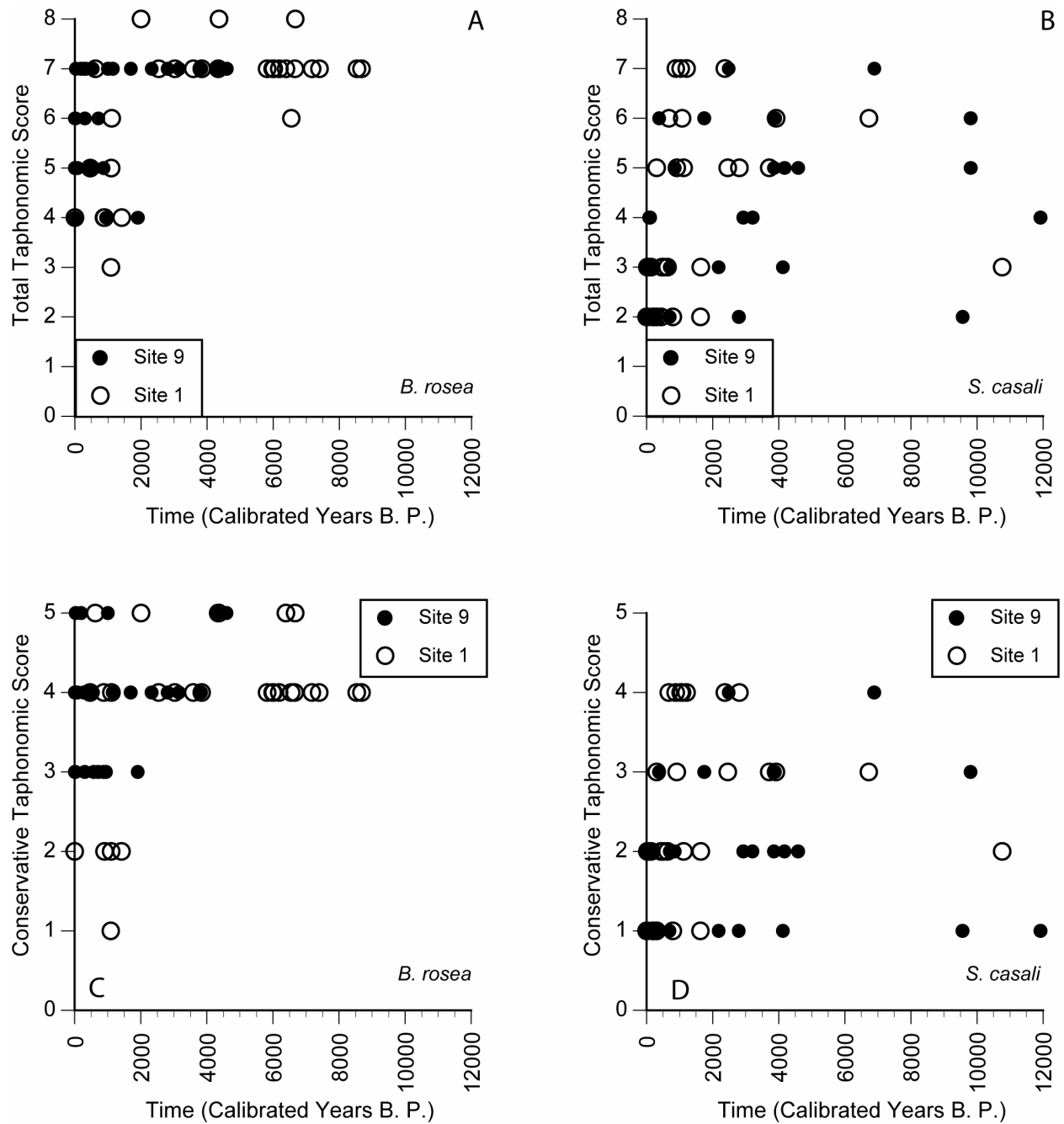


Figure 3 - 4. Taphonomic distribution diagrams comparing Site 9 (10 m, closed circles) to Site 1 (30 m, open circles). A-B: Total taphonomic scores for Sites *B. rosea* and *S. casali*, respectively. C-D: Conservative taphonomic scores for Sites *B. rosea* and *S. casali*, respectively.

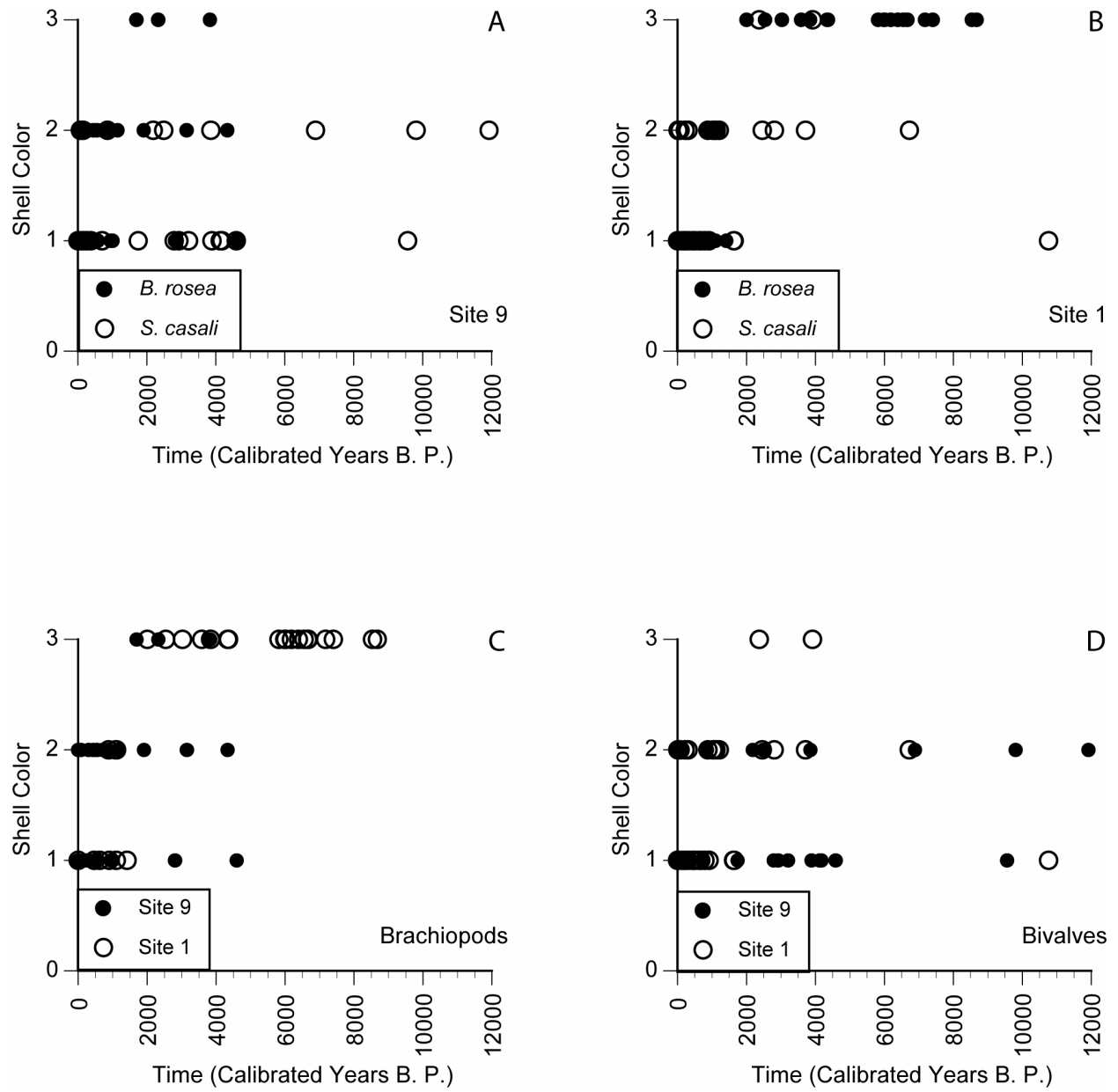


Figure 3 - 5. Shell color distribution diagrams comparing *B. rosea* and *S. casali* at Site 9 (10 m, A) and Site 1 (30 m, B). Collection Sites 1 and 9 are compared for *B. rosea* (C) and *S. casali* (D).

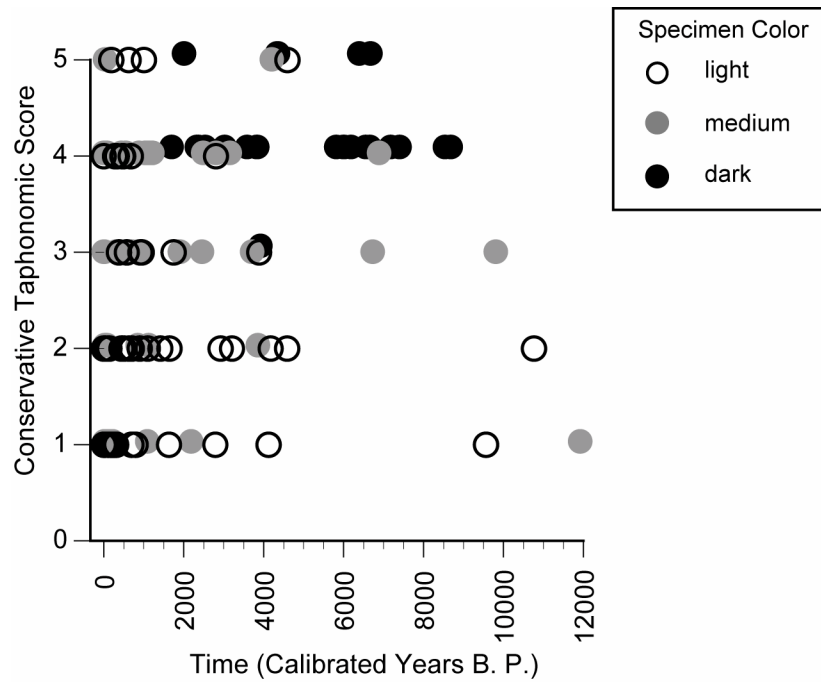


Figure 3 - 6. Conservative taphonomic distribution plotted by specimen color for all samples of *B. rosea* and *S. casali*.

Table 3 - 1. Sampling site data. Temperatures are averages of monthly bottom water measurements from 2000.

Site	9	1
Depth	10 m	30 m
Latitude	23° 26' 41"	23° 28' 53"
Longitude	45° 02' 07"	44° 55' 21"
Temp C°	22.0	19.4
Salinity ‰	34.0	35.0
Sedimentary Characteristics		
Carbonate %	25	25
Organic Matter %	7	3
Mean Grain Diameter (mm)	0.91	0.68
Grain Sorting	Poor	Moderate
No. analyzed shells: <i>Bouchardia</i>	5	4
No. analyzed shells: <i>Semele</i>	3	6

Table 3 - 2. D/L Asp values, power transformed D/L Asp values and calibrated age (years BP) for all samples in the data set. Both composite taphonomic scores (including all scored taphonomic categories) and conservative scores (only taphonomic categories which can occur after death of the specimen) are listed for each specimen, with higher scores indicating greater amounts of shell degradation. Shell color was graded on a scale of 1 (light) to 3 (dark) as compared to natural specimens.

Sample	D/L Asp	D/L Power Function	Calibrated Age (yr BP)	Composite Score	Conservative Score	Color
<i>B. rosea</i> , Site 9 (10 m)		Age = (Asp ^{2.6} - 0.01266)/ 4.633E-05				
91001	0.276	0.035	486	5	4	1
91003	0.351	0.066	1146	7	4	2
91004	0.194	0.014	30	7	5	2
91005	0.473	0.143	2808	7	4	1
91006	0.230	0.022	199	5	4	2
91007	0.191	0.014	18	6	4	2
91008	0.269	0.033	437	5	4	2
91009	0.252	0.028	326	7	4	1
91011	0.244	0.026	278	7	4	1
91013	0.337	0.059	1003	7	5	1
91014	0.564	0.226	4596	7	5	1
91016	0.552	0.213	4331	7	5	2
91017	0.285	0.038	552	5	4	2
91018	0.098	0.002	0	5	4	1
91019	0.183	0.012	0	6	3	2
91020	0.493	0.159	3150	7	4	2
91021	0.288	0.039	575	5	3	1
91022	0.331	0.056	945	4	3	1

Table 3.2 (continued)

Sample	D/L Asp	D/L Power Function	Calibrated Age (yr BP)	Composite Score	Conservative Score	Color
91023	0.305	0.046	711	6	3	2
91024	0.248	0.027	302	6	3	2
91025	0.414	0.101	1906	4	3	2
91026	0.176	0.011	0	6	4	2
91027	0.175	0.011	0	4	3	2
91030	0.228	0.021	189	7	5	1
91031	0.323	0.053	870	5	3	2
91032	0.534	0.196	3951	7	4	3
91033	0.283	0.038	537	7	4	2
91034	0.443	0.120	2326	7	4	3
91036	0.191	0.014	18	6	3	2
91038	0.398	0.091	1694	7	4	3
<i>B. rosea</i>, Site 1 (30 m)		Age = (Asp^{2.6} - 0.01043)/ 3.824E-05				
13001	0.095	0.002	0	4	2	1
13002	0.599	0.264	6626	8	5	3
13003	0.322	0.053	1101	5	2	1
13004	0.513	0.176	4338	7	5	3
13005	0.577	0.239	5987	7	4	3
13006	0.600	0.265	6656	6	4	3
13007	0.323	0.053	1112	6	4	2
13008	0.571	0.233	5819	7	4	3
13009	0.491	0.157	3842	7	4	3
13010	0.413	0.100	2351	7	4	3

Table 3.2 (continued)

Sample	D/L Asp	D/L Power Function	Calibrated Age (yr BP)	Composite Score	Conservative Score	Color
13011	0.658	0.337	8535	7	4	3
13012	0.578	0.240	6015	7	4	3
13013	0.662	0.342	8675	7	4	3
13014	0.301	0.044	880	4	4	2
13015	0.624	0.293	7400	7	4	3
13016	0.479	0.148	3585	7	4	3
13018	0.451	0.126	3026	7	4	3
13019	0.617	0.285	7178	7	4	3
13021	0.321	0.052	1090	3	1	2
13022	0.269	0.033	588	5	4	1
13023	0.273	0.034	622	7	5	1
13025	0.591	0.255	6389	7	5	3
13026	0.514	0.177	4362	8	5	3
13027	0.391	0.087	2003	8	5	3
13028	0.349	0.065	1415	4	2	1
13029	0.600	0.265	6656	7	4	3
13030	0.584	0.247	6186	7	4	3
13031	0.303	0.045	900	4	2	1
<i>S. casali</i>, Site 9 (10 m)		Age = (Asp^{3.1} - 0.00013503)/ 1.137E-05				
91042	0.489	0.109	9562	2	1	1
91043	0.138	0.002	178	2	1	1
91044	0.283	0.020	1745	6	3	1
91045	0.366	0.044	3888	6	3	1

Table 3.2 (continued)

Sample	D/L Asp	D/L Power Function	Calibrated Age (yr BP)	Composite Score	Conservative Score	Color
91046	0.132	0.002	153	2	1	1
91047	0.329	0.032	2791	2	1	1
91048	0.525	0.136	11921	4	1	2
91049	0.493	0.112	9807	5	3	2
91050	0.493	0.112	9807	6	3	2
91051	0.334	0.033	2925	4	2	1
91052	0.109	0.001	80	4	2	2
91053	0.386	0.052	4587	5	2	1
91054	0.103	0.001	65	2	1	2
91055	0.117	0.001	103	2	1	1
91057	0.373	0.047	4124	3	1	1
91058	0.118	0.001	105	4	1	1
91059	0.365	0.044	3855	5	2	2
91060	0.375	0.048	4175	5	2	1
91061	0.128	0.002	138	3	2	1
91062	0.172	0.004	363	6	3	1
91063	0.211	0.008	695	2	1	1
91064	0.212	0.008	700	3	2	1
91065	0.132	0.002	151	2	1	2
91066	0.156	0.003	265	2	1	1
91068	0.225	0.010	851	5	2	2
91069	0.440	0.078	6890	7	4	2
91070	0.344	0.037	3206	4	2	1
91071	0.071	0.000	12	2	1	1

Table 3.2 (continued)

Sample	D/L Asp	D/L Power Function	Calibrated Age (yr BP)	Composite Score	Conservative Score	Color
91072	0.074	0.000	16	2	1	1
91073	0.141	0.002	191	2	1	1
91074	0.117	0.001	102	4	2	1
91075	0.317	0.028	2474	7	4	2
91076	0.087	0.001	33	3	1	1
91078	0.304	0.025	2182	3	1	2
91079	0.095	0.001	47	3	2	1
<i>S. casali</i>, Site 1 (30 m)		Age = (Asp^{3.1} - 0.00065487)/ 6.44E-06				
13050	0.424	0.070	10761	3	2	1
13051	0.235	0.011	1642	3	2	1
13052	0.308	0.026	3918	6	3	3
13053	0.101	0.001	26	3	2	1
13054	0.178	0.005	631	3	2	1
13055	0.124	0.002	139	3	2	1
13056	0.164	0.004	465	3	2	1
13059	0.215	0.008	1212	7	4	2
13061	0.048	0.000	0	2	1	1
13062	0.303	0.025	3712	5	3	2
13063	0.098	0.001	14	2	1	2
13064	0.147	0.003	306	5	3	2
13066	0.263	0.016	2370	7	4	3
13067	0.112	0.001	74	3	2	2
13068	0.210	0.008	1120	5	2	2

Table 3.2 (continued)

Sample	D/L Asp	D/L Power Function	Calibrated Age (yr BP)	Composite Score	Conservative Score	Color
13069	0.365	0.044	6725	6	3	2
13070	0.266	0.016	2458	5	3	2
13071	0.273	0.018	2657	5	4	2
13072	0.168	0.004	509	3	2	1
13073	0.207	0.008	1075	6	4	2
13074	0.235	0.011	1630	2	1	1
13075	0.222	0.009	1360	7	4	2
13076	0.109	0.001	57	3	2	2
13077	0.075	0.000	0	2	1	1
13078	0.198	0.007	915	5	3	1
13079	0.101	0.001	26	2	2	2
13080	0.137	0.002	226	2	1	1
13081	0.083	0.000	0	2	1	1
13082	0.161	0.003	438	2	2	1
13083	0.190	0.006	793	2	1	1
13085	0.205	0.007	1031	7	4	2
13086	0.148	0.003	310	2	1	1
13087	0.119	0.001	107	2	1	2
13088	0.184	0.005	708	6	4	1

Table 3 - 3. Summary of taphonomic characters included in the calculation of the total and conservative taphonomic scores. The character ‘color’ was not included in the scores, but was noted for each shell for separate analysis.

Taphonomic Character	Total Taphonomic Score	Conservative Taphonomic Score
Disarticulation	X	X
Fragmentation	X	X
Edge Completeness	X	
Removal of Gloss	X	
External Surface Alteration	X	
Internal Surface Alteration	X	X
Visibility of Muscle Scars	X	X

Table 3 - 4. Summary of sample site data. Mean, median and range of ages, taphonomic scores (Score), conservative taphonomic scores (C. Score) and shell colors are tabulated separately for brachiopod *B. rosea* and bivalve *S. casali* from combined collection sites, Site 9 and Site 1.

All Sites		Brachiopods, N = 58	Bivalves, N = 69
mean	Age = Score = C. Score = Color =	2525.5 6.17 3.84 2.10	1964.6 3.77 2.04 1.43
median	Age = Score = C. Score = Color =	1129.0 7 4 2	695.0 3 2 1
range	Age = Score = C. Score = Color =	8675 5 4 2	11921 5 3 2
Standard deviation	Age =	2596.8	2868.0
Site 9 (10 m)		Brachiopods, N = 30	Bivalves, N = 35
mean	Age = Score = C. Score = Color =	1104.6 6.03 3.87 1.77	2520.0 3.69 1.77 1.31
median	Age = Score = C. Score = Color =	544.5 6 4 2	700.0 3 2 1
range	Age = Score = C. Score = Color =	4596 3 2 2	11921 5 3 1
Standard deviation	Age =	1361.7	3339.8
Site 1 (30 m)		Brachiopods, N = 28	Bivalves, N = 34
mean	Age = Score = C. Score = Color =	4047.8 6.3 3.8 2.5	1392.8 3.9 2.3 1.6
median	Age = Score = C. Score = Color =	4090.0 7 4 3	653.5 3 2 1.5
range	Age = Score = C. Score = Color =	8675.0 5 4 2	10761.0 5 3 2
Standard deviation	Age =	2756.6	2189.2

Table 3 - 5. Spearman correlation coefficients for specimen ages, taphonomic scores, conservative taphonomic scores and specimen colors. All variables are significantly correlated.

Spearman Correlation Coefficients				
	Age	Taphonomic Score	Conservative Taph. Score	Color
Age	1.00	0.52 <.0001	0.38 <.0001	0.46 <.0001
Taphonomic Score		1.00	0.91 <.0001	0.60 <.0001
Conservative Taph. Score			1.00	0.53 <.0001
Color				1.00

Table 3 - 6. Results of the Wilcoxon and Kolmogorov-Smirnov two sample tests comparing brachiopod *B. rosea* and bivalve *S. casali* from combined collection sites, and separately for Site 9 and Site 1.

Variable	Wilcoxon			Kolmogorov-Smirnov		
	Z	2-tailed	1-tailed	D	KS	Pr>KSa
all sites						
Age =	1.76	0.08	0.04	0.20	0.10 1.15	0.14
Score =	7.01	<.0001	<.0001	0.53	0.27 2.99	<.0001
C. Score =	7.68	<.0001	<.0001	0.63	0.31 3.53	<.0001
Color =	4.72	<.0001	<.0001	0.35	0.17 1.97	0.0009
Site 9						
Age =	-1.16	0.3	0.12	0.23	0.12 0.94	0.34
Score =	5.16	<.0001	<.0001	0.59	0.29 2.35	<.0001
C. Score =	6.33	<.0001	<.0001	0.80	0.40 3.22	<.0001
Color =	3.00	0.003	0.001	0.35	0.18 1.42	0.04
Site 1						
Age =	4.06	<.0001	<.0001	0.50	0.23 1.95	0.001
Score =	4.85	<.0001	<.0001	0.56	0.28 2.20	<.0001
C. Score =	4.58	<.0001	<.0001	0.62	0.31 2.41	<.0001
Color =	4.13	<.0001	<.0001	0.62	0.31 2.43	<.0001

Table 3 - 7. Results of the Wilcoxon and Kolmogorov-Smirnov two sample tests comparing collection Site 1 and Site 9 for combined taxa, and separately for brachiopod *B. rosea* and bivalve *S. casali*.

Variable	Wilcoxon			Kolmogorov-Smirnov		
	Z	2-tailed	1-tailed	D	KS	Pr>KSa
all taxa						
Age =	2.11	0.03	0.02	0.23	0.11 1.29	0.07
Score =	0.75	0.5	0.2	0.12	0.06 0.70	0.7
C. Score =	1.19	0.2	0.1	0.13	0.06 0.73	0.7
Color =	2.99	0.003	0.001	0.29	0.15 1.65	0.009
<i>B. rosea</i>	Z	2-tailed	1-tailed	D	KS	Pr>KSa
Age =	4.40	<.0001	<.0001	0.53	0.26 2.00	0.0007
Score =	1.39	0.2	0.08	0.21	0.11 0.81	0.5
C. Score =	0.58	0.6	0.3	0.18	0.09 0.68	0.7
Color =	3.42	0.0006	0.0003	0.58	0.29 2.20	0.0001
<i>S. casali</i>	Z	2-tailed	1-tailed	D	KS	Pr>KSa
Age =	0.812	0.4	0.2	0.25	0.13 1.05	0.2
Score =	0.30	0.8	0.4	0.10	0.05 0.40	0.997
C. Score =	2.17	0.03	0.01	0.22	0.11 0.92	0.4
Color =	1.69	0.09	0.05	0.19	0.09 0.77	0.6

Chapter 4 – Environmental and Ecological Trends across the Miocene-Pliocene Contact in the Williamsburg, Virginia Area

Abstract

Late Cenozoic sedimentary units preserved in the Atlantic Coastal Plain offer a rich source of paleontological data. Fine-scale sampling of these fossiliferous units can provide direct quantitative insights into changes in faunal composition through time (including diversity trends and extinction events), and also yield information about paleoenvironmental and paleoecological trends. The Miocene Cobham Bay Member of the Eastover Formation and Pliocene Sunken Meadow Member of the Yorktown Formation were investigated using an extensive bulk sampling program to assess how environmental and ecological parameters changed in the region across the Miocene-Pliocene boundary regionally traceable erosional disconformity. A total of 54 bulk samples and 51,244 specimens representing 110 genera were collected and analyzed using qualitative and quantitative methods. Multivariate faunal ordinations and sedimentological analyses suggest that faunal composition and environmental conditions have changed slowly through the studied time interval, with a remarkably gradual rather than abrupt trend across the Miocene and into the Pliocene: data do not suggest any notable turnover event, elevated extinction rates or abrupt shifts in relative abundance of common taxa at the boundary. These quantitative and qualitative lines of evidence do not support previously published suggestions for major biotic changes across the boundary and suggest that the Miocene-Pliocene boundary does not represent a long lasting major disconformity. This is consistent with recent Strontium dating efforts, which suggest that the two members cannot be distinguished in age along the contact.

Introduction

Transitions in Neogene global climate has prompted numerous researchers to study faunal changes, migration and evolution during this time (e.g. the Panama Paleontology Project (PPP); Neogene Marine Biota of Tropical America (NMITA); CORONA; European bioprovincial studies on spatial and temporal faunal patterns occurring during the Miocene (Kowalewski et al. 2002) and Miocene-Pliocene Messinian Salinity Crisis in the Mediterranean region). Although faunal transitions have been studied for the Pliocene-Pleistocene of the North American Atlantic Coastal Plain (Stanley and Campbell 1981; Stanley 1986; Allmon et al. 1993), the Miocene-Pliocene transition as recorded in mid-Atlantic Coastal Plain macrofossil deposits has yet to be explored. Quantitative analyses of faunal diversity and ecological trends from various paleogeographical and temporal settings during the Neogene are necessary to fully understand biotic transitions and climatic responses during this time. This study aims to provide a rigorous quantitative assessment of macrofaunal and sedimentological changes across the Miocene-Pliocene boundary (between the Cobham Bay Member of the upper Miocene Eastover Formation and the lower Pliocene Sunken Meadow Member of the Yorktown Formation), while using an internally consistent taxonomic identification scheme.

The unconsolidated and highly fossiliferous deposits of the mid-Atlantic Coastal Plain provide a suitable system for paleontological investigations of the late Cenozoic marine fossil record. Despite that, and the fact that the mid-Atlantic Coastal Plain has a long history of paleontological research, current studies suggests that many formations are patchily studied, or only investigated for a few groups of organisms. Moreover, while biostratigraphic revisions have been made in recent decades (Blackwelder and Ward 1976; Ward and Blackwelder 1980; Blackwelder 1981; Ward 1992a, b), the bulk of macrofaunal taxonomic investigations occurred

in the 19th and early 20th centuries (e.g. numerous works by T. A. Conrad, W. H. Dall, J. A. Gardner, H. C. Lea, W. C. Mansfield, and T. Say, among others), with fewer whole-fauna taxonomic and ecological studies being conducted in more recent decades (Ward 1992a; Campbell 1993). As a result, species identifications may vary between taxonomic workers, from region to region, and across stratigraphic boundaries, leading to the lack of a comprehensive, generally agreeable stratigraphic biozonation between regions for marine macrofossils (Ward 1992a). Even more strikingly, quantitative paleoecological studies are essentially lacking in the literature, so few numerical estimates of diversity, faunal composition, extinction events and related issues exist for the region, but see Campbell (1993) and Daley (1999).

The Miocene-Pliocene boundary of the mid-Atlantic Coastal Plain (Salisbury Embayment, Fig. 4.1), has traditionally been viewed as a significant erosional event, removing approximately 1.5 million years, or much of the Messinian in southern Virginia based on biostratigraphic relationships and a Miocene glauconite date (6.46 ± 0.15 my) from the eastern shores of Virginia (Ward and Blackwelder 1980). Paleontological studies of shelly marine fauna from this time suggest faunal turnover, primarily at the species level (Ward 1992a).

Study Area and Geologic Setting

The Eastover Formation was named and described by Ward and Blackwelder (1980). Prior to publication by Ward and Blackwelder (1980), the sediments belonging to the Eastover were described as belonging to the older Calvert, Choptank and St. Marys, or younger Yorktown formations. The Eastover Formation represents a sequence of upper Miocene sediments that crop out in Virginia, Maryland and North Carolina. It was deposited during the late Miocene (Tortonian to Messinian), and represents a marine pulse culminating a long term, second order

sea level fall (Vail and Mitchum 1979; Culver and Goshorn 1996; Ward and Powars 2004). Molluscan faunas in the Eastover Formation are believed to represent a warm temperate environment (Ward and Blackwelder 1980), but foraminiferal fauna suggest cool water temperatures (Culver and Goshorn 1996). The Eastover Formation contains an assemblage of micro and macrofauna recognizable as distinct from the older St. Marys and younger Yorktown assemblages (Ward and Blackwelder 1980; Ward 1992a; Culver and Goshorn 1996; de Verteuil and Norris 1996).

The Eastover Formation is divided into two members: the Claremont Manor and the Cobham Bay (Ward and Blackwelder 1980). In this study, only the Cobham Bay Member, that formed in an open marine, normal salinity, shallow (few to 60 m) inner shelf environment (Ward 1992a; Culver and Goshorn 1996) will be considered. The Cobham Bay member in the study area (Fig. 4.1) is a shelly, grain-supported fine to medium quartz sand and silty sand, with grains most commonly consisting of bivalve shells. Although the Cobham Bay is a sandy facies, shelly sand beds become interbedded with low diversity, often nearly monospecific siltier beds to the north and northeast. Only strata proximal to the type section near Cobham Bay along the James River (Fig. 4.1b, Sites 1 - 6) will be considered for analysis to ensure maximum facies comparability with strata of the Sunken Meadow.

The Sunken Meadow Member of the Yorktown Formation is also a grain-supported, shelly quartzose sand, believed to represent a warm temperate environment (Ward and Blackwelder 1980). Depositional conditions have been described as a shallow, open marine, shifting sand environment (Johnson et al. 1980; Ward and Blackwelder 1980). Macrofaunal horizons are poorly sorted and show no grading within bedding, suggesting that faunal patchiness would be preserved, and transport and winnowing are likely to have been negligible

(Miller 1997; Barbour Wood and Miller 2002; Holland 2005; Webber 2005; Zuschin et al. 2005). Water temperatures are warmer than in the Cobham Bay of the Eastover Formation based on foraminiferal diversity (Culver and Goshorn 1996). Along the James River (Fig 4.1b.), the unit is thin, often measuring less than two meters in thickness, and is abundantly shelly with well-preserved fauna, even in the sand sized range.

The contact between the two units in the study area is sharp, and may be locally marked by a thin bone lag interspersed with overlying Sunken Meadow sediments and fauna. Elsewhere in the depositional basin, the contact may also be marked by small quartz pebbles, phosphate nodules and bioturbation (Ward and Blackwelder 1980). An increase in the rate of encrustation by barnacles, particularly on the bivalve *Chesapecten* is often observed around the boundary separating the two studied units. Faunal changes are also evident upon close inspection, and most pronouncedly marked by the disappearance of the bivalve *Isognomon sp.*, gastropod *Turritella plebia plebia*, and the appearance of the bivalve *Pecten clintonius*, though the species are not always found adjacent to the boundary. The Sunken Meadow sediments are also cleaner and better sorted (Ward and Blackwelder 1980) as well as less phosphatic and glauconitic (de Verteuil and Norris 1996) than in the Cobham Bay, but the contact between the units is often difficult to pinpoint, and has been a subject of a debate (Johnson and Goodwin 1969; Johnson et al. 1980).

Few radiometric dates are available for the sampled units. A glauconite from the upper part of a subsurface unit from an unspecified location in the eastern shores of Virginia believed to be the Eastover was dated at 6.46 +/- 0.15 million years by J. P. Owens (Ward and Blackwelder 1980). The age equivalence of beds in this unit relative to beds that crop out in the study area is unknown, but changes in basin floor geometry, regional dip and the amount of

erosion along the contact across the basin as noted by Ward and Blackwelder (1980) make exact age equivalence to uppermost Miocene beds in the study area (Fig. 4.1) improbable. The next available glauconite radiometric date is from the Rushmere Member of the Yorktown Formation, overlying the Sunken Meadow Member, which was dated at 4.4 +/- 0.2 million years, with the Sunken Meadow Member being approximately dated via biostratigraphy (Ward and Blackwelder 1980). Given available data, duration of the Miocene-Pliocene unconformity in the study area is not known.

Materials and Methods

Bulk field samples were collected in replicate from six localities (Fig. 4.1). Samples were either collected bed by bed, or, when bedding was massive or obscured, at finely spaced intervals (≤ 0.5 m). This protocol was designed to maximize the stratigraphic resolution of sampling and ensure good vertical coverage of sampled successions. At collection Sites 1 – 4 (Fig. 4.1b), multiple stratigraphic sections were sampled where outcrops permitted. During collection, the outcrop surface was scraped to remove residual overburden and trenched along the perimeter of the sample. Chisels were driven into the outcrop and leveraged simultaneously to pop out intact blocks of shell-laden sediment in attempt to maintain original shelly packing and reduce physical destruction of samples during collection, transportation and sample processing. To further minimize post-collection biases, sediment replicates were transferred into multiple clean double-layered plastic bags housed in 75-lb polypropylene sand bags for additional support during transportation, though some specimen fragmentation and destruction likely occurred despite those efforts (Flessa et al. 1992).

Faunal data from samples reported to have been collected in bulk from the Virginia Museum of Natural History in Martinsville were also incorporated into this study (collection Sites 2-6, Figure 4.1b). Extensive pilot analyses suggest that bulk field and preexisting Museum collections from the study area are indistinguishable statistically in terms of diversity and faunal composition (Barbour Wood and Kowalewski 2005; Barbour Wood et al. 2005). Moreover, all analyses presented here produce remarkably similar results when Museum samples are excluded. Thus, both sources of data are combined below to maximize the statistical power of numerical analyses.

In the lab, each field-collected replicate was weighed (generally 5 – 10 kg) and wet sieved. For each sample, specimens passing through a #10 sieve (2 mm openings) were placed in containers for storage. Molluscan specimens retained by the sieve were sorted and tabulated to the finest taxonomic level possible, typically to the species or genus level for bivalves and gastropods by a single operator (Barbour Wood), using taxonomic identifications of L. W. Ward to reduce operator error in identification. Though already sorted, museum samples were treated in the same way. For bivalve fauna, each disarticulated valve was counted as a single individual. Corrections to the data set for the number of bivalved individuals have not been made as bivalves and gastropods are not being analyzed jointly in multivariate ordinations presented below. Non-molluscan fauna was also identified in the samples, but was comparatively rare and therefore excluded from all analyses. Samples were conservatively culled by removing rare genera representing < 0.05% in total specimen abundance and by excluding samples containing less than 100 specimens. This procedure removed approximately half of the genera (50 out of 104), but only 367 specimens. Multivariate ordinations performed with rare genera included (not shown) do not differ notably from those presented below. The final data matrix, including Museum

samples, contained 110 samples (62 Miocene and 48 Pliocene) including 54 genera and 51,244 specimens. A summary of samples collected from each site can be found in Table 4.1.

Samples are housed at the Virginia Museum of Natural History. Sediments remaining from the sieving process, ranging from fine sands to clays, were air or oven dried, bagged, and also housed at the Virginia Museum of Natural History for storage. These sediments were noted to contain microfossils, but were not processed further for the purpose of this research. Sediment grain size analysis was conducted for one stratigraphic section from Site 3 and one from Site 4 (Fig. 4.1) by passing sediments through 1.0, 0.5, 0.25, 0.125 and 0.074 mm sieves.

Genera and species were coded using ecological categories defined by the Neogene Marine Biota of Tropical America (NMITA) group and Kowalewski et al. (2006) for 1) attachment and stability (free-lying in sediment, epibyssate, endobyssate/semi-infaunal, cemented, or infaunal); 2) burrow depth (epifaunal, semi-infaunal, shallow infaunal or deep infaunal) to assess substrate relationships of infaunal taxa; 3) life mode (infaunal siphonate, epifaunal, infaunal asiphonate, epifaunal recliner, nestler or borer); 4) feeding (suspension feeding, within sediment deposit feeding; surface deposit feeding; carnivore, mucus tube feeding and/or chemosymbiotic); 5) mobility (active, sedentary or immobile); and 6) ornamentation (heavily ribbed or ornamented, somewhat ornamented, or smooth). A chi-square test was applied to test for significant differences in proportion of specimens in a given ecological category for samples grouped relative to the Miocene-Pliocene boundary (using Proc Freq procedure in SAS/STAT, Version 9.1.3). To compare changes in occupation of individual ecological category modes (e.g. the percentage of infaunal organisms) from the Miocene to the Pliocene, abundances for specimens of taxa occupying the modes within each ecological category were tallied and percent transformed for each sample. The Mann-Whitney U test on

medians was calculated using the program PAST (Hammer et al. 2001) for the percent of taxa occupying each ecological mode to test the null hypothesis of no change in median ecological mode occupation in the Miocene as compared to the Pliocene. A summary of results for the chi-square and Mann-Whitney U tests are shown in Appendix 4A.

Multivariate statistical techniques were applied to the relative abundance data matrix for exploratory purposes. The program PC-ORD Version 4.10 (McCune and Mefford 1999) was used to run detrended correspondence analysis, or DCA (Hill and Gauch 1980), reciprocal averaging, or RA (Hill 1973) and Non-metric Multidimensional Scaling, or NMS (Kruskal and Wish 1978). All those ordination techniques produced a similar grouping of samples. Only results from DCA are shown here, as it is commonly used to analyze ecological and gradient data (Scarponi and Kowalewski 2004; Holland 2005). PC-ORD outputs DCA axes scores for both samples and taxa, and the program Deltagraph Version 5.6 (Red Rock Software 2001) was used for graphing.

Results

Ordinations

Results of the DCA ordination are plotted as Figure 4.2, with the primary axis, DC1, accounting for 40.5 % and 46.5 % of variation, and secondary axis, DC2, accounting for 30.7 % and 23.0 % of variation at the species and genus level, respectively. Samples are coded by collection age, and show the most prominent separation by age along the primary axis (Fig. 4.2), with Miocene samples primarily plotting high on the DC1 axis, and Pliocene samples plotting exclusively on the low portion of the DC1 axis for both species and genus level ordinations. Miocene samples show a greater amount of variation in DC1 score than those of Pliocene age

(Fig. 4.2). To reduce potential taxonomic noise and maintain a maximum possible number of samples, further analyses will involve only genus level data. Figure 4.3a illustrates the pattern of change in sample DC1 scores across the Miocene-Pliocene boundary for all samples. High DC1 scores represent older Miocene samples, or those collected low in the section, followed by a gradual trend upward through Miocene strata corresponding with a decrease in DC1 values, continuing into the Pliocene.

DCA allows for samples and taxa to be ordinated simultaneously. Figure 4.4a illustrates the taxonomic plot for all genera. Although sample points have been removed to display ordination of genera more clearly, the convex hulls outlining the areas occupied by Miocene and Pliocene samples (i.e. Fig. 4.2b) have been marked with dashed lines for reference. Abundances of genera were summed for Miocene and Pliocene samples and values were percent transformed separately for the two time intervals (for example, a genus represented by 6 Miocene specimens and 24 Pliocene specimens would be assigned percent values of 20% for Miocene and 80% for Pliocene). The percent of Pliocene representation of each genus (e.g. 80% in the preceding example) was plotted and contoured in Figure 4.4b. This illustrates that taxa with high DC1 scores (those plotting on the right side of Figure 4.3a) are contained exclusively or primarily in Miocene samples, or farthest stratigraphically from the Miocene-Pliocene boundary, and taxa ordinating low on the DC1 axis are primarily found in Pliocene samples. The progressive decrease in DC1 scores from the oldest collected Miocene strata to those in the Pliocene corresponds to the gradual increase in sample composition of genera found in both the Miocene and Pliocene, with Miocene samples collected most proximal to the Miocene-Pliocene boundary being quite similar in taxonomic composition to Pliocene samples (Figs. 4.2b and 4.3).

The change in taxonomic composition of samples across the Miocene-Pliocene boundary is very gradual (see especially Figs. 4.3b-d). Pliocene Sunken Meadow Member samples appeared to be very restricted in taxonomic composition initially, until approximately 100 cm above the boundary (Fig. 4.3a) where Pliocene samples began to show more variable taxonomic compositions as illustrated by variability in DC1 scores. Thus, ordination plots suggest that the taxonomic composition of samples changed in a gradual manner through the Cobham Bay Member (Figs. 4.3 and 4.4b) with no notable shifts in faunal composition around the Miocene-Pliocene boundary.

Ecological Changes

Ecological category occupation changed across the Miocene-Pliocene boundary. Results of the chi-squared test (Appendix 4A) comparing the Miocene and Pliocene samples in terms of all ecological categories (2 by 7 homogeneity table) suggest a statistically significant difference in ecological specimen structure between the two compared time intervals ($p < 0.0001$ for all categories). Ecological modes within each category (e.g. byssally attached, cemented and unattached organisms in the attachment category) were also tested for change across the boundary. Figure 4.5 illustrates changes in occupation for all modes with total (Miocene + Pliocene) specimen abundances greater than 2%. The ecological results suggest the following changes from the Miocene to the Pliocene (Appendix 4A, Fig. 4.5). Attachment and stability: free-lying and cemented taxa increase, while epibyssate and infaunal taxa decrease. Endobyssate/semi-infaunal taxa also decrease, but not significantly. Infaunal burrowing depth: semi-infaunal taxa increase while shallow infaunal (significantly) and deep infaunal taxa (not significantly) decrease. Life mode: infaunal asiphonate (significantly) and epifaunal (not

significantly) increase while infaunal siphonate and epifaunal recliner taxa significantly decrease. Feeding: no significant changes were observed, though suspension feeders increased and surface deposit feeders decreased. Mobility: immobile (significantly) and actively mobile (not significantly) taxa increased while sedentary taxa significantly decreased. Finally, heavily ornamented taxa significantly decreased. Moderately ornamented and smooth taxa both increased, but not significantly so.

Sediment Analyses

Sediment analyses suggest that substrates were becoming progressively finer grained upward through the Cobham Bay Member approaching the Miocene-Pliocene boundary (Fig. 4.6). This fining upward trend strongly mimics decreasing DC1 scores in the Miocene (e.g. Fig. 4.3) suggesting that DC1 scores may reflect changes in substrate, which in turn may reflect decreasing bottom water energy levels or increasing depth. Above the boundary, the grain size trend reverses, as sediments coarsen upward within the Pliocene Sunken Meadow strata of the Yorktown Formation toward the overlying Rushmere Member (Fig. 4.6). The Pliocene DC1 scores do not show a reverse in trend from those in the Miocene. They are, however, initially low proximal to the Miocene-Pliocene boundary and thereafter become more variable (Fig. 4.3a), ranging from low to medium scores on the DC1 axis. Thus, if DC1 does at least partly indicate changes in substrate, the Pliocene coarsening upward trend does not mimic the DC1 axis as strongly as in the Miocene, but genus scores do become more variable. Substrate and bathymetric preferences are not widely available for genera within similar environments to the study area. However, data for average collection depths along the United States Atlantic and Gulf of Mexico coasts were gathered for nineteen genera with extant morphologically similar

species from various web sources. A significant, though weak, correlation between DC1 score and bathymetry was found (adjusted $r^2 = 0.36$, $p = 0.004$).

Discussion

Faunal composition of samples changes gradually over time from the Miocene Cobham Bay Member to the Pliocene Sunken Meadow Member. Observed faunal changes are likely tracking environmental parameters changing over time. Changes in substrate evident via grain size analysis in tested samples possibly reflect water energy and/or depth, and may have produced an upward gradient in faunal associations. Changes in substrate appear to mostly mimic changes in DC1 scores, especially in the Miocene part of the studied succession. It is possible that either Pliocene taxa were more tolerant of environmental change, or that other environmental factors yet to be analyzed (e.g. salinity, temperature) may have affected faunal composition (see examples in Scarponi and Kowalewski 2004).

Similarities in taxonomic composition among Miocene and Pliocene samples collected closer to the boundary can either be explained by stratigraphic mixing (burrowing or winnowing) across the boundary, or by a real temporal gradient (i.e., gradual change in taxonomic composition across the boundary). The latter explanation implies that the Miocene-Pliocene boundary must represent a short-term unconformity only. Due to the presence of infaunal taxa in life position and large, thick and abundant epifaunal taxa (e.g. oysters and scallops) found throughout the section, as well as the lack of grading or scouring surfaces, any winnowing or significant disturbance by post-erosional burrowing is unlikely. The presence of a gradual change throughout the collected Miocene sections, mimicked in all sampled sections including

museum collections (Fig. 4.3a-d), further suggests that the gradual change in taxonomic composition across a minor short-term disconformity is a more likely explanation.

The lack of a noticeable break or shift in taxonomic composition between these two sandy members is also surprising because both were likely deposited in a proximal position relative to the paleoshoreline based on sandy depositional facies and macrofaunal work (Culver and Goshorn 1996). As proximal depositional settings are more likely to experience erosion during sea level regression than deeper, more distal ones, this suggests that the amount of time missing along the Miocene-Pliocene boundary in the vicinity of the collection area is likely to be brief, at least on an evolutionary scale. Moreover, Strontium dates obtained from shells of the genus *Chesapecten* collected from Site 4 of the study area (Fig. 4.1) suggest that uppermost Cobham Bay strata are indistinguishable in age from those in the Sunken Meadow (Badiali 2005). It is likely, however, that deposits in different parts of the basin may have been subject to differential amounts of post-depositional uplift and erosion or sediment bypass leading to variable amounts of missing time along the unconformity. Although macrofaunal turnover is present along the boundary, it occurs primarily at the species level, which, as discussed above, may be problematic for a number of reasons.

Observed trends may also mimic the microfossil record, which shows little change across the Tortonian-Messinian and Messinian-Zanclean boundaries. Bergren et al. (1995) note that the planktonic foraminiferal and calcareous nannoplankton records show no significant change across the Tortonian/Messinian boundary (located within planktonic foraminifera Zone N17 and calcareous nannofossil Zone NN11), or across the Miocene-Pliocene boundary (Messinian-Zanclean; within planktonic foraminifera Zone N18 and calcareous nannofossil Zone NN12). De Verteuil and Norris (1996) collected samples from the Claremont Manor and Cobham Bay

Members of the Eastover and Sunken Meadow Member of the Yorktown from the study area (Fig. 4.1b, Site 4) and correlate the majority of calcareous nannofossil Zone NN11 to their dinoflagellate cyst zone DN10, which encompasses all of the Eastover, including the Tortonian-Messinian boundary. However, no zones were created for the Pliocene limiting interpretation and correlation of the Miocene-Pliocene boundary.

Changes in ecological partitioning over time, currently analyzed by broad specimen age (Miocene Cobham Bay Member or Pliocene Sunken Meadow Member) cannot be directly compared to changes in substrate, which may accommodate an environmental gradient. The relationship between changes in grain size over time (as delineated by stratigraphic collection horizon) is not unidirectional: the Cobham Bay fines upward toward the Miocene-Pliocene boundary, and the Sunken Meadow coarsens upward through sampled strata, but ultimately sediment analyses suggest that both members are represented by the same range in grain sizes. Due to the overall similarities through the deposition of the two units, no *net change* in substrate at the depositional member level can be called upon as a cause for observed changes in ecological modes, though due to differences in data collection and analyses, within-member correlations may still be present, but as of yet undetected.

Conclusions

Extensive high-resolution bulk sampling has allowed us to document quantitative changes in the faunal composition of fossil associations throughout two stratigraphic units separated by a regionally-recognized unconformity believed to represent the Miocene-Pliocene boundary: the Cobham Bay Member of the Miocene Eastover Formation and Pliocene Sunken Meadow Member of the Yorktown Formation. Faunal composition and sediment grain size both

appear to have changed gradually not only within each member, but also across the erosional Miocene-Pliocene boundary. It is likely that genera were tracking continuous environmental changes occurring over time. Moreover, a gradual taxonomic change across the boundary suggests that the Miocene-Pliocene disconformity is unlikely to represent a significant temporal gap in deposition, despite the fact that the studied succession represents a proximal depositional setting (likely, a shallow-water embayment). This interpretation is supported by recent strontium dating (Badiali 2005), which suggests that the two members cannot be distinguished in age along the contact.

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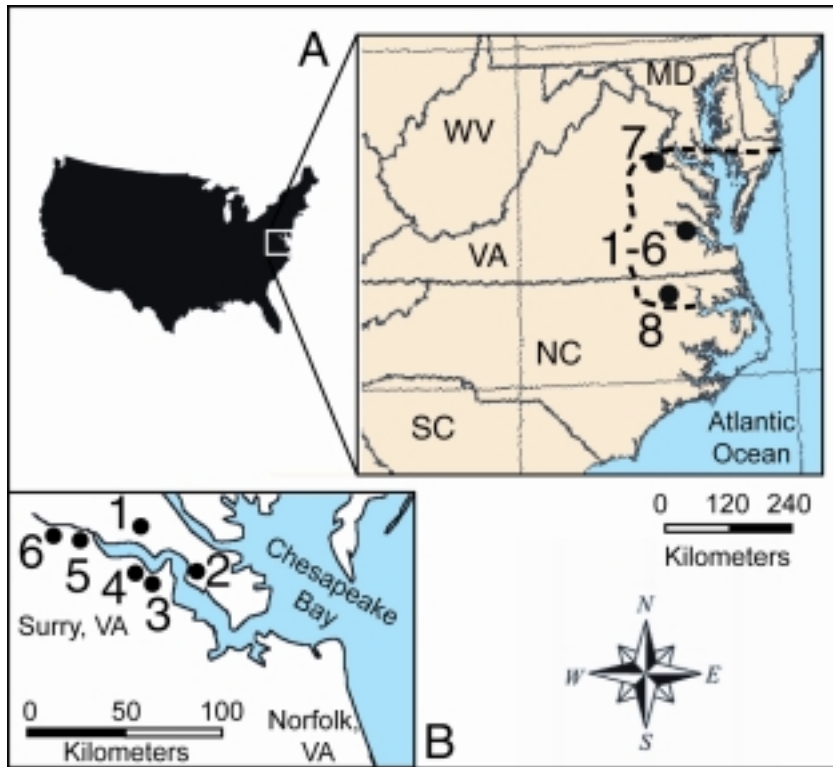


Figure 4 - 1. Overview of the collection area. A. Collection Sites shown in comparison to depositional extent (dashed line) of the Miocene Eastover deposits in the Salisbury Basin. B. Inset shows the location of Sites 1 – 6 sampled along the James River in the Surry, VA and Williamsburg, VA areas.

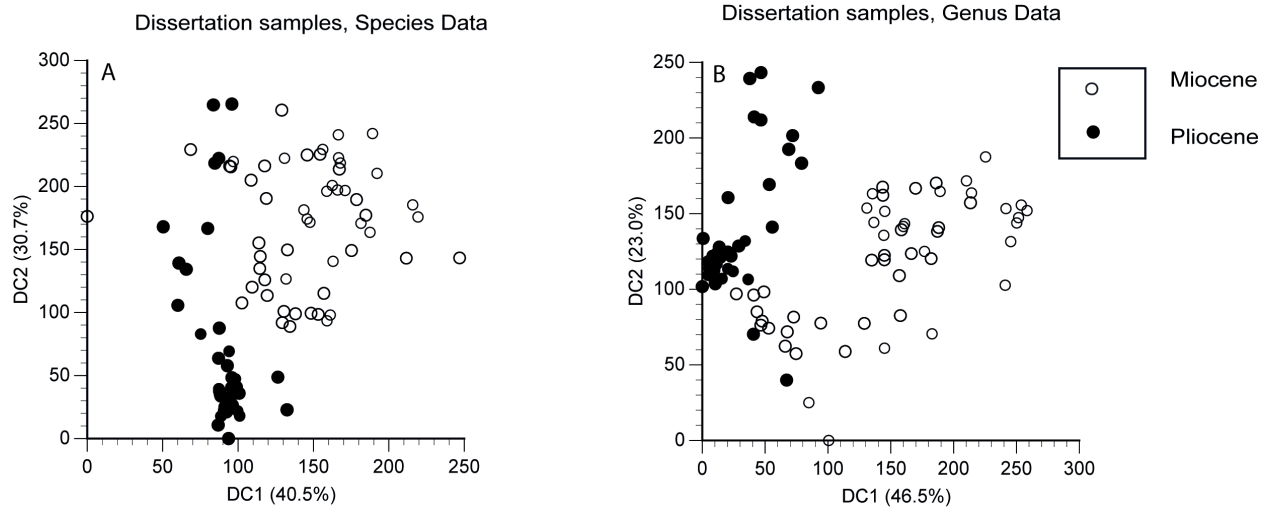


Figure 4 - 2. Detrended correspondence analysis plots for Miocene samples (open circles) and Pliocene samples (closed circles) at both the species (plot A) and genus level (plot B). For both genus and species-level data, Pliocene samples generally plot with lower DC1 scores than those collected in the Miocene.

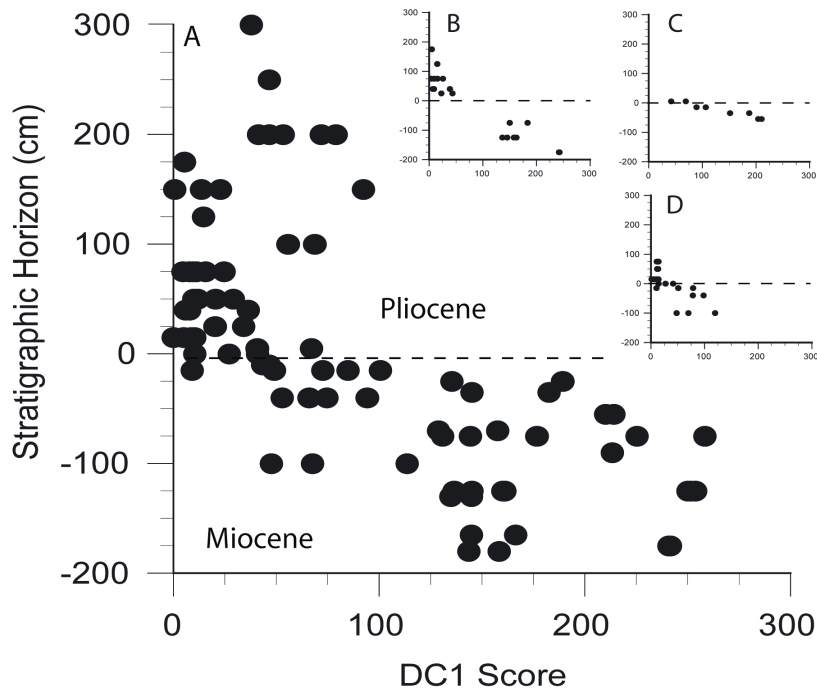


Figure 4 - 3. DC1 sample scores from Sites 2 – 4 plotted against stratigraphic collection horizon, where 0 cm and the dashed line represent the Miocene/Pliocene boundary. Inset B shows samples from collection Site 3, Chippokes State Park, where boundary samples were not collected. Insets C – D show samples from different sections at Site 4, Cobham Bay, both of which were collected continuously across the boundary.

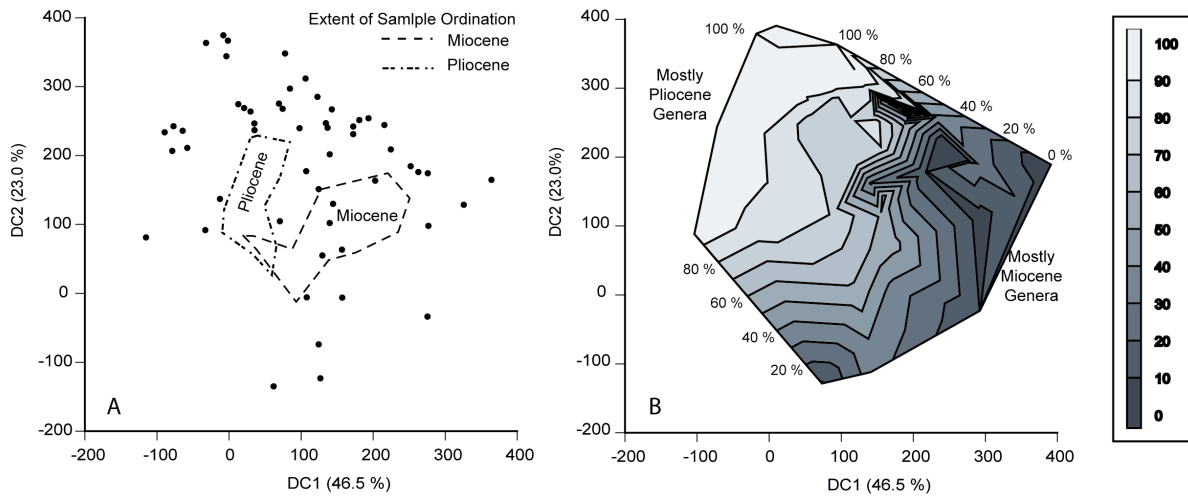


Figure 4 - 4. Detrended correspondence analysis plots. A. Ordination of Miocene and Pliocene genera (closed circles) plotted within the same space as samples. Convex hulls delineating the area occupied by Miocene samples is depicted by a dashed line and Pliocene sample are marked by a stippled dashed line. B. DCA plot depicts the percent Pliocene sample abundance represented by each genus, where a genus plotted at 0% is only contained in Miocene samples, and one plotted at 100% is only contained in Pliocene samples.

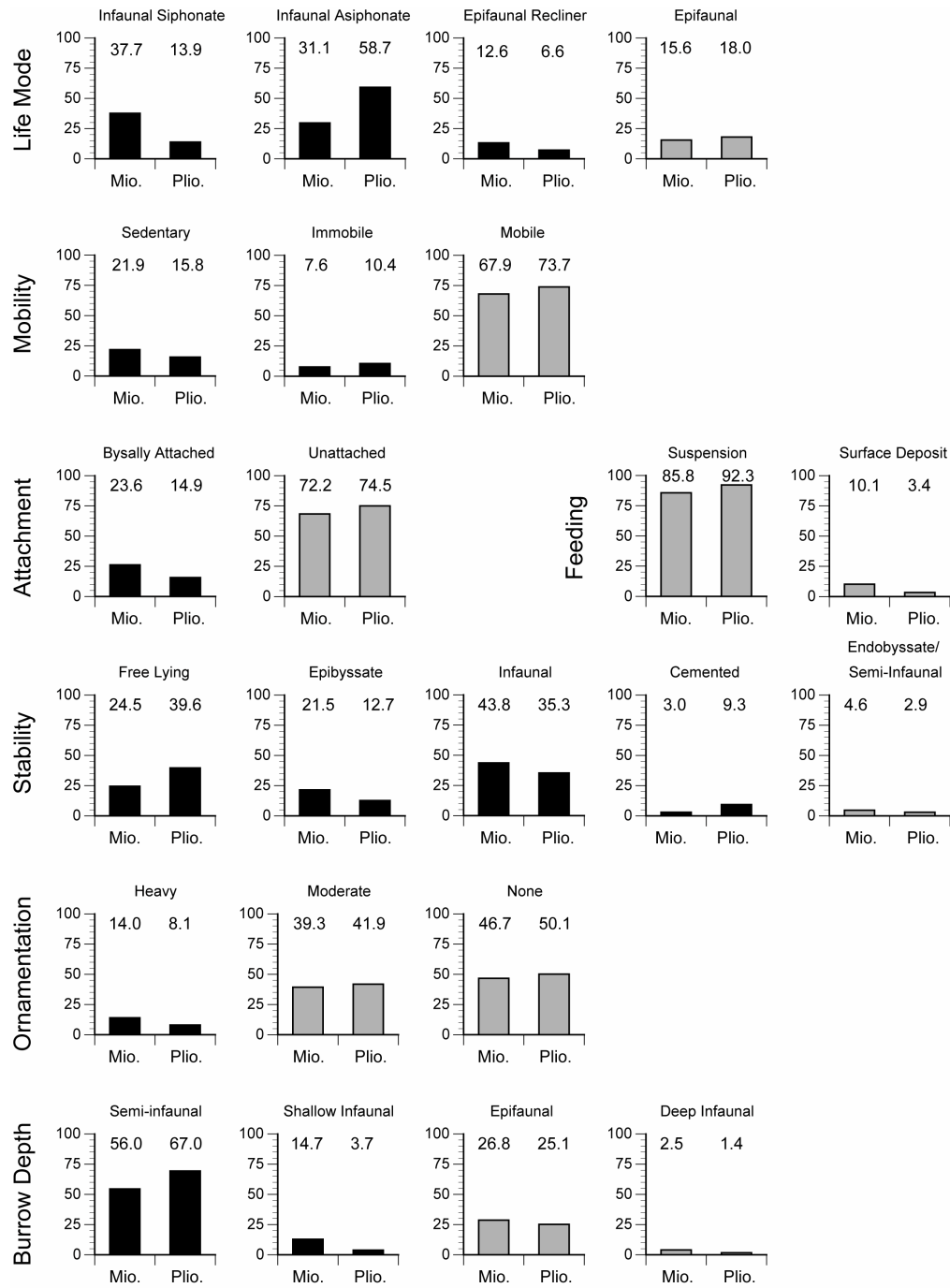


Figure 4 - 5. Plots show guild occupation with percent specimen abundances (noted above each bar) greater than 2% for each ecological category. Guilds showing a significant change in occupation (Mann-Whitney U test) across the Miocene/Pliocene boundary are plotted as black bars, and those which are not significant are plotted as gray bars.

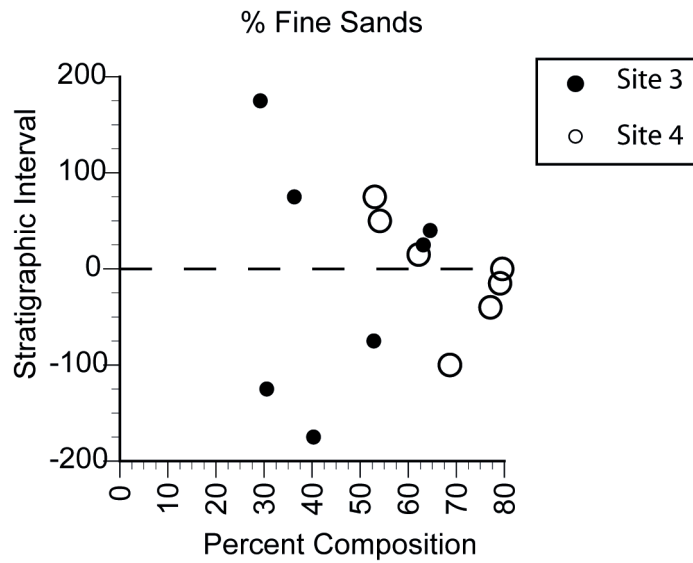


Figure 4 - 6. Percent fine-grained sands (# 120 US Standard Sieve Series, 0.125 mm opening) plotted against stratigraphic collection horizon, where 0 cm and the dashed line represent the Miocene/Pliocene boundary. Medium-grained sands decrease and fine and very fine-grained sands increase in abundance upward through the stratigraphic section approaching the Miocene/Pliocene boundary. Medium-grained sands increase and fine and very fine-grained sands decrease in abundance upward into the Pliocene throughout the Sunken Meadow Member.

Table 4 - 1. Summary of collections obtained from each site.

Field Locality (From Fig. 1)	Collection Type	No. Sampled Sections	No. Replicate Samples
1 Lake Matoaka Spillway	Field	1	6 Miocene
	Field	3	15 Pliocene
2 Carter's Grove	Museum	-	1 Pliocene
	Field	2	8 Miocene 12 Pliocene
3 Chippokes State Park	Museum	-	1 Miocene
	Field	5	36 Miocene 14 Pliocene
4 Cobham Bay	Museum	-	4 Miocene 3 Pliocene
	Museum	-	1 Miocene 3 Pliocene
5 Mt. Pleasant	Museum	-	3 Pliocene
6 Claremont Manor	Museum	-	3 Pliocene
7 Stratford Hall	Field	1	Miocene
8 Meherrin River	Field	3	Miocene
Totals			50 Miocene 41 Pliocene

Susan L. Barbour Wood

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Education

Virginia Tech: B.S. 1997 - Geological Sciences

- Advisor Richard Bambach

University of Cincinnati: M.S. 2002 - Geological Sciences

- Advisor Arnold I. Miller
- Thesis: Barbour Wood, Susan L., 2002. *Microstratigraphic analysis of an amalgamated horizon in the Type Cincinnati: Implications for spatio-temporal resolution in the fossil record.*

Virginia Tech: Ph.D. 2006 – Geosciences

- Advisor Michał Kowalewski

Supplemental Education

Friday Harbor Marine Laboratory, University of Washington: 1997

- Molluscan Paleobiology: participated in a rigorous five week lecture and laboratory course on modern and fossil mollusks
- Course involved observation of dredged live marine mollusks and other organisms, dissection, comparative anatomy, SEM work, weekly presentations and independent research with a final report

Teaching Awards and Experience

Sunderman Teaching Award, University of Cincinnati, 2000. This award was given to one student per year for excellence in teaching based on faculty review and student evaluations. I received this for award for Oceanography and Earth in Upheaval.

C. G. "Jake" Tillman Teaching Endowed Award, Virginia Tech 2005. This award was given to two students per year (one for upper level courses and one for lower level courses) for excellence in teaching based on faculty review and student evaluations. I received this award for teaching the Paleontology Laboratory.

Undergraduate Student Mentor, Virginia Tech: 2005-2006

- Mentorship in research with two undergraduate students interested in geobiology, one in biogeochemistry and two in geoscience education
- Aided students in creating single semester to year-long projects to illustrate scientific methods and research practices geared toward publication

- Students presented findings (15-minute GSA style) at the annual Geosciences Research Symposium (Department of Geosciences, Virginia Polytechnic Institute and State University), and at either regional or annual Geological Society of America meetings

2002-2006: Laboratory Instructor, Virginia Tech

- Created lab outline and syllabus, set up and maintained specimens/material for weekly labs, created weekly lesson plans and administered short lecture to introduce taxa/concepts covered in each lab, created exams and lab exercises, and graded student work
- **Guest Lecturer**, presented multiple lectures (in the lecture section) per course

Paleontology, Virginia Tech: Spring 2005

- Unaided responsibility for approximately 30 students in two lab sessions per week

Earth and Life Through Time (Historical Geology), Virginia Tech: Spring 2002, Spring-Fall 2003, Fall 2005-Spring 2006

- Lab Coordinator (2003, 2005-2006)
- Lab Instructor (2002-2006): Unaided responsibility for approximately 24 students per lab session (1-3 sessions each semester)

Lab developer, Earth and Life Through Time (Historical Geology), Virginia Tech: 2002 – 2005

- Co-created, edited and produced exercises and supplementary material for the Earth and Life Through Time (Historical Geology) lab manual
- Collected and restocked sedimentary rocks and other lab materials as necessary

Lab developer, Field Methods, Virginia Tech: 2003

- Co-created and led a field-based lab exercise in the Type Cincinnati (Upper Ordovician, Cincinnati, Ohio) to teach field-based fossil collection, identification, and analytical techniques to Freshmen geoscience students

1999-2001: Teaching Assistant and Laboratory Instructor, University of Cincinnati

Evolution of Life: Planet Earth, University of Cincinnati, Spring 2000

Earth in Upheaval, University of Cincinnati, Winter 2000

Oceanography-Planet Earth, University of Cincinnati, Fall 1999

Environmental Geology I-III, University of Cincinnati, Fall 1998 - Spring 1999

Curriculum Developer and Activity Leader, Geological Education Outreach (GEO)

Program, Department of Geosciences, Virginia Tech: 1997 – 1998

- Co-developed and led weekly workshops on hands-on fossil, mineral and earthquake activities for 1st -6th grade students at local elementary schools according to Standards of Learning (SOL) requirements for each grade

Research Grants

Doctoral research, Virginia Tech:

- 2005 **Virginia Museum of Natural History Graduate Student Grant** for graduate research awarded to one student per year
- 2003 **American Museum of Natural History Theodore Roosevelt Memorial Fund** for graduate research
- 2003 **Byron Nelson Cooper Memorial Fellowship**, Virginia Tech, competitive grant for graduate research
- 2003 **Graduate Research Development Project Grant**

Master's research, University of Cincinnati:

- 1999 **Geological Society of America Student Research Grant**
- 1999 **Paleontological Society Research Grant with Top Ranked Research Proposal** (Mid-American Paleontological Society (MAPS) Award)
- 1999 **University Research Council Award**, University of Cincinnati, competitive grant for graduate research

Awards and Professional Recognition

- 1997 **Sigma Gamma Epsilon W.A. Tarr award**, Virginia Tech, for public service and leadership
- 1996 **Lowry Geoscience Scholarship Fund**, Department of Geology, Virginia Tech
- 1996 **Dinamation International Society Scholarship Fund**
- 1996 **Alfred and Rose Miniaci Scholarship**

Research Experience

2002-2006 Doctoral student, Virginia Tech

- 2002-Present: Research Assistant, Virginia Tech
- Effects of environmental change on ecological and diversity patterns over time
- Determination of how different types of data collections (e.g. bulk field, museum, etc.) affect portrayal of paleobiological trends
- Morphological change in the genus *Astarte* over a time of potential environmental stress
- Climatic and environmental interpretations using geochemical methods
- Age dating shells using amino acid racemization and carbon dating

1998-2001 Master's student, University of Cincinnati

- Spatial and temporal patterns of fossil assemblages within and across storm deposits

- Reconstruction of sea floor patchiness and determination of the potential for storms to disrupt community structure over time

1996-97 Undergraduate student, Virginia Tech

- Rates of predatory drilling in the Yorktown Formation (Pliocene), Virginia and predation trends through time on multiple common bivalve genera consisting of different shell structures, thicknesses, internal volumes and ecologies
- Depositional environments and sea level changes through the Mississippian Greenbrier Formation, Virginia

Publications

Barbour Wood, Susan L., Richard A. Krause, Jr., Michał Kowalewski, John F. Wehmiller, and Marcello G. Simões, 2006 (in press). Aspartic acid racemization dating of Holocene calcitic brachiopods and aragonitic bivalves from the southern Brazilian shelf, South Atlantic. *Quaternary Research*.

Kowalewski, Michał, Wolfgang Kissling, Martin Aberhan, Franz Fürsich, Daniele Scarponi, **Susan L. Barbour Wood** and Alan P. Hoffmeister, 2006 (in press). Ecological, taxonomic, and taphonomic components of the post-Paleozoic increase in sample-level species diversity of marine benthos. *Paleobiology*.

Barbour Wood, Susan L., Michał Kowalewski, Rowan Lockwood and Lauck W. Ward. Did environmental change cause extinction or patchiness? Analyzing faunal trends across the Miocene/Pliocene boundary. Expected to be submitted to *Palaeos* for publication June 2006.

Barbour Wood, Susan L. and Arnold I. Miller. Spatio-temporal resolution of an Ordovician storm horizon. Expected to be submitted to *Palaeos* for publication July 2006.

Barbour Wood, Susan L., Richard A. Krause, Jr., Michał Kowalewski, John F. Wehmiller and Marcello G. Simões. The search for a taphonomic clock: A comparison of rates of time averaging and taphonomic decay between brachiopods and bivalves. Expected to be submitted to *Lethaia* for publication July 2006.

Barbour, Susan L., 1999. Multi-scale analysis of spatial faunal variability and microstratigraphy in the Fairview Formation (Upper Ordovician), Northern Kentucky. In Algeo, T.J. and Brett, C.E. eds., *Sequence, cycle & event stratigraphy of Upper Ordovician & Silurian strata of the Cincinnati Arch region*. Field Trip Guidebook in conjunction with the 1999 Field Conference of the Great Lakes Section SEPM-SSG (Society for Sedimentary Geology) and the Kentucky Society of Professional Geologists, October 8th – 10th, 1999, p.117-122.

Published Abstracts

- Barbour Wood, Susan L.** and Michał Kowalewski, 2005. Late Cenozoic molluscan diversity and ecology: Patterns from the fossil record of Virginia. *Geological Society of America Abstracts with Programs*, vol. 37, no. 7, p. 461.
- Krause, Richard A., Jr., **Susan L. Barbour Wood**, Chris Romanek, Michał Kowalewski, Marcello G. Simões and John F. Wehmiller, 2005. The multi-centennial dynamics of an upwelling system revealed by stable isotope and trace element sclerochronology of amino-acid dated bivalve and brachiopod shells. *Geological Society of America Abstracts with Programs*, vol. 37, no. 7, p. 525.
- Barbour Wood, Susan L.**, Michał Kowalewski and Lauck W. Ward, 2005. High discordance of molluscan diversity and evenness patterns from the Late Cenozoic fossil record of Virginia? *North American Paleontology Convention Programme and Abstracts 25* (Supp. to 2): 17-18.
- Kowalewski, Michał, Marcello G. Simões, **Susan L. Barbour Wood**, Richard A. Krause, Jr., S. C. Rodriguez, John F. Wehmiller, David L. Rodland and Monica Carroll, 2005. Holocene terebratulid brachiopods from the southern Brazilian Shelf (South Atlantic): Ecology, taphonomy, and time-averaging. *Fifth International Brachiopod Congress*, Copenhagen, Denmark.
- Barbour Wood, Susan L.**, Michał Kowalewski and Lauck W. Ward, 2004a. Quantifying collection biases in bulk, museum and literature-based molluscan sample data. *Geological Society of America Abstracts and Programs*, vol. 36, no. 5, p. 456.
- Barbour Wood, Susan L.**, Richard A. Krause, Jr., Michał Kowalewski, John F. Wehmiller and Marcello G. Simões, 2004b. Time averaging on a shallow subtropical shelf: The search for a taphonomic clock. *Geological Society of America Abstracts and Programs*, vol. 36, no. 2, p. 134.
- Krause, Richard A., Jr., **Susan L. Barbour Wood**, John F. Wehmiller, Michał Kowalewski, and Marcello G. Simoes, 2004. A comparative analysis of time averaging for bivalves and brachiopods from a modern tropical shelf. *Geological Society of America Abstracts with Programs*, vol. 36, no. 5, p. 383.
- Barbour Wood, Susan L.**, Richard A. Krause, Jr., Michał Kowalewski, John F. Wehmiller, Marcello G. Simões and Glenn A. Goodfriend, 2003. A comparison of rates of time averaging between the bivalve *Macoma cleryana* and brachiopod *Bouchardia rosea* on a shallow subtropical shelf. *Geological Society of America Abstracts and Programs*, vol. 35, no. 6, p. 273.
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- Barbour, Susan L.**, 1998. Prey selectivity and paleoecology of gastropod predatory borings in bivalves of the Yorktown Formation (Pliocene) of Virginia. *Geological Society of America Abstracts and Programs*, vol. 30, no. 4, p. 2.

Work Experience

- 2000-2001 **Environmental Geologist:** URS Corporation
1998 **Collections Technician:** Virginia Museum of Natural History, Martinsville, VA
1994-1997 **Research and Laboratory Assistant:** Carbonate Laboratory, Virginia Tech

Volunteer and Outreach Activities

Curations Volunteer at the Virginia Museum of Natural History: 2002 – Present

- Aided in collecting and processing fossil samples
- Ph.D. research collections donated to the Virginia Museum of Natural History
- Assisted in setting up and running public and private research field trips, and involved in scientific discussion, history and outcrop description with participants on public trips

Student Teaching, Geological Education Outreach (GEO) Program: 1997 – 1998

- Taught hands-on fossil, mineral and earthquake classes for 1st - 6th grade students at Montgomery County, VA elementary schools according to Standards of Learning (SOL) requirements for each grade

Student Teaching, Virginia Museum of Natural History: 1997

- Assisted in teaching and activities in a week long archaeology and paleontology course for K-7th grade students

Archaeology Field Assistant, Virginia Museum of Natural History: 1997

- Assisted in field setup, coordination of participants, excavation and other site activities in a five-week archaeology dig at Saltville, VA

Technical Skills

- Proficient in computer repair and in many computer applications including image acquisition, calibration and measurement using Scion NIH; Adobe PhotoShop, Illustrator and Acrobat; data analysis and graphics production using PC-ORD, SAS/IML, Microsoft Excel, Harvard Chart and DeltaGraph; and other Microsoft based software packages
- Experienced in webpage design and management using Macromedia, FrontPage and Adobe PhotoShop
- Experienced in thin section and acetate peel production, microdrilling for isotopic work, laser ablation and chemical lab techniques related to the entire process of dating shells by amino acid racemization using gas chromatography

Professional References

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- Arnold I. Miller (geobiology), M.S. Thesis Advisor, Department of Geology, University of Cincinnati, 500 Geology/Physics Building, Cincinnati, OH 45221-0013, *Phone*: 513.556.4022, *Fax*: 513.556.6931, *e-mail*: arnold.miller@uc.edu (personal, teaching, and research reference)
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- Alton C. Dooley, Jr. (geobiology, vertebrate paleontology), Virginia Museum of Natural History, 1001 Douglas Avenue, Martinsville, VA 24112, *Phone*: 276.666.8600, *E-mail*: butchd@vmnh.net (personal, Museum volunteer and research reference)
- Rod Brame, Ph.D. (geobiology), Earth Science Teacher, T.C. Williams High School, 330 King Street, Alexandria, Virginia 22302, *Phone*: 703.824.6800, *e-mail*: roderic.brame@acps.k12.va.us (personal, teaching and student collaboration reference)