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# A continuous multi-millennial record of surficial bivalve mollusk shells from the São Paulo Bight, Brazilian shelf



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## ABSTRACT

To evaluate the potential of using surficial shell accumulations for paleoenvironmental studies, an extensive time series of individually dated specimens of the marine infaunal bivalve mollusk *Semele casali* was assembled using amino acid racemization (AAR) ratios (n = 270) calibrated against radiocarbon ages (n = 32). The shells were collected from surface sediments at multiple sites across a sediment-starved shelf in the shallow sub-tropical São Paulo Bight (São Paulo State, Brazil). The resulting <sup>14</sup>C-calibrated AAR time series, one of the largest AAR datasets compiled to date, ranges from modern to 10,307 cal yr BP, is right skewed, and represents a remarkably complete time series: the completeness of the Holocene record is 66% at 250-yr binning resolution and 81% at 500-yr binning resolution. Extensive time-averaging is observed for all sites across the sampled bathymetric range indicating long water depth-invariant survival of carbonate shells at the sediment surface with low net sedimentation rates. Benthic organisms collected from active depositional surfaces can provide multi-millennial time series of biomineral records and serve as a source of geochemical proxy data for reconstructing environmental and climatic trends throughout the Holocene, not just the present.

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## Introduction

Biomineralized skeletal remains of bivalves, brachiopods, forams, and other shelled organisms collected at, or directly below, the sediment–water interface typically include many long-dead specimens in many marine settings (e.g., Flessa et al., 1993; L. Martin et al., 1996; R.E. Martin et al., 1996; Anderson et al., 1997; Meldahl et al., 1997; Flessa, 1998). When large collections of specimens are dated individually, they can provide a time series of biominerals that contain a wealth of information on past taphonomic, sedimentary, ecological, and climatic processes. With the rapid progress in advanced analytical instrumentation, it is now feasible to acquire large geochronological data sets to analyze the age structure of surficial shell accumulations. Analyzing amino acid racemization (AAR) ratios in biominerals and calibrating the rate of AAR using a subset of specimen independently dated by AMS-<sup>14</sup>C is a particularly cost-effective method of determining the ages of

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large numbers of specimens (e.g., Demarchi et al., 2011). This method has been used in numerous studies focused on evaluating timeaveraging (age mixing) for multiple types of biogenic materials (Wehmiller et al., 1995; Goodfriend and Stanley, 1996; Kowalewski et al., 1998; Carroll et al., 2003; Kidwell et al., 2005; Barbour Wood et al., 2006; Kosnik et al., 2007; Krause et al., 2010). Miller et al. (2013) provide a recent review of the principles and applications of AAR geochronology.

This study presents the results of an extensive dating effort, based on radiocarbon-calibrated AAR rates, obtained on shells of the aragonitic bivalve *Semele casali* Doello-Jurado, 1949, from the southern Brazilian shelf. It builds directly on two previous studies: Carroll et al. (2003) reported estimates of time-averaging for 82 shells of the calcitic brachio-pod *Bouchardia rosea* from our study area calibrated using five AMS-<sup>14</sup>C ages. Subsequently, Barbour Wood et al. (2006) developed a series of AAR calibrations for *B. rosea* and the bivalve *S. casali* using seven and nine AMS-<sup>14</sup>C ages, respectively, and assessed the importance of the variation in reservoir effects and species identity on the precision and accuracy of AAR estimates (Table 1). Krause et al. (2010), using 103 AAR ages for *B. rosea*, 75 AAR ages for *S. casali*, and three additional

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Site information for the analyzed specimens, including the bathymetry, collection method, and number of specimens analyzed for AAR values and AMS-<sup>14</sup>C age in the three geochronological studies conducted in the region.

Site number	Water depth (m)	Latitude	Longitude	Collection method	Number of AAR analyses	Number of AMS- <sup>14</sup> C analyses	Study
Site 1	10	23º26′41″ S	45⁰02′07″ W	Dredge	3	3	Barbour Wood et al. (2006)
Site 1	10	23º26′41″ S	45⁰02′07″ W	Dredge	35	2	Krause et al. (2010)
Site 2	10	23º21′83″ S	44º52'20" W	Dredge	20	0	Current study
Site 3	10	23º23′44″ S	44º49'64" W	Dredge	23	6	Current study
Site 4	15	23º23′32″ S	44º51′05″ W	Dredge	35	0	Current study
Site 5	15	23º22′88″ S	44º52′95″ W	Dredge	1	0	Current study
Site 6	20	23º28′37″ S	45°00′29″ W	Dredge	4	0	Current study
Site 7	20	23º45′53″ S	45º14′78″ W	Dredge	1	0	Current study
Site 8	25	23º29′39″ S	44º59′16″ W	Dredge	11	0	Current study
Site 9	25	23º24′15″ S	44º50'42" W	Dredge	68	17	Current study
Site 10	30	23º28′53″ S	44º55′21″ W	Dredge	6	6	Barbour Wood et al. (2006)
Site 10	30	23º28′53″ S	44º55'21" W	Dredge	31	1	Krause et al. (2010)
Site 11	30	23°59′93″ S	45º23′93″ W	Dredge	2	0	Current study
Site 12	35	23º25′35″ S	44º46'24" W	Dredge	19	0	Current study
Site 12	35	23º25′35″ S	44º46'24" W	Van Veen Grab	5	0	Current study
Site 13	45	23º32′52″ S	44º44'20" W	Dredge	2	0	Current study
Site 14	57	24º03′32″ S	46º07′05″ W	Box Corer	9	0	Current study

AMS-<sup>14</sup>C ages, evaluated differences in age structure between the two species, assessed temporal completeness and shape of AAR-derived age distributions of shells, and updated the AAR calibration (Table 1). This study focuses on *S. casali* and is based on the final dataset of 275 AAR ages and 23 additional AMS-<sup>14</sup>C ages (Table 1). This substantially larger dataset was used to create a calibration curve (power function) that integrates all of the data on *S. casali* from the study area. This robust dataset allows for (1) exploring the quality of the paleoenvironmental record afforded by a time series of numerous, individually dated mollusk shells; (2) assessing time-averaging across numerous sites within a single locality and evaluating variations in localized patterns of age distributions; and (3) assessing variation in time-averaging across a depth gradient.

## Methods and materials

## Study area

Table 1

Shells of the bivalve species *S. casali* were collected from surficial sediments in the shallow marine embayments of the São Paulo Bight marine province (Fig. 1). The São Paulo Bight extends from 23 to 28°S at the northernmost part of the southern Brazilian margin. This arcshaped embayment encompasses (from north to south) the Picinguaba,

Ubatuba, Caraguatatuba, Sao Sebastiao and Santos Bays. River input to São Paulo Bight is minimal and reworking of late Quaternary sediments prevails (Mahiques et al., 2011). The South Brazilian (west boundary) current is the primary water mass, comprising warm, saline waters with an average annual surface temperature of 24°C and a salinity of 34–35‰ (Campos et al., 1999). The surficial sediments are composed primarily of terriginous siliciclastics ranging in size from coarse sands to gravel in shallow water sites and from medium to coarse sands in deeper collection sites (Campos et al., 1999). The Holocene sediments are typically barrier sands ~8 to ~21 m thick which overlay thick (~30 m) organic-rich muds that are interpreted to be estuarine in origin (Lessa et al., 2000).

## Specimens

*S. casali* is a small (<20 mm), relatively thin-shelled infaunal deposit feeder. *S. casali* was selected for this investigation because it is abundant throughout the study area and has a wide bathymetric range of 10 to 180 m (Narchi and Domaneschi, 1977). This species has a modern latitudinal range from 20° to 35°S. The specimens were collected from 14 sites in the study area at multiple water depths (Table 1; Fig. 1). Most shells were collected by dredging, and one sample each was collected using a van Veen grab and a box corer (Table 1). Dredging recovers



Figure 1. Map of the São Paulo Bight marine province in São Paulo State, southeastern Brazil, showing the 14 collection sites (stars).

specimens from the sediment surface and shallow subsurface (32 cm maximum) from across a broad area. The van Veen grab and box corer also collect surficial samples; however, they sample a single point and extend 20–30 cm into the shallow subsurface. The 14 collection sites were located in eight distinctly different water depths, ranging from 10 to 57 m, which we clustered into three depth categories (<20 m, 20–30 m, and >30 m). The sediment for each site was wet sieved and all whole valves of the bivalve *S. casali* were removed for analysis. The number of specimens recovered from the sample at each site ranged from a single valve (at two of the sites) to 68 valves (Table 1). They were generally well-preserved in the samples as disarticulated, unfragmented valves ranging from 10 to 19 mm in length (anterior to posterior).

## Sample preparation and analysis

Specimens were cleaned with a Dremel® Multi-Pro™ Model 395 to remove encrusting epibionts and authigenic minerals. All shells were acid-leached to remove about one-third of the mass, then rinsed in purified H<sub>2</sub>O without bleach. Subsamples of shell material were removed from the exposed internal shell layer at the same position near the valve hinge on each specimen. A subset of specimens (n = 26) were resampled and reanalyzed for AAR. These valves were used to calculate the intra-valve variation in amino acid D/L values. Subsamples were hydrolyzed in 6 M HCl under N<sub>2</sub> for 6 h at 115°C. This process maximizes hydrolysis while minimizing induced racemization (Kaufman and Manley, 1998). During the hydrolysis phase, asparagine (Asn) and glutamine (Gln) undergo deamidation to aspartic acid (Asp) and glutamic acid (Glu), respectively (Hill, 1965; Zhao et al., 1989) and may contribute small fractions to the final Asx and Glx values (Asp + Asn = Asx, Glu + Gln = Glx) (Kaufman and Manley, 1998). Samples were evaporated in vacuo and rehydrated with weak HCl, sodium azide, and a synthetic amino acid used as an internal standard. Samples were then transferred to auto-injection vials for analysis.

The valves were analyzed for AAR at two laboratories. A total of 75 specimens were analyzed at the University of Delaware (UD) in a previous study (Barbour Wood et al., 2006) using an Agilent 6890 Gas Chromatograph. The remaining 200 specimens were analyzed at Northern Arizona University (NAU) using reverse phase liquid chromatography with a Hewlett-Packard HP1100 liquid chromatograph and programmable fluorescence detector (Kaufman and Manley, 1998). Analyses on 33 specimens were conducted at both facilities to ensure the repeatability of the AAR ratios (Krause et al., 2010 explains how the data sets from the two laboratories were combined). Both laboratories reported values for D/L of Asx and Glx. In addition, the NAU laboratory reported values for serine (Ser), and alanine (Ala). Asx was selected as the primary geochronological index because of its abundance in mollusk-shell protein, its superior chromatographic resolution and because it racemizes at a high rate providing a better temporal resolution for relatively young materials compared with other amino acids (Goodfriend et al., 1996).

Glx D/L values were used in concert with Asx D/L values as part of the data-screening process. Although racemization rates differ between these two amino acids, they are expected to covary within individual specimens (Kosnik and Kaufman, 2008). Outliers likely represent confounding factors such as analytical errors, or, possibly, aberrant early diagenetic changes perhaps related to microbial activity. Outliers were identified as those that exceeded the  $\pm 2\sigma$  deviation of the residuals of the reduced major axis regression of D/L Asx versus D/L Glx. Additional criteria used to screen the specimens include a high concentration of the labile amino acid, Ser, which is indicative of contamination by modern amino acids, as well as analytical reproducibility (Kosnik and Kaufman, 2008). These screening criteria were applied only to the new valves analyzed in this study (n = 200) and resulted in the removal of five specimens; the AAR data from the previous studies had already been screened and were used as reported (Barbour Wood et al., 2006; Krause et al., 2010).

## Radiocarbon analyses

Of the 275 *S. casali* shells analyzed for AAR, 35 were sent for AMS-<sup>14</sup>C dating (Table 2). Ten valves were analyzed at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at Woods Hole Oceanographic Institute and the other 25 valves were dated by the Keck Carbon Cycle Accelerator Mass Spectrometry Facility at the University of California–Irvine (UCI-KCCAMS) (Table 2). Radiocarbon ages were calibrated to calendar years with CALIB version 5.0 (Stuiver et al., 2005) using the databases SHCal04 (Southern Hemisphere) and marine04.14c (Hughen et al., 2004; McCormac et al., 2004). A mean marine reservoir age of 408  $\pm$  18 yr ( $\Delta$ R 8  $\pm$  17 yr) was assumed, as established by Angulo et al. (2005). All ages were calibrated relative to AD 1950, and all valves with ages ranging from AD 1950 and younger are considered to be modern in this study (AD 1950 = 0 cal yr BP).

### Calibration of D/L values and data analysis

Numerous mathematical functions have been applied to calibrate the rate of AAR using paired analysis of <sup>14</sup>C age and D/L values (Clarke and Murray-Wallace, 2006). A power function is an appropriate model to fit the data because racemization is a reversible reaction, with highest rates during the early stage of the reaction followed by decreasing rates as the chiral states move toward equilibrium. While using independently dated specimens does not directly measure the rate of racemization as is the case in heating experiments, it has been demonstrated as a viable option for numerous studies of fossil materials (Goodfriend, 1992; Goodfriend et al., 1996; Collins et al., 1999). Live-collected specimens can also be used to determine the initial D/L value (Kosnik et al., 2008). Although no live specimens were available here, the lowest Asx D/L value likely represents the most recently deceased specimen. The lowest Asx D/L value in the dataset was treated as the initial D/L value and subtracted from all specimens in the dataset to set the modern specimens of the power function to zero cal yr BP. The power function was determined using R Version 3.01 (R Development Core Team, 2008) by iteratively raising the exponent of the D/L values to determine the best fit of Asx D/L values with AMS-<sup>14</sup>C ages (Kosnik et al., 2008). A power function was also calculated for Glx and Ala values as well as a subset of Asx values for the valves that had been analyzed for all amino acids in order to determine the differences between calibrated ages using different amino acids.

In order to determine whether distributions of valve ages differed by water depth, the samples were compiled into three depth ranges: shallow (10–15 m), moderate (20–30 m), and deep-water (>35 m) sites. Age distributions from the three categories were compared visually and statistically with a non-parametric Kruskal–Wallis one-way analysis of variance using SAS® software (Hammer et al., 2001). Further, a bootstrap simulation was conducted using SAS® software by iteratively resampling the three depth classes with replacement using the total population of ages. The simulation was conducted with 1000 iterations. The three depth classes were compared to one another at each iteration and maximum, minimum, range, and standard deviation of median ages, mean ages, skewness and kurtosis were recorded.

## Results

A total of 275 specimens were initially analyzed for AAR values. Additionally, 35 were analyzed for AMS-<sup>14</sup>C ages (Table 1). An inspection of the covariance between Asx and Glx D/L values was conducted as part of the screening process in accordance with Kosnik and Kaufman (2008) (Fig. 2A). This screening process removed five specimens (shell# 42508, 161515, 161507, 431501, and 451010) from the dataset that exceeded  $\pm 2\sigma$  deviation in the residuals of the regression (Fig. 2A;

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AMS-<sup>14</sup>C ages used to calibrate Asx D/L values. Analyses were conducted at two laboratories (National Ocean Sciences Accelerator Mass Spectrometry Facility and Keck Carbon Cycle Accelerator Mass Spectrometry Facility). AMS-<sup>14</sup>C ages were calibrated to calendar years using CALIB version 5.0 (Stuiver et al. (2005)).

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Specimen number	14C Lab	14C lab number	Specimen depth (m)	Fraction modern	14C ag	ge	Calibrated age	D/L Asx	D/L Glx	References
91071	NOSAMS	OS-42389	10	1.11	>Modern		0	0.071	N/A	Barbour Wood et al. (2006)
91062	NOSAMS	OS-39672	10	0.91	745	$\pm 35$	378	0.160	N/A	Barbour Wood et al. (2006)
91075	NOSAMS	OS-42453	10	0.71	2770	$\pm 30$	2484	0.246	N/A	Barbour Wood et al. (2006)
13077	NOSAMS	OS-39670	30	0.95	375	$\pm 35$	0	0.072	N/A	Barbour Wood et al. (2006)
13081	NOSAMS	OS-42384	30	0.93	555	$\pm 30$	183	0.083	N/A	Barbour Wood et al. (2006)
13087	NOSAMS	OS-42385	30	0.93	590	$\pm 25$	222	0.111	N/A	Barbour Wood et al. (2006)
13088	NOSAMS	OS-39671	30	0.87	1130	$\pm 30$	676	0.173	N/A	Barbour Wood et al. (2006)
13075	NOSAMS	OS-43396	30	0.85	1350	$\pm 50$	883	0.160	N/A	Barbour Wood et al. (2006)
13071	NOSAMS	OS-39673	30	0.68	3050	$\pm 35$	2808	0.273	N/A	Barbour Wood et al. (2006)
91077	NOSAMS	OS-43397	10	0.90	855	$\pm 50$	474	0.143	N/A	Krause et al. (2010)
91050	UCI-KCCAMS	29524	10	0.82	1595	$\pm 15$	1151	0.228	N/A	Krause et al. (2010)
13050	UCI-KCCAMS	29522	30	0.85	1315	$\pm 25$	851	0.188	N/A	Krause et al. (2010)
182531	UCI-KCCAMS	62185	25	0.95	435	$\pm 20$	0	0.088	0.034	Current Study
182542	UCI-KCCAMS	62187	25	0.93	585	$\pm 20$	217	0.129	0.052	Current Study
182517	UCI-KCCAMS	62184	25	0.86	1210	$\pm 20$	738	0.154	0.072	Current Study
182551	UCI-KCCAMS	62190	25	0.86	1250	$\pm 20$	782	0.178	0.083	Current Study
182537	UCI-KCCAMS	62186	25	0.84	1370	$\pm 20$	911	0.206	0.089	Current Study
182558	UCI-KCCAMS	62192	25	0.76	2160	$\pm 20$	1747	0.229	0.112	Current Study
182502	UCI-KCCAMS	62183	25	0.65	3465	$\pm 20$	3341	0.269	0.136	Current Study
182510	UCI-KCCAMS	72303	25	0.57	4510	$\pm 15$	4714	0.273	0.140	Current Study
182505	UCI-KCCAMS	72304	25	0.51	5415	$\pm 15$	5787	0.313	0.161	Current Study
182544	UCI-KCCAMS	62188	25	0.45	6450	$\pm 20$	6929	0.301	0.160	Current Study
182556	UCI-KCCAMS	62191	25	0.44	6545	$\pm 20$	7057	0.330	0.168	Current Study
182550	UCI-KCCAMS	62189	25	0.39	7480	$\pm 20$	7936	0.377	0.202	Current Study
182528	UCI-KCCAMS	63897	25	0.78	2040	$\pm 15$	1597	0.212	0.098	Current Study
182535	UCI-KCCAMS	63898	25	0.88	1070	$\pm 20$	634	0.167	0.076	Current Study
182541	UCI-KCCAMS	63899	25	0.79	1925	$\pm 15$	1461	0.189	0.089	Current Study
182557	UCI-KCCAMS	63900	25	0.91	785	$\pm 25$	425	0.140	0.062	Current Study
182560	UCI-KCCAMS	63901	25	0.78	2005	$\pm 15$	1558	0.218	0.102	Current Study
451002	UCI-KCCAMS	63902	10	0.83	1540	$\pm 20$	1089	0.195	0.080	Current Study
451012	UCI-KCCAMS	63903	10	0.51	5375	$\pm 25$	5730	0.406	0.201	Current Study
451013	UCI-KCCAMS	63904	10	0.53	5045	$\pm 20$	5383	0.346	0.165	Current Study
451021	UCI-KCCAMS	63905	10	0.58	4410	$\pm 20$	4553	0.324	0.149	Current Study
451022	UCI-KCCAMS	63906	10	0.67	3175	$\pm 20$	2958	0.269	0.120	Current Study
451005	UCI-KCCAMS	72302	10	0.70	2820	$\pm 15$	2574	0.279	0.129	Current Study

open circles). Asx D/L values from the two previous studies were taken as reported and used in concordance with the new amino acid ratios, giving a total of 270 specimens in the final dataset (Appendix 1). Of the 35 AMS-<sup>14</sup>C ages, three valves at 0 cal yr BP were removed from the calibration as they were too young to be accurately dated given the reservoir age, leaving a total of 32 independently dated valves (Table 2).

A power function was used to fit the AMS-<sup>14</sup>C ages and the corresponding Asx D/L values to develop an age equation (Fig. 2B). The lowest Asx D/L value of 0.045 (shell# 91042 and 91065) was treated as an initial amino acid D/L value and subtracted from all specimens. The resulting power function has an  $r^2$  value of 0.92 (Fig. 2B):

 $t = 60282.18 * (Asx D/L - 0.045)^{1.9594}$ 

where t = specimen age in years. This combined-data age equation was used to date all 270 specimens, including slightly revised AAR ages for previously reported data (Fig. 3).

As a measure of the age uncertainty, the standard error of the regression model was calculated based on the regression of the Asx D/L values against AMS- $^{14}$ C ages and yielded an error of 9%. The uncertainty in the ages increases with age, reaching 936 yr for the oldest specimen (10,307 cal yr BP). Another source of uncertainty—the intra-shell variability—was assessed by subsampling and re-analyzing 26 of the specimens for their Asx D/L values and calculating the corresponding difference in age estimates. The reanalyzed specimens ranged in age from 0 (modern) to 5600 yr, and their mean age difference was 298 yr (median = 186 yr).

The resulting age distribution of all shells is right skewed (skewness = 2.14), with shells ranging in age from modern to 10,307 cal yr BP. Of the 270 specimens, 23 (8.5%) represent the youngest

centennial bin (0–100 cal yr BP or AD 1850 to present). The collection includes 79 specimens (29%) younger than 500 cal yr BP. Almost half of the specimens (49%) are <1000 cal yr BP, with a median age for the entire dataset of 1041 cal yr BP. The age distribution shows that the shells make up a nearly complete centennial record (92.5% of the centuries are represented) as far back as 4000 cal yr BP, with only three centennial bins lacking a dated shell (2600, 3800 and 3900 cal yr BP). At binning resolution of 500 yr, the record is 100% complete for 6000 yr (i.e., all 500-yr bins from 0 to 6000 cal yr BP included dated shells; Fig. 3). For the time range of specimens analyzed from São Paulo Bight, the record is 65.9% complete at 250-yr time bins (14 bins of 41 bins lack dated shells) and 81.0% complete with 500-yr time bins (Figs. 3A, B).

The age distributions of specimens are notably different among sample sites (Fig. 4). While all sites display a pattern generally similar to the overall distribution of ages, with a right-skewed distribution and a greater abundance of modern specimens, three sites exhibit a nearly flat age distribution (Fig. 4; Sites 3, 4, and 8). A flat distribution was found in all three water-depth categories. One of these sites was entirely devoid of specimens younger than 500 cal yr BP (Fig. 4; Site 3).

The deepest-water sites (>30 m) contained the three oldest valves in this study (10,307, 9913 and 9288 cal yr BP); however, the relative age distributions of shells from the three depth categories are similar to one another (Figs. 5A–C), and the median shell ages do not vary significantly across the three depth categories (Kruskal–Wallis test:  $\chi^2 = 1.58$ , p = 0.45). A bootstrap resampling analysis with replacement of the three depth categories was conducted in order to model hypothetical age distributions. These hypothetical distributions model the three depth categories as three equivalent populations (i.e., depth invariant) by iteratively sampling random specimens from the entire data set. These hypothetical distributions were then compared to the actual depth distributions to test whether the hypothetical and actual

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**Figure 2.** (A) Comparison between Asx and Glx D/L values for each shell analyzed in this study. Five specimens (open circles) were considered outliers and rejected because the residuals of the major axis regression of D/L values against age exceeded 2*o* deviation. (B) Extent of Asx racemization (D/L) compared with the AMS-<sup>14</sup>C age of 32 specimes analyzed for both Asx D/L and <sup>14</sup>C. A power function was used to calibrate the rate of racemization to derive the age equation. Water depths of the collection site for each specimen are indicated.

depth categories are equivalent as would be expected for specimens collected from the same population (i.e., depth invariant) or whether the actual data are distinct from the hypothetical models (i.e., depth dependent). Median age, skewness, and kurtosis were used to classify each hypothetical depth category as these values describe the central tendency and shape of the distribution. To compare the differences between the three hypothetical depth categories at each iteration, the standard deviation of mean ages, median ages, skewness, and kurtosis were calculated. The standard deviation of these values for each iteration was then recorded to create a distribution of hypothetical outcomes from random specimen selected from the same population (Figs. 5D-E). The standard deviation, mean ages, median ages, skewness, and kurtosis of the actual depth categories were then compared to the hypothetical model (arrows in Figs. 5D-E). The three depth categories had a standard deviation of median ages of 98 yr with a range of 186 yr (870 to 1057 yr). The standard deviation of mean ages was 160 yr with a range of 300 yr (1442 to 1743 yr). The standard deviation of skewness among the depth categories was 0.60 with a range of 1.13 (1.38 to 2.50). The standard deviation of kurtosis was 2.03 with a range of 3.82 (1.74 to 5.56). The actual values observed for the data are well within the range of expected standard deviations predicted by the hypothetical models of specimens pooled from the same population.

To assess the influence of depth on the rate of AAR, age equations were calculated for the three depths for which AMS-<sup>14</sup>C ages were available (10 m, 25 m, and 30 m). Each of these depth-specific equations was applied to the entire data set of amino acid ratios to derive three separate age distributions (Table 3). Multiple statistical metrics were used to compare the ages attained from the depth-specific equations to the combined equation to address the possible influence of depth on AAR rates (Table 3). The three depth-specific equations created age



**Figure 3.** Age distribution of the 270 analyzed specimens of *S. casali*. Ages were determined using a single calibration equation calculated using 32 AMS-<sup>14</sup>C-dated shells that were also analyzed for amino acid racemization (Fig. 2B). Specimens range in age from modern to >10,000 cal yr BP. Specimens were grouped into two different bin sizes (A) 250 yr intervals, and (B) 500-yr intervals. The structure of the age frequency is maintained when the bin size is varied, showing this nearly continuous distribution through time.

distributions that were similar for the entire dataset and for the combined equation regardless of depth (Table 3).

While D/L Asx values were analyzed for all AMS-<sup>14</sup>C dated specimens, D/L values for other amino acids were available for only some of those specimens. These data were used to calculate calibrated age equations for Glx and Ala. The resulting ages are similar to those using Asx, despite fewer calibration points (Table 4). The distribution of Glx-inferred ages has a similar structure to Asx ( $r^2 = 0.9174$ ), but the Glx age estimates are younger than those obtained using the Asx calibration (Table 4). Ala-inferred ages are highly consistent with the Asx ages ( $r^2 = 0.9274$ ). Ser cannot be used for AAR geochronology because it typically reaches a maximum value of about 0.4, then decreases with age. Ser values are reported because they can be indicative of contamination. To further assess the differences in amino acids, Asx was reevaluated and a new calibration curve recalculated using only the AMS-14C-dated specimens for which Glx and Ala was also available (n = 22). This new calibration was applied to date only the specimens for which other amino acid values were analyzed on the valve (n = 195) to make the age distributions comparable (Table 4; Asx subset). The difference in ages for valves calibrated using Asx (subset) versus Glx has a mean value of 379 yr (median = 217 yr). When comparing Asx (subset) to Ala, the mean difference in ages is 429 yr (median = 345 yr).

## Discussion

Geochronology and implications for future research

The AAR dated shells, collected from the taphonomically active zone (TAZ, sensu Davies et al., 1979), reveal a right-skewed temporal

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Figure 4. Distribution of specimen ages by collection site for all sites with 10 or more specimens. Age distributions differ among sites. While most are dominated by young shells from most recent centuries, a few of the sites include relatively few young shells (Sites 8 and 4) or completely lack (Site 3) modern specimens.

distribution that includes valves with long (multi-millennial) residence times (Fig. 3). The dated shells comprise a remarkably complete time series, with nearly every century represented by at least one specimen, back to 4000 cal yr BP (missing only the 2600 and 3800 and 3900 cal yr bins). Right-skewed age distributions including old shells near the sediment surface have been observed in many recent studies (Kowalewski et al., 1998; Carroll et al., 2003; Kidwell et al., 2005; Kosnik et al., 2007), though the temporal range for the material analyzed here exceeds what has been observed previously in other depositional settings (see Kowalewski, 2009 for a comparison of age distributions for various species). The dated shells were collected across a depth gradient from which we can assess whether temporal mixing varies significantly with water depth. Previous studies suggest that mean specimen age and extent of time-averaging increase with increasing distance from shore (Flessa and Kowalewski, 1994). For this study, the specimen depth categories were coarsely grouped because samples from some depths included only a few specimens. Comparison of the age distributions based on the three depth categories suggests similar scales and structures of time-averaging. The non-parametric Kruskal–Wallis one-way analysis of variance suggests that the three depth assemblages were not significantly different ( $\chi^2 = 1.58$ , p = 0.45). Further, the age distributions of

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**Figure 5.** Age distributions grouped by specimen collection depth. Depth categories include (A) shallow (<20 m), (B) moderate (20–30 m), and (C) deep (>30 m). Frequency is given as a percent of the total number (n) of specimens from each depth category. All bathymetric ranges display similar age distributions. A bootstrap analysis with replacement was conducted to determine the potential age distribution of specimens sampled from the same population. The frequency of the standard deviation of the median ages (D) and standard deviation of skewness (E) between the three depth categories was recorded for 1000 iterations of the bootstrap analysis. The arrows in panels D and E indicate the actual standard deviation of the median ages = 162 yr, standard deviation of actual skewness = 0.6163). The actual standard deviation of median ages was located well within the potential values determined by the bootstrap analysis using specimens sampled from the same population. The frequency is given as a not skewness was located well within the potential values determined by the bootstrap analysis using specimens sampled from the same population of actual median ages and skewness was located well within the potential values determined by the bootstrap analysis using specimens sampled from the same population. The bootstrap analysis using specimens sampled from the same population. The bootstrap analysis using specimens sampled from the same population. The bootstrap analysis failed to demonstrate that the three depth categories are significantly different from one another.

shells from the three depth categories had similar skewness, median, mean, and kurtosis with low among-group standard deviations (Table 3). By using a bootstrap resampling method (see the Methods and materials section), it was possible to further assess whether timeaveraging varied significantly with depth by comparing the actual depth distributions to resampled distributions in which any age value from the entire dataset is possible regardless of depth. This bootstrap resampling tested the null hypothesis that the actual age distributions came from the same, depth-invariant age distribution. The actual values for the standard deviation of mean, median, skewness and kurtosis fell within the distribution of possible values as determined by the bootstrap resampling analysis, providing no statistical evidence for the significance of actual differences observed among the three depth categories (Figs. 5D, E). Thus, time-averaging appears relatively comparable across the sampled bathymetric range, suggesting spatially uniform rates of accumulation and reworking for the surficial shell material.

Whereas the age distributions are similar along the bathymetric gradient, there is notable variation from site to site. A few individual sites reveal a paucity of modern material and one of the sites (Site 3) is completely devoid of modern specimens (Fig. 4). This notable local patchiness in time-averaging processes is difficult to interpret. The shape of age distributions and the scale of time-averaging are affected by multiple factors (sedimentation rates, depth and frequency of reworking, intensity of destructive taphonomic processes, biological productivity, and intrastratal biological activity), which may have varied locally contributing to the observed variation in age structures from one site to another.

#### Table 3

Summary of specimen ages calculated using depth-specific equations. Three age equations were calculated based on the AMS-<sup>14</sup>C ages on valves of three depths and were applied to the Asx D/L values from all the valves of this study to determine the effect of depth on racemization rates at this locality. Mean, median, standard deviation, skewness and kurtosis were calculated from the ages of the entire dataset using the three depth-specific equations and were then compared to the combined age equation.

AMS-14C sample depths	N <sup>a</sup>	A <sup>b</sup>	Xc	r <sup>2d</sup>	Mean age (cal yr BP)	Median age (cal yr BP)	Standard deviation	Skewness	Kurtosis
10 m	10	35343.09	1.49	0.97876	2022	1604	1678	1.44	2.65
25 m	16	86071.83	1.81	0.96877	2884	2011	2880	1.92	4.84
30 m	6	41379.15	1.59	0.98177	1999	1526	1762	1.59	3.28
All depths	32	60282.18	1.96	0.92398	1584	1033	1711	2.14	6.06

<sup>a</sup> Number of AMS <sup>14</sup>C specimens at a given depth.

<sup>b</sup> Rate constant of the power function.

<sup>c</sup> Power exponent of D/L in the power function.

 $^{\rm d}~r^2$  fit of the power function to the AMS  $^{14}\!C$  ages.

### Table 4

Summary of specimen ages calculated using different amino acids. A subset of valves with both aspartic acid and glutamic acid values was used to determine a new Asx equation that was comparable to the other amino acids.

Amino acid
N<sup>a</sup>
A<sup>b</sup>
X<sup>c</sup>
r<sup>2d</sup>
Lowest D/L value
Maximum age (cal yr BP)
Mean age (cal yr BP)
Median age (c

Amino acid	N	A	X	r <sup>20</sup>	Lowest D/L value	Maximum age (cal yr BP)	Mean age (cal yr BP)	Median age (cal yr BP)	Standard deviation	Skewness	Kurtosis
Asx	32	60282.18	1.96	0.9240	0.045	10,307	1584	1033	1711	2.14	6.06
Glx	22	147354.40	1.72	0.9576	0.020	8529	1501	954	1598	1.98	4.48
Ala	22	39267.01	1.54	0.9835	0.022	10,630	1522	812	1837	2.25	5.93
Asx subset	22	51008.09	1.79	0.9269	0.050	9975	1806	1209	1783	1.99	5.05

<sup>a</sup> Number of AMS <sup>14</sup>C specimens with corresponding AAR values.

<sup>b</sup> Rate constant of the power function.

<sup>c</sup> Power exponent of D/L in the power function.

 $^{\rm d}$  r<sup>2</sup> fit of the power function to the AMS  $^{14}$ C ages.

The unusually old age of our specimens from the study area, collected at or near the sediment surface, is unexpected given that the valves of S. casali are small and thin (see also Valentine et al., 2006). The valves collected for this study had little taphonomic alteration with limited abrasion, dissolution, and minor epibiont encrustation. Such minor alteration would not be expected for valves that have resided continuously within the TAZ at or slightly under the sediment surface for thousands of years. The prevalence of relatively well preserved valves suggests that these specimens were buried for most of their *post-mortem* history, as even short exposure above the sediment surface would quickly degrade such thin, fragile valves leaving no material behind to analyze. Agefrequency distributions of the thicker specimens of the calcitic brachiopod Bouchardia rosea from this same locality reveal a similar rightskewed age structure with a similar age range (from 0 to 8000 cal yr BP), despite the notably smaller sample size (n = 103) (Carroll et al., 2003; Krause et al., 2010).

The similar age distribution for these two taphonomically distinct biominerals suggests that extrinsic factors rather than intrinsic shell characteristics are responsible for controlling the scale and structure of time-averaging in the study area. As noted by multiple authors (see references in Mahiques et al., 2011), the southwestern Atlantic upper margin, including the São Paulo Bight, is marked by low sedimentation rates. Hence, the most likely explanation for our results is shell burial below the TAZ with minimal intermittent re-exposure into this destructive zone, which conforms to interpretations of extensive time-averaging proposed previously (Flessa et al., 1993; L. Martin et al., 1996; R.E. Martin et al., 1996; Meldahl et al., 1997; Kowalewski et al., 1998; Carroll et al., 2003; Olszewski, 2004). Valves can be buried under the sediment rapidly (particularly infaunal bivalves such as S. casali) and exhumed intermittently back to the surface (Clifton, 1971; Parsons-Hubbard et al., 1999). With the low exhumation and turnover rates, older valves can be preserved for long periods of time. Thus the extensive time-averaging documented here may typify other marine sedimentstarved settings regardless of the type of biomineralized material.

The dating efforts reported here demonstrate that the surficial accumulations from the southeast Brazilian Bight provide multi-millennial records suitable for reconstructing long-term environmental change. Geochemical analyses of biomineralized shell materials provide multiple proxies (e.g., trace elements, stable isotopes) that reflect the conditions in which the shell-secreting organisms lived. As geochemical methods and resolution continue to improve, and dating techniques become more efficient and inexpensive, biomineralized materials from time-averaged shell accumulations should provide an increasing wealth of environmental proxy data.

## Methodological implications

When AMS-<sup>14</sup>C ages are plotted against Asx D/L values for data pooled across all sites, the two data series are tightly correlated (Fig. 2B). The consistent racemization rates observed here across a depth gradient are not unexpected given that all sampled sites, regardless of their depth, occur within the same fully mixed water mass and are unlikely to have

experienced a notable temperature gradient (Campos et al., 2000). In addition, the spatial uniformity in racemization rates suggests that the shallower sites could not have been subaerially exposed because such events would notably change the thermal history of the affected specimens and prevent an effective application of a single calibration equation. This again is not unexpected in our study area. All sites have remained submerged since the Holocene post-glacial transgression, and sea level has remained relatively unchanged for the past 5000 yr (L. Martin et al., 1996; R.E. Martin et al., 1996; Angulo and Lessa, 1997; Angulo et al., 1999, 2004; Lessa et al., 2000; Baker et al., 2001) providing potentially favorable conditions for developing a reliable single calibration for sites varying in water depth. Indirectly, thus, the results provide an independent confirmation of oceanographic and sea-level histories of the region derived previously using other lines of evidence (references cited above).

To further assess the use of a single calibration, three depth-specific calibration equations were calculated from the three depths for which AMS-<sup>14</sup>C ages were available. These three equations were applied to the entire dataset and the age distributions were compared to the single, depth invariant equation (Table 3). The three depth-specific calibrations produced age distributions that were similar in structure to the pooled calibration as demonstrated by a number of statistical metrics (Table 3).

Considering multiple sites at multiple depths concurrently rather than separately reduces the needed number of AMS-<sup>14</sup>C ages, as sitespecific calibrations are no longer necessary. The use of a single calibration equation could average values and obscure real differences between sites and depths. As demonstrated in this study with the three depth-specific AMS-<sup>14</sup>C calibrations, the use of the single calibration did not change the overall age distributions noticeably from those calculated based on depth (Table 3). This suggests that the lack of difference in time-averaging between depths is real and not an artifact of the single calibration equation. Further, the use of a single calibration formula for the entire region did not prevent us from detecting local, site-to-site variability in age distributions of dated shells (Fig. 4). In study areas with greater spatial variability in thermal history, more intensive depth-specific AMS-14C dating would be necessary to calibrate AAR rates. However, for fully mixed water masses unaffected by substantial local sea-level changes, a single calibration for multiple sites appears to suffice. Because AMS-<sup>14</sup>C ages are the more cost-prohibitive aspect of large geochronological studies, reducing the number of analyses required to calibrate AAR rates facilitates the development of large geochronological datasets.

## Summary and conclusions

Using amino acid racemization ratios calibrated against AMS-<sup>14</sup>C ages (n = 32), 270 *S. casali* valves were dated individually and age-frequency distributions were assembled for 14 sites within the São Paulo Bight, southeastern Brazil (Fig. 1). Specimens range in age from modern to 10,307 cal yr BP. For most sites, and for pooled data, age distributions are right skewed and provide a nearly continuous geochronological record for the past 4000 yr at the centennial scale of resolution

(92.5%). At the millennial scale of resolution, the dated shells provide a nearly complete record for the entire Holocene (90%). Due to limited transport, intermittent exposure and burial and a spatially consistent thermal history throughout the study area, a single calibration can be applied to all specimens measured for AAR.

Periodic burial of modern material throughout the Holocene, with low exhumation and turnover rates of older valves buried in the shallow subsurface, allowed for near-surficial survival of many old specimens providing a long and remarkably continuous time series of dated shells. Shelfal settings characterized by low sedimentation rates and stable relative sea level during the Holocene highstand facilitate preservation and mixing of shelly specimens from multiple millennia. These conditions should be present in many marine settings increasing the likelihood of assembling long time-series of dated shells for a variety of biomineralized materials, which can then be used as a source of geochemical proxy data for tracking regional environmental and climatic trends throughout the Holocene. Use of geochemical data from biomineralized materials as a proxy for environmental conditions is an established and increasingly widespread strategy in late Quaternary studies. This and previous studies demonstrate that AAR dating of surficial shell accumulations allows for assembling extensive time series of biomineral solids suitable for paleoenvironmental and paleoclimatic studies spanning multi-centennial to multi-millennial time scales. Shells that lay on modern seafloors do not just record the present, but represent a wealth of past data that can span many millennia.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.yqres.2013.12.007.

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