## SEASONAL VARIATIONS IN PERUVIAN MARINE RESERVOIR AGE FROM PRE-BOMB ARGOPECTEN PURPURATUS SHELL CARBONATE

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**ABSTRACT.** Marine upwelling along coastal Peru can be intense and variable, making radiocarbon dating marine and coastal systems complex. Historical and proxy records of upwelling along coastal Peru are few, and long-lived species such as corals do not grow in the cold coastal waters. Mollusk shell carbonate, however, can record both the magnitude of the local marine reservoir correction,  $\Delta R$ , and of seasonal oscillations in the ventilation age of coastal waters. If large, these seasonal oscillations would complicate radiocarbon dating of marine organisms. To examine this possibility, we sampled for  $\delta^{13}$ C,  $\delta^{18}$ O, and <sup>14</sup>C content a set of pre-bomb *Argopecten purpuratus* shells collected from coastal Peru during 1908 and 1926. Intrashell variations of up to 216 <sup>14</sup>C yr were noted, but these were not consistently correlated with seasonal changes in  $\delta^{18}$ O or  $\delta^{13}$ C. Only an 11 yr difference was observed in the weighted average  $\Delta R$  of Callao Bay shells collected during normal (1908) and El Niño (1926) years. Despite the intrashell <sup>14</sup>C variation noted, weighted average  $\Delta R$  values from all 3 sample sites and from normal and El Niño years all overlap at 1  $\sigma$ . We report  $\Delta R$  values of 183 ± 18 and 194 ± 23 yr from Callao Bay (12°4′S), 165 ± 24 yr from Salaverry (8°14′S), and 189 ± 23 yr from Sechura Bay (5°45′S).

#### INTRODUCTION

Marine upwelling along coastal Peru has a significant effect on the apparent ventilation age of local seawater. In the absence of El Niño, deep, nutrient-rich upwelling predominates. During an El Niño event, however, the upwelling source shifts to shallow, warmer, nutrient-depleted super-thermocline water of younger ventilation age (e.g. Huyer et al. 1987; Toggweiler et al. 1991). Upwelling also varies based on local winds (e.g. Huyer et al. 1987). Because of the different ventilation ages of the different sources of upwelling water, the marine reservoir age may vary depending on the pattern of upwelling.

Corals are excellent isotopic recorders, providing long continuous marine isotopic records. Highresolution studies in the tropical central Pacific (Grottoli et al. 2003) and tropical eastern Pacific (Druffel et al. 2004) show that corals record surface ocean radiocarbon content on a subannual scale. Unfortunately, suitable corals do not exist in the eastern Pacific cold tongue near Peru.

Mollusk shells are alternative isotopic recorders, typically used to determine local marine reservoir ages (e.g. Taylor and Berger 1967; Southon et al. 1990). Mollusks are abundant in Peruvian archaeological middens throughout the Holocene (e.g. Sandweiss et al. 1996, 2001; Sandweiss 2003) and in earlier fossil assemblages (e.g. Hsu et al. 1989). Their disadvantage is that they are short-lived and thus provide only brief records of marine conditions.

Generally, measurements on marine shell assume a homogeneous intrashell <sup>14</sup>C content (e.g. Ascough et al. 2005b; Cage et al. 2006). Although perhaps generally true, variation may be significant in regions with large seasonal changes in upwelling intensity, such as along the Peruvian coast. The research we report here focuses on whether these variations are detectable within modern prebomb mollusk shell carbonate, and whether they are significant for calculations of the modern

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regional marine reservoir correction,  $\Delta R$ . A similar approach has been taken by Cullen et al. (2006), studying pre-bomb shells from the Santa Barbara Basin. Their findings indicate that intrashell variations in <sup>14</sup>C content are significant.

Several investigations have documented regional variation in the marine reservoir age over time (e.g. Southon et al. 1990; Eiríksson et al. 2004; Hutchinson et al. 2004; Ascough et al. 2005a). The few marine reservoir age studies for Peru suggest significant changes during the Holocene are possible. Owen (2002) found late Holocene reservoir ages to be 670 to 760 yr in far southern Peru. Fontugne et al. (2004) also investigated the marine reservoir age in far southern Peru and found it to be about 600 yr in the late Holocene and 500 to 1300 yr in the early to mid-Holocene.

The question of what constitutes a suitable species for upwelling and <sup>14</sup>C analysis remains open. Rollins et al. (1986, 1987) showed that the El Niño of 1982–1983 was recorded in the shells of Peruvian *Chione subrugosa* and *Trachycardium procerum* as notches or bands of closely spaced growth lines that were compressed as a consequence of physiological stress. Andrus et al. (2005) showed that a record of this event was also recorded isotopically in a modern *T. procerum* valve from near Casma, Peru (~9.30°S). The isotopic profile along a growth axis revealed a decrease of about 1.5‰ in  $\delta^{18}$ O and a <sup>14</sup>C increase of about 8 percent modern carbon (pMC) coincident with the El Niño event. The <sup>14</sup>C increase reflected shell growth in <sup>14</sup>C-enriched surface waters, the enrichment accentuated by the presence of bomb-derived radiocarbon.

Smaller oscillations with amplitudes of about 1% in  $\delta^{18}$ O and 2.1 pMC are also recorded in the modern *T. procerum* shell. A similar isotopic investigation of a 5800 BP archaeological *T. procerum* shell showed amplitudes in variation of 1.8% in  $\delta^{18}$ O and 1.5 pMC (Andrus and Hodgins, unpublished data). These may reflect seasonal changes in upwelling intensity, although the influences of biology, local environment, and diagenesis need to be considered.

In the research we report here, we quantify the variation in stable isotopes and  $^{14}$ C content in prebomb *Argopecten purpuratus* (Peruvian or Chilean bay scallop) shells. This species is distributed widely along the west coast of South America, from 5°S to 37°S (Wolff and Mendo 2000). It lives between 0 and 30 m depth (Stotz and González 1997; Cantillanez et al. 2005) and has a natural life span of 4 to 5 yr. Modern fishing practice harvests individuals of 90 mm length, a size obtained within 14 to 16 months if cultured, or up to 27 months in natural beds (González et al. 2002). Scallops are motile, but capture and release experiments by Wolff and Mendo (2000) from May 1983 to May 1984 (an El Niño year) recovered all individuals within 100 m of the release point. The species is warm-water tolerant: studies have shown dramatic increases in *Argopecten* populations after El Niño events (Wolff 1987, 1988; Wolff and Mendo 2000). *Argopecten* have long been exploited as a food source and so occur in Peruvian coastal archaeological sites (e.g. DeVries and Wells 1990).

It will be important to understand isotopic variations in modern shells of known provenance before investigating archaeological shells of unknown age. If, for example, El Niño significantly alters the ventilation age preserved in mollusks, it will be important to recognize this effect and correct for it when estimating the reservoir effect from ancient shells.

## MATERIAL AND METHODS

The A. purpuratus (Figure 1) shells analyzed in this study are part of a Smithsonian Institution collection comprising a variety of species collected alive on known dates during the early 20th century. We are investigating A. purpuratus because they are abundant in the collection and cover a range of locations and collection dates. We sampled 8 A. purpuratus valves for  $\delta^{13}$ C,  $\delta^{18}$ O, and  $^{14}$ C content.



Figure 1 *A. purpuratus* valve. Growth bands are visible under low magnification within the distal portion of the valve.

Our samples were collected alive in 1908 and October and November 1926 from 3 locations (Sechura Bay, 5°45'S; Salaverry, 8°14'S; and Callao Bay, 12°4'S; see Figure 2). Two *A. purpuratus* valves from different individuals were sampled for each combination of geographic and temporal setting.



Figure 2 Map showing locations of A. purpuratus collection sites

The 1908 and 1926 collection dates allow us to examine differences in shells between normal and El Niño years. Both 1907 and 1908 were normal years. An El Niño event occurred in 1926, as shown by a >2 °C positive sea surface temperature (SST) anomaly in the Kaplan Extended SST Anomaly data set (Kaplan et al. 1998).

For stable isotope measurements, each valve was milled using a fixed dental drill and carbide dental bur at multiple locations along a single growth axis, powdering the carbonate within a roughly 0.5-mm-diameter hemispherical divot. The resulting powder was collected, reacted with dehydrated phosphoric acid *in vacuo*, and analyzed for  $\delta^{13}$ C and  $\delta^{18}$ O using a Finnigan MAT 252 mass spectrometer with a Kiel III automated sampling device. At least 1 internal NBS-19 calcite laboratory standard was run for every 19 shell carbonate samples. One-sigma precision on repeated standards is  $\pm 0.1\%$  for  $\delta^{18}$ O and  $\pm 0.06\%$  for  $\delta^{13}$ C.

Because  $\delta^{18}$ O can be used as a water temperature proxy (e.g. Epstein et al. 1953; Kim and O'Neil 1997; Dettman et al. 1999; Chauvaud et al. 2005), the  $\delta^{18}$ O curve produced by stable isotope sampling was then used to determine where to take larger (~5 mg) samples for <sup>14</sup>C in order to capture the expected greatest range in <sup>14</sup>C. Carbonate for <sup>14</sup>C measurement was collected along paths parallel to growth lines to a width and depth of about 0.5 mm. To compare the effects of sampling depth, 4 additional <sup>14</sup>C samples were taken from 2-mm-deep divots. The collected carbonate was reacted with phosphoric acid at room temperature *in vacuo*. The reaction was allowed to proceed to completion and the CO<sub>2</sub> produced was cryogenically isolated and graphitized using standard procedures (Slota et al. 1987).

# **RESERVOIR CORRECTION CALCULATIONS**

Because of both upwelling of <sup>14</sup>C-depleted deep water and slow mixing of carbon across the oceanatmosphere interface, the marine surficial mixed layer is depleted in <sup>14</sup>C relative to the atmosphere. Marine mollusks tend to precipitate carbonate in isotopic equilibrium with local seawater (Mook and Vogel 1968), and seawater dissolved inorganic carbon is the dominant source of carbon in shell carbonate, although a small proportion (usually <10%) of metabolized food carbon is also incorporated (Lorrain et al. 2004). The difference between contemporaneous marine and atmospheric <sup>14</sup>C ages can be reported as the marine reservoir age, R, or as the marine reservoir correction,  $\Delta R$ (Stuiver et al. 1986).

The <sup>14</sup>C marine reservoir age, R(t), is the difference between local marine and atmospheric <sup>14</sup>C ages at calendar age *t*. This can be expressed as

$$R(t) = M_m(t) - A(t)$$

where  $M_m(t)$  is the measured <sup>14</sup>C age of a marine organism of known calendar age, t, and A(t) is the atmospheric <sup>14</sup>C age, obtained from a terrestrial calibration curve such as IntCal04 (Reimer et al. 2004) for a historic sample of known age. If R(t) for a given year and location are known, it can be used with  $M_m(t)$  to calculate the equivalent A(t), which can then be calibrated using a terrestrial calibration curve to find the calibrated age of the marine organism. R(t) can vary significantly from year to year because high-frequency changes in atmospheric <sup>14</sup>C are not instantaneously mirrored by the marine reservoir (Stuiver et al. 1986).

The marine reservoir correction,  $\Delta R$ , is a more accepted and less time-dependent way to describe marine <sup>14</sup>C depletion. Stuiver et al. (1986) developed a marine <sup>14</sup>C calibration curve for a theoretical global ocean, requiring a local reservoir age correction that can vary over both time and place,  $\Delta R$ ,

to be applied to marine <sup>14</sup>C-dated samples (Stuiver and Braziunas 1993) because the real ocean is not uniform. This correction is calculated from a marine sample of known age as

$$\Delta R(t) = M_m(t) - M_{calib}(t)$$

where  $M_{calib}(t)$  is from the Marine04 calibration curve of Hughen et al. (2004). Once  $\Delta R$  is known for an area at a time of interest, ages of marine samples can be corrected for local effects by adding  $\Delta R$  before calibration with the Marine04 curve.

#### RESULTS

 $\Delta R$  on individual shell carbonate samples ranges from 45 ± 85 to 261 ± 55 yr (Table 1).  $\Delta R$  within single shells varied by up to 216 yr. At Callao Bay, the only site for which we have samples from both 1908 and 1926,  $\Delta R$  weighted averages for each collection date overlap within 1  $\sigma$ : 183 ± 18 and 194 ± 23 yr in 1908 and 1926, respectively. Farther north, the Salaverry (1926) weighted average  $\Delta R$  is 165 ± 24 yr and the Sechura Bay (1908) weighted average  $\Delta R$  is 189 ± 23 yr, both overlapping with the Callao Bay  $\Delta R$  averages within 1  $\sigma$ .

Most  $\delta^{18}$ O and  $\delta^{13}$ C records from *A. purpuratus* valves collected at the same place and time are not identical but show similar amplitudes and patterns of variation (seen clearly in Figures 3, 5, and 6). The variation seen in Figure 4a is similar to that in the distal portion of the larger shell profiled in Figure 4b. Shells collected at the same place but different times (contrasting growth during normal conditions and during El Niño) show different patterns of variation: those that grew during El Niño show strong, erratic negative excursions in  $\delta^{18}$ O and positive excursions in  $\delta^{13}$ C (e.g. Figures 5 and 6, particularly 5a). In most *A. purpuratus* valves sampled,  $\delta^{18}$ O and  $\delta^{13}$ C covary within 10 to 20 mm of the umbo, but vary inversely across the rest of the valve.



Figure 3 Stable isotope analyses of 2 *A. purpuratus* valves from different scallops collected live at Sechura Bay in 1908. Solid circles with 1- $\sigma$  error bars represent <sup>14</sup>C measurements, expressed as  $\Delta R$ . Solid squares represent  $\delta^{18}O$ , open diamonds represent  $\delta^{13}C$ , and error bars show 1- $\sigma$  precision on repeated NBS-19 standards. Patterns of variation and amplitudes in both valves are similar. The isotopic signals covary near the umbo, but vary inversely beyond 20 mm from the umbo.

			Distance from	δ <sup>18</sup> Ο	8 <sup>13</sup> C	<sup>14</sup> C content	<sup>14</sup> C age	Reservoir age	Reservoir correction
Lab nr	Shell nr	Collection location and date	(mm) oqum	(‰)	(%)	(pMC)	(BP)	$R(t) (yr)^{a}$	ΔR (yr) <sup>b</sup>
AA69000	207760A	Callao Bay (12°4'S), 1908	8.5	-0.2	0.8	$92.30 \pm 0.52$	643 ± 44	550 ± 45	$195 \pm 50$
AA68793	207760A		8.5			$92.79 \pm 0.41$	60I ± 35	$508 \pm 36$	<i>153</i> ± 42
AA69001	207760A		44.8	1.7	0.7	$92.02 \pm 0.57$	$668 \pm 50$	$575 \pm 50$	$220 \pm 55$
AA68794	207760A		44.8			$91.56 \pm 0.50$	$708 \pm 44$	615±45	$260 \pm 50$
AA68797	207760B		14.5	0.1	1.3	$93.30 \pm 0.60$	557 ± 51	$464 \pm 51$	$109 \pm 56$
AA68798	207760B		58.5	1.3	1.2	$93.06 \pm 0.54$	$578 \pm 47$	$485 \pm 48$	$130 \pm 53$
AA68800	207760B		84.0	0.1	1.1	$92.38 \pm 0.49$	$637 \pm 42$	$544 \pm 43$	$189 \pm 48$
AA68799	207760B		90.0	1.6	0.9	$92.14 \pm 0.55$	$657 \pm 48$	$564 \pm 49$	209 ± 54
						weighte	ed average:	538 ± 16	<b>183 ± 18</b>
AA69380	207761A	Sechura Bay (5°45'S), 1908	13.2	0.4	1.1	$93.47 \pm 0.57$	543 ± 47	$450 \pm 48$	95 ± 53
AA69379	207761A		55.7	1.8	1.0	$91.62 \pm 0.63$	$703 \pm 54$	$610 \pm 54$	255 ± 59
AA74686	207761C		10.5	0.2	1.0	$92.39 \pm 0.38$	$636 \pm 32$	543 ± 33	188 ± 40
AA74687	207761C		38.1	1.6	0.8	$92.09 \pm 0.38$	$662 \pm 32$	$569 \pm 33$	$214 \pm 40$
						weighte	d average:	545 ± 20	189 ± 23
AA68998	368498A	Callao Bay, 7 Nov. 1926	26.0	-0.3	2.1	$94.02 \pm 0.99$	$496 \pm 82$	$360 \pm 82$	45 ± 85
AA68791	368498A		26.0	0.0	1.1	$92.27 \pm 0.52$	$646 \pm 45$	$510 \pm 46$	$195 \pm 51$
AA68792	368498A		84.4	1.3	1.0	$92.05 \pm 0.49$	$666 \pm 42$	$530 \pm 43$	$215 \pm 48$
AA68999	368498A		84.6	1.8	1.2	$92.02 \pm 0.64$	$668 \pm 55$	532 ± 55	$217 \pm 60$
AA68795	368498B		17.0	-0.2	1.8	$91.52 \pm 0.57$	$712 \pm 50$	576±50	$261 \pm 55$
AA68796	368498B		70.0	1.5	0.9	$92.81 \pm 0.51$	$600 \pm 44$	$464 \pm 45$	$149 \pm 50$
						weighte	d average:	$510 \pm 21$	$194 \pm 23$
AA69382	368560A	Salaverry (8°14'S), Oct. 1926	38.4	1.5	1.0	93.35 ± 0.59	552 ± 50	$416 \pm 50$	101 ± 55
AA69381	368560A		49.6	0.2	1.5	$92.92 \pm 0.59$	589 ± 49	453 ± 49	138 ± 55
AA69429	368560B		34.0	1.9	0.7	$92.00 \pm 0.42$	$670 \pm 36$	534 ± 37	$219 \pm 43$
AA69430	368560B		38.5	-0.2	0.5	$92.61 \pm 0.42$	$617 \pm 36$	481 ± 37	$166 \pm 43$
						weighte	d average:	481 ± 21	$165 \pm 24$



Figure 4 Stable isotope analyses of *A. purpuratus* valves from scallops collected live at Callao Bay in 1908. Solid circles with 1- $\sigma$  error bars represent <sup>14</sup>C measurements, expressed as  $\Delta R$ . Solid squares represent  $\delta^{18}$ O, open diamonds represent  $\delta^{13}$ C, and error bars show 1- $\sigma$  precision on repeated NBS-19 standards.



Figure 5 Stable isotope analyses of *A. purpuratus* valves from scallops collected live at Callao Bay in late 1926, following the early 1926 El Niño event. Solid circles with 1- $\sigma$  error bars represent <sup>14</sup>C measurements, expressed as  $\Delta$ R. Solid squares represent  $\delta^{18}$ O, open diamonds represent  $\delta^{13}$ C, and error bars show 1- $\sigma$  precision on repeated NBS-19 standards. Shell 368498A in particular shows rapid oscillations in  $\delta^{13}$ C and  $\delta^{18}$ O during a possible period of growth during El Niño.

Some, but not all, shells that grew during El Niño show possible growth hiatuses, reflected in abrupt changes in isotopic variation, in shell curvature, or both. The possible growth hiatus shown isotopically as an abrupt change in  $\delta^{18}$ O in Figure 6b approximately corresponds to a slight break in shell curvature at 35 mm from the umbo. A more prominent break in shell curvature on this valve at 60 mm from the umbo, however, does not correspond to an abrupt isotopic shift.

Three of 4 deeper <sup>14</sup>C samples contained the same amount (at 1  $\sigma$ ) of <sup>14</sup>C as the shallower samples (Table 1), while the fourth deep-and-shallow sample pair (AA68998 and AA68791) had disparate <sup>14</sup>C contents. In this pair, the deeper sample appears 150 <sup>14</sup>C yr older than the shallow sample.



b. Shell 368560B collected at Salaverry (8°14' S), 1926



Figure 6 Stable isotope analyses of *A. purpuratus* valves collected live at Salaverry in October 1926, following the early 1926 El Niño event. Solid circles with 1- $\sigma$  error bars represent <sup>14</sup>C measurements, expressed as  $\Delta R$ . Solid squares represent  $\delta^{18}O$ , open diamonds represent  $\delta^{13}C$ , and error bars show 1- $\sigma$  precision on repeated NBS-19 standards. The abrupt drop or subsequent abrupt increase in  $\delta^{18}O$  in the middle of valve 368560B may represent a growth hiatus. Growth curves from Wolff (1987) suggest this individual was part of the spring cohort, and, based upon size, June or July 1926 as the time of the hiatus.

### DISCUSSION

Based on counting the approximately daily growth bands (Clark 1974; Chauvaud et al. 2005) and on examining what we suspect is an annual cycle in  $\delta^{13}$ C and  $\delta^{18}$ O, we conclude that the *A. purpuratus* shells we sampled are 1 to 1.5 yr old, while the largest shell, 207760B (Figure 4b), may approach 2 yr old. This conclusion is supported by growth rate studies in Wolff (1987). Although shells of this age allow us to investigate seasonal variations in isotopic content, they preclude direct analyses of interannual variations. Longer-lived mollusks would be more useful for such studies.

Chauvaud et al. (2005) experimentally determined a linear relationship between water temperature, water  $\delta^{18}$ O, and scallop (*Pecten maximus*) calcite  $\delta^{18}$ O:

$$T = 14.84 - 3.75(\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{water}})$$

where *T* is water temperature in °C,  $\delta^{18}O_{calcite}$  is expressed in %° relative to VPDB, and  $\delta^{18}O_{water}$  is expressed in %° relative to SMOW. This equation is very similar to the Kim and O'Neil (1997)  $\delta^{18}O_{calcite}$ -temperature equation based on abiogenic calcite precipitation. If we assume that the Chauvaud et al. (2005) relationship holds for *A. purpuratus*, and assuming that  $\delta^{18}O_{water}$  changes due to salinity are much less than the variation measured in  $\delta^{18}O_{calcite}$ , then the 1.37 to 2.10%° variation in shell  $\delta^{18}O$  corresponds to recorded water temperature variations of 5.2 to 8.0 °C over the lives of the scallops. This is in reasonable agreement with expected annual water temperature variations along coastal Peru: Puerto Chicama (8°S), for example, experienced a SST range of about 5 °C during normal years and greater than 11 °C during strong El Niño years from 1980–99 (see http://www.jisao.washington.edu/data\_sets/chicama\_sst/). These variations exceed the range in SST measured by Coker (1918) suggesting annual temperature variations of 2–5 °C during 1907–08 along coastal Peru.

We hypothesized that part of the cause of marine temperature variations along coastal Peru is varying intensity of upwelling of deep cold water, with coldest water temperatures (and highest shell  $\delta^{18}$ O values) corresponding to the greatest contribution of upwelling. This upwelled water is <sup>14</sup>Cdepleted relative to warmer surficial water, so we expected shell samples with high  $\delta^{18}$ O to be relatively depleted in <sup>14</sup>C. We also expected shell that grew during the 1926 El Niño, when upwelling was significantly diminished and <sup>14</sup>C-enriched runoff may have increased, to be enriched in <sup>14</sup>C compared with shell that did not grow during this event.

<sup>14</sup>C ages within single shells varied by up to 216 <sup>14</sup>C yr, several times larger than the typical  $\sigma$  on individual <sup>14</sup>C measurements (Table 1). However, no clear pattern in <sup>14</sup>C with respect to shell  $\delta^{18}$ O maxima and minima was noted (Figures 3–6). As shells were only sampled for <sup>14</sup>C measurement at  $\delta^{18}$ O maxima and minima, the possibility exists that the points of minimum and maximum <sup>14</sup>C content were missed. Despite these large intrashell variations, no significant differences in weighted-average <sup>14</sup>C age were observed between shells that lived during El Niño and during normal conditions.

The lack of major differences in weighted average <sup>14</sup>C age between shells that grew during normal and during El Niño conditions is difficult to explain. Although *A. purpuratus* thrives in El Niño conditions, possible growth hiatuses noted in shells that grew during the 1926 El Niño event (e.g. Figure 6b) suggest that these scallops may occasionally stop growing even under favorable conditions. This is consistent with observed growth cessations in the scallop *P. maximus* that occur after environmental change, handling, or during phytoplankton blooms (Chauvaud et al. 2005). Perhaps, then, *A. purpuratus* shell carbonate does not record the full range of marine isotopic variation over the life of the organism. Other possibilities for the lack of clear differences between normal and El Niño <sup>14</sup>C weighted averages, such as these scallops migrating or living in areas sheltered or buffered from changing upwelling, are unlikely.

As with  $\delta^{18}$ O,  $\delta^{13}$ C shows no clear correlation with <sup>14</sup>C. An inverse correlation between  $\delta^{13}$ C and  $\delta^{18}$ O is apparent except near the umbones of the *A. purpuratus* shells we sampled. This suggests that, like  $\delta^{18}$ O,  $\delta^{13}$ C is influenced (perhaps indirectly) by temperature over much of the lives of these scallops. The covariance in these isotope ratios near the umbones suggests the additional influence of a biological or metabolic process that changes during ontogeny. This process may be species specific, as Peruvian *T. procerum* (Andrus et al. 2005) and *Mesodesma donacium* (Carré et al. 2005) shells do not show a similar relationship between  $\delta^{13}$ C and  $\delta^{18}$ O.

The  $\Delta R$  values we report are lower than the two  $(243 \pm 49, 670 \pm 44 \text{ yr})$  previously reported for Peru (Table 2). The 670 yr  $\Delta R$ , however, was treated as an outlier by Stuiver et al. (1986), and Owen (2002) suggests it may not have been collected live or may have been affected by an extreme local hard water effect. Our weighted average  $\Delta R$  values of  $165 \pm 24$  to  $194 \pm 23$  yr are not far out of line with the remaining 243 yr value previously reported. As geography may influence the marine reservoir age, local marine <sup>14</sup>C variations might also explain the difference between the  $\Delta R$  values. (The exact collection location of the shell with  $\Delta R = 243$  yr is unknown.)

	Collection			
Location	date	Species	$\Delta R$ (yr)	Reference
Guayaquil, Ecuador (3°S)	1927	Cerithidea valida	$-216 \pm 37$	Taylor and Berger 1967
Guayaquil, Ecuador	1927	Thais biserialis	$84 \pm 45$	Taylor and Berger 1967
Northern Peru (about 10°S)	1930–1940	Strombus peruvianus	$243 \pm 49$	Taylor and Berger 1967
Peru (about 14°S)	1930–1940	Oliva peruviana	670 ± 44	Taylor and Berger 1967
Angofagasta, Chile (24°S)	1925	Concholepas concholepas	$175 \pm 34$	Taylor and Berger 1967
Valparaiso, Chile (33°S)	1930–1940	Tegula aler	$313 \pm 76$	Taylor and Berger 1967
Valparaiso, Chile	1939	Mytilus sp.	$43 \pm 52$	Ingram and Southon 1996

Table 2 Reported modern values for  $\Delta R$  based on <sup>14</sup>C dates on marine shells from the west coast of South America. Latitudes for ambiguous Peruvian locations estimated in Stuiver et al. (1986).

Due to the range of up to 216 <sup>14</sup>C yr in ages from a single shell and the possibility of growth cessations, researchers using <sup>14</sup>C ages from marine organisms in an area with variable upwelling should exercise caution. Recent findings by Cullen et al. (2006) support this as well. Samples collected for <sup>14</sup>C dating, whether whole-shell or small portions of a shell, may not be representative of the overall marine environment in which the mollusks grew due to growth rate changes and hiatuses. Also, regional  $\Delta R$  values may have been calculated on shells that grew during atypical upwelling conditions. More research is needed on the influences of seasonality and upwelling on shell <sup>14</sup>C. The best sampling strategy for marine shells in a variable upwelling environment remains unclear and is a focus of our ongoing work.

## CONCLUSION

Based on our <sup>14</sup>C dating of multiple *A. purpuratus* valves, we report modern pre-bomb  $\Delta R$  values of 183 ± 18 and 194 ± 23 yr at Callao Bay, 12°4′S (shells collected in 1908 and 1926); 165 ± 24 yr at Salaverry, 8°14′S; and 189 ± 23 yr at Sechura Bay, 5°45′S. When multiple <sup>14</sup>C samples are averaged, interannual variations in  $\Delta R$  are minimal; a difference of only 11 yr was calculated between shell carbonate precipitated in Callao Bay during the normal years 1907–8 and the strong El Niño of 1926.

The results reported here suggest that intrashell variations in <sup>14</sup>C can be significant (>200 <sup>14</sup>C yr), but these do not correlate clearly with seasonal cycles in SST as reflected by mollusk carbonate  $\delta^{18}$ O. Moreover, rapid fluctuations in  $\delta^{18}$ O apparent within some valves argue against  $\delta^{18}$ O oscillations stemming solely from seasonal SST changes. Because of this intrashell <sup>14</sup>C variation, we advise caution in using <sup>14</sup>C for high-precision dating in environments with variable marine upwelling such as Peru.

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