POTENTIAL USE OF ARCHAEOLOGICAL SNAIL SHELLS FOR THE CALCULATION OF LOCAL MARINE RESERVOIR EFFECT

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ABSTRACT. Shellmounds are archaeological sites found across the Brazilian coast and form an important record of the human occupation of this area during the Holocene. The presence of both terrestrial and marine remains within the same archaeological context enables the comparison of different carbon reservoirs. There is only a small number of similar studies for the coast of south-southeastern Brazil. Previous work was based on the analysis of pre-bomb shells from museum collections and paired charcoal/marine shells from archaeological sites. This article assesses the potential use of terrestrial shells as representative of atmospheric carbon reservoir in the calculation of the marine reservoir effect (MRE) of the southeastern Brazilian coast. The presence of both terrestrial and marine shells over several archaeological layers represents a great potential for calculating reservoir corrections and their temporal variation.

INTRODUCTION

Radiocarbon dating of terrestrial organic materials lies on the assumption that the \(^{14}\)C level in the sample is in equilibrium with the corresponding atmospheric carbon reservoir. Many paleoenvironmental, geological, and archaeological studies have used land snail shells to reconstruct occupation history and past climatic and environmental conditions at the sites under study (Xu et al. 2011; Yanes et al. 2011, 2012; Zaarur et al. 2011; Rech et al. 2012; Rakovan et al. 2013).

When dating snails, it is the mineral matrix of the shell, mostly composed of calcium carbonate in the form of aragonite, that is dated. The use of land snails as dating material is restricted to a group of snails that do not incorporate old carbon from limestone or calcareous sediments, which would lead to old apparent ages (Tamers 1970; Evin et al. 1980; Goodfriend and Hood 1983; Goodfriend and Stipp 1983; Yates 1986; Goodfriend 1987; Goodfriend et al. 1999; Zhou et al. 1999; Quarta et al. 2007; Romaniello et al. 2008; Xu et al. 2011).

The biological pathways for the incorporation of old carbon are not well understood. Goodfriend and Hood (1983) suggested that atmospheric CO\(_2\), plants, and \(^{14}\)C-depleted limestone are the three possible sources of carbon during the formation of aragonite shells in terrestrial gastropods. However, in a recent study there was no difference in the carbonate isotopic composition of *Helix aspersa* (Müller, 1774) fed with a CaCO\(_3\) diet compared to a CaCO\(_3\)-free diet, suggesting that the most relevant source of carbon is metabolic CO\(_2\) from food sources incorporated through direct digestion and breakdown of urea (Stott 2002). The mechanisms of incorporation and distribution of carbon isotopes are not necessarily the same for all terrestrial species (Barnhardt 1992; Stott 2002). Furthermore, there is evidence that the use of \(\delta^{13}\)C to calculate the old carbon effect in terrestrial species is flawed (Xu et al. 2011). For dating purposes, each terrestrial gastropod species should be tested for incorporation of old carbon and discarded if necessary. Some terrestrial gastropods of the most common genera in North America, such as *Catinella*, *Columella*, *Discus*, *Gastrocopta*, and *Succinea*, have been shown to yield reliable \(^{14}\)C dates, regardless of the local geologic substrate (Pigati et al. 2010).

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THE MARINE RESERVOIR EFFECT

The marine reservoir effect (MRE) is defined as an offset between the marine and atmospheric reservoir $^{14}$C content and has an average value of 405 ± 22 $^{14}$C yr (Hughen et al. 2004), known as the global marine reservoir effect, or $R_g$. The MRE has also a local component, a $\Delta R$ value, that represents the difference between the reservoir age and the mean global age (Stuiver and Braziunas 1993) and takes into account time and space variations, which depend on many factors like the carbon exchange between ocean carbonates and atmospheric CO$_2$, upwelling currents, circulation patterns, and coastal topography (Gordon and Harkness 1992; Ascough et al. 2004). Quantification of the local marine reservoir effect is important in the establishment of accurate archaeological chronologies (Fernandes et al. 2012).

Traditionally, pre-bomb marine shells or pairs of associated archaeological samples, such as marine shells and charcoal from the same depositional context, have been used to determine the difference between the terrestrial and marine carbon reservoirs (Kennett et al. 1997; Culleton 2006; Culleton et al. 2006; Soares and Dias 2006, 2007; Ascough et al. 2009; Russell et al. 2010; Petchey et al. 2013). However, in some archaeological sites, samples of charcoal are scarce or not present at all. In that case, terrestrial gastropods may be used as an alternative, provided that they yield reliable $^{14}$C ages.

The aim of this work is to assess the potential use of the gastropod Thaumastus achilles (Pfeiffer, 1852) from the Bulimulidae family as a reliable representative of the atmospheric carbon reservoir in the analysis of the MRE in the southeastern Brazilian coast. Prior to using any land snail taxon in such studies, its reliability has to be evaluated. The incorporation of “old” ($^{14}$C-free) material will depend upon the diet of each animal (Rubin et al. 1963). T. achilles is known to feed from trees and shrubs (Breure 1979) and its presence in South America is attested for several thousands of years. Very abundant in the southeastern coast of Brazil, it was collected and eaten regularly by fisher-gatherer populations. The availability of both terrestrial and marine shells found over several archaeological layers presents great potential for calculating MRE corrections from paired samples.

Very few similar studies are available for the coast of Brazil, and these are mostly based on pre-bomb shells from museum collections. A number of $^{14}$C dates of marine shells from the northern coast of Ilha de Santa Catarina (27°30′S, 48°00′W), in Santa Catarina State, were used to estimate a mean reservoir age using samples with similar ages from a museum collection (Nadal de Masi 2001). Charcoal-shell pairs from an archaeological site at Jabuticabeira (27°36′S, 48°30′W), in Santa Catarina State, were used to estimate a reservoir correction (Eastoe et al. 2002). Angulo et al. (2005) used museum samples and previously published determinations from shells of known age to estimate a reservoir correction considering all available data in the same region (Nadal de Masi 2001; Eastoe et al. 2002). Analyzing museum samples from Ilha do Francês (27°25′S, 48°28′W to 27°41′S, 48°29′W), in Santa Catarina State, and Ilha do Mel (25°30′S, 48°17′W to 25°35′S, 48°23′W), in Paraná State, they obtained $\Delta R$ values between 112 ± 41 and −55 ± 41 $^{14}$C yr, with a mean of 33 ± 24 $^{14}$C yr. Considering previous works, a new $\Delta R$ mean value was estimated by Angulo et al. (2005) to be 8 ± 17 $^{14}$C yr for the Brazilian southern and southeastern marine surficial coastal waters. A large range of $\Delta R$ values was taken into account for this new value, and it should not be representative of such a large coast extension. More recently, Macario et al. (2015) and Alves (2015) obtained $\Delta R$ values of −140 ± 66 $^{14}$C yr for Saquarema (22°55′S, 42°30′W) and −127 ± 67 $^{14}$C yr for Rio das Ostras (22°31′S, 41°56′W), respectively, on the southeastern Brazilian coast. Thus, the purpose of this article is to use paired samples of marine and terrestrial mollusk shells, the former being a food source for fisher-gatherer populations, distributed over several archaeological layers in shellmounds around the coast, as a potential tool for calculating MRE corrections.
MATERIALS AND METHODS

In order to investigate the dead carbon incorporation through diet by T. achilles, we have ¹⁴C dated shells of three recently dead animals collected in Cabo Frio (23°53′S, 42°29′W), Rio de Janeiro State.

To evaluate the potential use of terrestrial shells as representative of atmospheric carbon reservoir for MRE on the southeastern Brazilian coast, specimens from the Manitiba I shellmound, located in Saquarema (22°55′66″S, 42°29′00″W), Rio de Janeiro State (Figure 1), were selected from the zooarchaeological collection of the National Brazilian Museum at the Rio de Janeiro Federal University (MN-UFRJ). The Manitiba I shellmound, like most of the shellmounds located in the city of Saquarema, is positioned on a sandbank, between the lagoon and the sea, strategically close to marine resources (Kneip 2001). With a total area of 6000 m², it is the largest shellmound in the region. Excavations in 1999 and 2000 covered an area of 140 m² and seven archaeological layers were identified, with the base 3.36 m above the mean sea level. Only two funerary structures were recovered, in contrast to other shellmounds in the same area, with at least 19 funerary structures each. The spatial distribution of artifacts and other archaeological remains characterize this shellmound as a living place with intense domestic and ceremonial activities (Kneip 2001). The available dates for the Manitiba I shellmound vary from 3810 ± 70 to 4270 ± 70 BP (Kneip 2001).

Samples of T. achilles shells, charcoal from hearths, and marine shell samples of Lucina pectinata (Gmelin, 1791) from the same archaeological context (Layer IV) were analyzed. All shell samples were cleaned with ultrapure water and chemically treated with 0.1M HCl to remove the outer layer, which could be contaminated. Hydrolysis was done by injecting H₃PO₄ with a gas-tight syringe into evacuated vials to obtain CO₂. The same procedure to obtain CO₂ was adopted for calcite blanks and IAEA C2 carbonate control samples. Charcoal samples went through ABA treatment at 90°C with 1M HCl acid and 1M NaOH. Pretreated organic samples were combusted in prebaked quartz tubes with silver wire and cupric oxide at 900°C for 3 hr in a muffle oven. The gas was purified by means of dry ice/ethanol traps in the graphitization line (Macario et al. 2013). Graphitization
was performed using the zinc/titanium hydrate method with iron catalyst (Xu et al. 2007). Torch-sealed Pyrex® tubes were heated at 460°C for 7 hr in a muffle oven. The graphitized samples were measured in a NEC 250kV Single Stage Accelerator System (SSAMS). Isotopic fractionation was corrected by measuring the δ13C on-line in the accelerator. Background was measured using processed calcite blanks for carbonate samples and processed graphite for organic samples. Graphite and calcite processed blanks yielded average ages of 35 and 38 ka, respectively. Average machine background was ~50 ka for the unprocessed graphite. Accuracy was checked by measuring IAEA reference materials within the 2σ range of consensus values.

For data analysis, we used the OxCal software v 4.2.3 (Bronk Ramsey and Lee 2013). Measurements of 14C contents of terrestrial/marine samples from the same archaeological context were subjected to an OxCal phase model, a grouping model with the assumption that the events are random samples from a uniform distribution between a start boundary and an end boundary (Buck et al. 1992). The modeled dates use Bayesian analysis (Bayes 1763).

In this preliminary study, a ΔR value was calculated by calibrating the terrestrial archaeological samples, land snails termed “T” and charcoal from hearths termed “C,” with the SHCal13 atmospheric curve (Hogg et al. 2013) and compared the 14C results for each of the marine archaeological samples termed “M,” calibrated with the Marine13 curve (Reimer et al. 2013) within the same phase, considering an undetermined ΔR ranging from −500 to +500 14C yr. The software code is presented in Figure 2.

Plot(manitiba)
{
  Sequence()
  {
    Boundary("Start 1");
    Phase("Manitiba I")
    {
      Curve("ShCal13","ShCal13.14c");
      R_Date("T1", 3748, 38);
      R_Date("T2", 3767, 29);
      R_Date("T3", 3649, 47);
      R_Date("T4", 3688, 25);
      R_Date("T5", 3659, 25);
      R_Date("C1", 3747, 22);
      R_Date("C2", 3598, 46);
      Curve("Marine13","Marine13.14c");
      Delta_R("Saquarema, RJ",U(-500,500));
      R_Date("M1", 3967, 43);
      R_Date("M2", 3666, 35);
      R_Date("M3", 3999, 28);
      R_Date("M4", 4080, 25);
      R_Date("M5", 3870, 26);
      R_Date("M6", 3839, 39);
    }
    Boundary("End 1");
  }
};

Figure 2 OxCal code for Phase model and ΔR determination

RESULTS AND DISCUSSION

The 14C concentration in modern snail shells was calibrated with the post-bomb atmospheric SH1-2 curve (Hua et al. 2013). The probability distributions for the calibrated dates are presented in Figure 3 and show that this species is in equilibrium with the present-day atmosphere, indicating that
there is no incorporation of dead carbon in their diet and that such species may provide reliable dating.

Figure 3 Radiocarbon concentration in the modern terrestrial (MT) mollusks
Concerning archaeological samples, the results from charcoal are in agreement with those from terrestrial snail shells. Even though there are statistical outliers in the $^{14}$C ages of both terrestrial and marine material, the small set of samples has led us to keep them, in an attempt to take into account this variability. Moreover, only after calibration could the results be properly compared; thus, a phase model approach was considered. Table 2 lists the conventional $^{14}$C dates, calibrated dates, and modeled dates using OxCal v 4.2.3 for the archaeological samples.

Table 2 $^{14}$C values of archaeological terrestrial and marine samples. T denotes terrestrial mollusk, M denotes marine mollusk, and C denotes charcoal samples.

<table>
<thead>
<tr>
<th>Lab ID</th>
<th>Sample</th>
<th>Sample description</th>
<th>$^{14}$C (yr BP)</th>
<th>$^{14}$C calibrated age (BP)</th>
<th>$^{14}$C modeled age (BP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140442</td>
<td>T1</td>
<td><em>Thaumastus achilles</em></td>
<td>3748 ± 38</td>
<td>3908–4217</td>
<td>3915–4152</td>
</tr>
<tr>
<td>140443</td>
<td>T2</td>
<td><em>Thaumastus achilles</em></td>
<td>3767 ± 29</td>
<td>3933–4224</td>
<td>3932–4157</td>
</tr>
<tr>
<td>140444</td>
<td>T3</td>
<td><em>Thaumastus achilles</em></td>
<td>3649 ± 47</td>
<td>3728–4084</td>
<td>3770–4086</td>
</tr>
<tr>
<td>140445</td>
<td>T4</td>
<td><em>Thaumastus achilles</em></td>
<td>3688 ± 25</td>
<td>3870–4085</td>
<td>3872–4084</td>
</tr>
<tr>
<td>140446</td>
<td>T5</td>
<td><em>Thaumastus achilles</em></td>
<td>3659 ± 25</td>
<td>3838–4070</td>
<td>3839–4069</td>
</tr>
<tr>
<td>140447</td>
<td>C1</td>
<td>Charcoal</td>
<td>3747 ± 22</td>
<td>3932–4149</td>
<td>3931–4148</td>
</tr>
<tr>
<td>140448</td>
<td>C2</td>
<td>Charcoal</td>
<td>3598 ± 46</td>
<td>3699–3977</td>
<td>3716–3982</td>
</tr>
<tr>
<td>140449</td>
<td>M1</td>
<td><em>Lucina pectinata</em></td>
<td>3967 ± 43</td>
<td>3270–4774</td>
<td>3820–4321</td>
</tr>
<tr>
<td>140450</td>
<td>M2</td>
<td><em>Lucina pectinata</em></td>
<td>3666 ± 35</td>
<td>2860–4332</td>
<td>3513–3930</td>
</tr>
<tr>
<td>140451</td>
<td>M3</td>
<td><em>Lucina pectinata</em></td>
<td>3999 ± 28</td>
<td>3324–4795</td>
<td>3865–4345</td>
</tr>
<tr>
<td>140452</td>
<td>M4</td>
<td><em>Lucina pectinata</em></td>
<td>4080 ± 25</td>
<td>3381–4839</td>
<td>3971–4417</td>
</tr>
<tr>
<td>140453</td>
<td>M5</td>
<td><em>Lucina pectinata</em></td>
<td>3870 ± 26</td>
<td>3109–4608</td>
<td>3692–4158</td>
</tr>
<tr>
<td>140454</td>
<td>M6</td>
<td><em>Lucina pectinata</em></td>
<td>3839 ± 39</td>
<td>3060–4561</td>
<td>3655–4136</td>
</tr>
</tbody>
</table>

Figure 3 Modeled dates of marine and terrestrial paired samples from the same archaeological context using OxCal v 4.2.3 (Bronk Ramsey and Lee 2013).
Calibrated modeled dates for terrestrial and marine samples leaving ΔR undetermined within a 1000 ¹⁴C yr range can be observed in Figure 3. Probability distributions for the beginning and ending of the phase are also shown. Based on this model, a local reservoir effect (ΔR value) of −82 ± 71 ¹⁴C yr was calculated from the Manitiba I shellmound (Figure 4).

The negative value for the ΔR correction found in this article decreases the total correction for the MRE in the studied region. Saquarema is affected by a well-known seasonal upwelling effect (Ikeda et al. 1974) that would yield positive values for the ΔR correction. However, the material sampled in this work could be influenced by freshwater due to the proximity of the lagoon. The result is also in agreement with the other results obtained for this region (Alves et al. 2015; Macario et al. 2015). These results show that it is possible to determine reliable ΔR values using terrestrial/marine samples, from an archaeological site, that were found in the same depositional context. Also, the study shows that there is no incorporation of dead carbon in the *T. achilles* diet, and this species may provide reliable dating.

**CONCLUSION**

Quantifying the marine reservoir effect provides a better understanding of local coastal processes. In the southeastern coast of Brazil, there are many archaeological shellmounds dating from 5 to 2 kyr cal BP that contain terrestrial and marine remains in the same archaeostratigraphic context. However, charcoal is not usually as thoroughly distributed as shells and, when this is the case, terrestrial gastropods with the potential to yield reliable ¹⁴C dates, such as *T. achilles*, can be used instead. A ΔR value of −82 ± 71 ¹⁴C yr was calculated for the Saquarema region from Manitiba I shellmound terrestrial/marine paired samples using an OxCal phase model.

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