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Fish bone diagenesis in southeastern Brazilian shell mounds and its importance for paleoenvironmental studies

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ABSTRACT

Brazilian shell mounds are relicts of prehistoric settlements characterized as distinct features on the sandy coastal plain, sandy bars of coastal lagoons and rocky island. They are composed of shells of edible marine mollusks, fish remains and wildlife bones intermixed with sand. In the coastal lagoon region of the Rio de Janeiro state these shell mounds range in age between 5100 and 1300 cal BP. In this study we analyzed the geochemistry of the bones of the whitemouth croaker that primarily offers insight on the nature of bone diagenesis and its use for radiochronology and as isotope paleo-thermometer. The x-ray diffractograms of bones from the Tarioba shell mound exhibit elevated calcite profiles in contrast to a reduced hydroxyapatite concentration. Two peaks of quartz and the presence of feldspar provide evidence of exogenous materials, *e.g.*, sand or silt particles, infilling hollow spaces within the fish bones. The Beirada and the Ponte do Girau shell mounds are characterized by the highest peaks of apatite relative to calcite, which is clearly different from the result obtained for Tarioba. The Manitiba profile is similar to the Tarioba profile except for calcite peaks that are approximately three times lower than those for Tarioba. At a depth of 25 cm in the Tarioba shell mound, the redox sensitive index of diagenetic alteration reaches its maximum value, suggesting a zone of accumulation in the soil horizon redox condition. The $\delta^{18}O$ derived temperatures profile based on mollusks showed a consistent range from 18.1 to 24.1 °C, indicating seasonal events of intense upwelling of the South Atlantic Central Water breaking the mean warm surface conditions of the Brazil Current. Diagenetic imprints of Tarioba shell mound suggest humid burial conditions with the loss of hydroxyapatite and the enrichment of exogenous calcite. Drier depositional environmental conditions are indicated in the Ponte do Girau and the Beirada shell mounds, while intermediary depositional environmental conditions characterize the Manitiba shell mound. In the period represented by the shell mound samples, the sea level exhibited significant oscillations and portions of the inner shelf were exposed, which may have resulted in an anomalous derived temperature records. These results are compatible with events of anomalous temperatures occurring in the sea level during the time span of occupation of these shell mounds.

1. Introduction

The southeastern Brazilian coast has numerous pre-historic shell mounds settlements or the so-called “sambaquis”, relicts of

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prehistoric settlements found scattered over the extensive sandy coastal plain and dunes, littoral sandy bars, coastal lagoons and rocky islands. All of them were under the influence of a seasonal coastal upwelling zone (Fig. 1), even though this region in the South America is characterized by the presence of an oligotrophic and warm western boundary current (Brazil Current). The shell mounds along the coastal lagoon region of the Rio de Janeiro state (*e.g.*, Tarioba, Manitiba, Beirada and Ponte do Girau) range in age between 5100 and 1300 cal BP (Kneip, 2001; Angulo et al., 2007; Tenório et al., 2010; Macario et al., 2014) and are primarily composed of shell of edible marine mollusks, fish remains and wildlife bones intermixed with sand and remains of precolonial civilization (Dias, 2001; Kneip, 2001; Tenório et al., 2010). Previous studies of the faunal remains found in these sites (Kneip, 2001; Souza et al., 2010) revealed that the primary fish target by the precolonial communities was the whitemouth croaker (Sciaenidae, *Micropogonias furnieri*). Radiocarbon isotope age dating from material of these shell mounds used mollusks (calcite), otoliths (aragonite) and charcoal, and have resulted in an accurate age and reservoir data (Macario et al., 2014, 2015; Carvalho et al., 2014).

The accuracy of the results of the isotopes geochemistry analysis depends on the sampled material to represent a mineralogically pristine composition (Zazzo and Saliège, 2011; West et al., 2012), and a careful assessment of the preservation of an original signal of the bone is also mandatory. Therefore, it is essential to study the geochemistry of such fish bones, in order to understand their nature and their potential use for radiochronology and as isotope paleothermometer. It is important to understand the influence of geochemical modifications in the bone matrix in order to arrive at paleoenvironmental interpretarions.

Here, we have analyzed X-ray diffractograms for crystallographic and quantitative multi-element analyses of bones of the whitemouth croaker (Sciaenidae, *M. furnieri*) from Rio de Janeiro shell mounds, to understand the geochemical composition and the diagenetic processes under burial conditions, and evaluate the climate and marine influence of the paleo-upwelling documented in these shell mounds. Isotopes analyses of mollusk shell samples in the two archaeo-estratigraphic sections of the Tarioba shell mound were used to reinforce the resulting paleoenvironmetal interpretations, because the mollusk tissues is mineralized by the deposition of a solid phase of $CaCO_3$, and not by crystals of calcium phosphate.

2. Fish bone diagenesis and geochemistry

Fish skeletons are generally characterized by an acellular bone structure, lacking the osteocytes that comprise the majority of bone cells in tetrapods (Witten and Huysseune, 2009). The diagenesis of the fish bones, is strongly dependent on environmental conditions, including micro-porosity, the presence of organic matter, bacteria and fungi in the soil, the temperature, hydrology and geochemical changes that occurred soon after burial (Petchey and Higham, 2000; Hedges, 2002; Jans et al., 2004; Stathopoulou et al., 2008; Szpak, 2011; Pitre et al., 2013). The relative stability of the collagen molecule in fish is much lower and more prone to chemical hydrolysis than in mammals (Szpak, 2011), in consequence the diagenetic process severely reduces the suitable substrate for radiocarbon dating (Brock et al., 2010). Because bone preservation could vary with burial depth, skeletal structure, soil humidity and climate, we have been exploring for specific

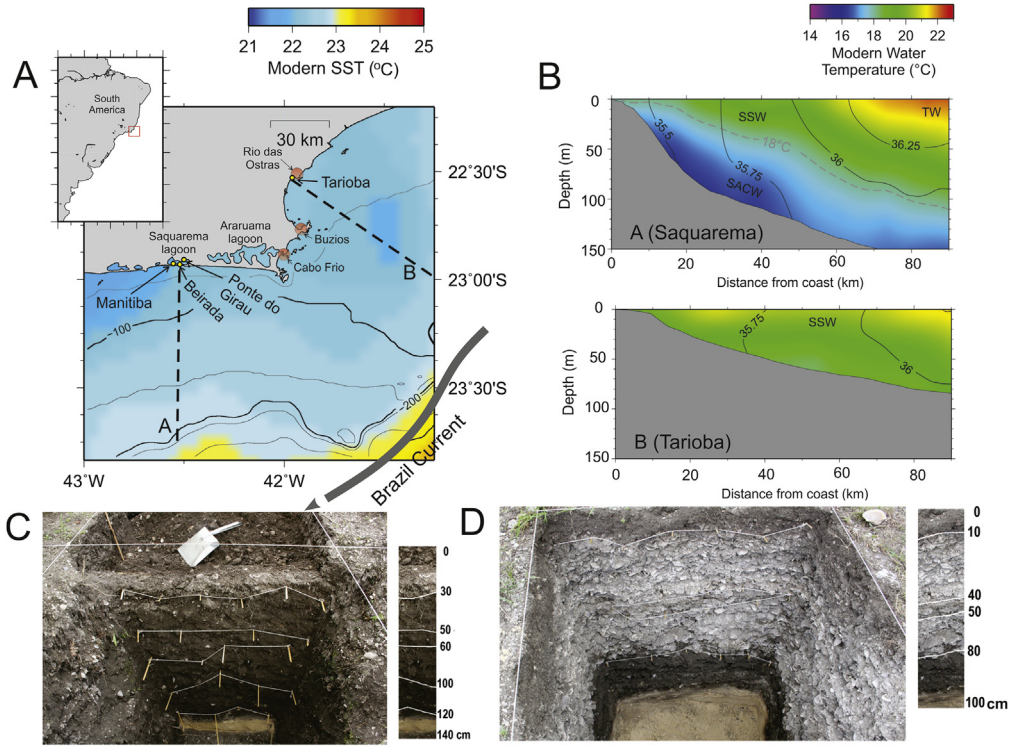

Fig. 1. (A) Study area along the southeastern Brazilian coast showing the locations of the shell mounds. The average modern sea surface temperature (SST-°C) is derived from the GHRSST/OSTIA program for the period from 2010 to 2012. (B) Two cross sections of the continental shelf (A – Saquarema; B – Tarioba) show the summertime temperature and salinity profiles based on 30 years of collected hydrographic data from the World Ocean Data Center (www.nodc.noaa.gov). The 18 °C isotherm in section A (Saquarema) is highlighted. Depth data were obtained from the ETOPO-2 dataset. (C) Detailed shell mound sections and outcrops in Tarioba A and (D) Tarioba B.