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STROMATOLITE GROWTH IN LAGOA VERMELHA, SOUTHEASTERN COAST OF BRAZIL: EVIDENCE OF ENVIRONMENTAL CHANGES

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ABSTRACT. Among the oldest remains of living beings to have inhabited the Earth's surface, there are the stromatolites—laminated sedimentary rocks associated with lithified mats of layered phototrophic microbial communities—which grow in specific environmental conditions. In the present work, we study a recent carbonatic stromatolite from Lagoa Vermelha (Rio de Janeiro, Brazil), a shallow coastal hypersaline lagoon. X-ray diffraction was associated to a depth chronological model defining three different sections based on changes in mineral composition of the stromatolite with increased dolomite content. Although a mean growth rate of 0.19 ± 0.03 mm/yr is observed, the model discloses decreasing growth rates among the sections. Since dolomite formation can be related to high availability of Mg⁺², confirmed by an expressive presence of (Ca, Mg)CO₃, the lower growth rates were associated to a more arid environment, until approximately 1440 cal AD, with higher temperatures and consequently promoting water evaporation and salinity enhancement.

KEYWORDS: climate, radiocarbon AMS dating, stromatolite, X-ray diffraction.

INTRODUCTION

Between marine and continental environments there are the coastal zones—wide areas that allow the coexistence of different depositional environments, such as tidal plains, deltas, beaches, dunes, estuaries, lagoons, etc. (Souza et al. 2005). Lagoons constitute 15% of the world's coastal zone and are among the most productive ecosystems in the biosphere (Barroso and Bernardes 1995). They occur along the whole Brazilian coast, mostly concentrated in the states of Rio de Janeiro and Rio Grande do Sul (Esteves 1998). Coastal lagoons can be freshwater, brackish, marine, or hypersaline environments, depending of water sources, climate and/or season. Hyper-salinity in coastal lagoons can be related to climate changes and human impact (Moreira-Turcq 2000). Such environments give origin to stromatolites, organosedimentary structures produced by trapping or capture followed by precipitation of sediments, resulting essentially from the metabolic activity of microorganisms, mainly cyanobacteria (Silva and Silva 2002). The study of the crystalline composition of these organisms and the understanding of their relation to the environment is important for the reconstruction of the paleoenvironment where they have grown. Moreover, this kind of study can give information about past climatic conditions.

In the present work, a stromatolite structure was analyzed by X-ray diffraction (XRD) and radiocarbon accelerator mass spectrometry (¹⁴C AMS), with the aim of evaluating its growth rate and to relate it to its mineralogical composition. Combining such information should permit inference of the climatic conditions during the period the stromatolite was developed.

Additionally, since there is no well-stablished sample-preparation protocol in the literature for such material, we discuss the applied methodology for ¹⁴C-AMS dating of stromatolites, allied to the XRD technique, in order to contribute to future research on this topic.

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MATERIAL AND METHODS

Samples of stromatolites were collected at the southern margin of a hyper-saline lagoon, Lagoa Vermelha (22°55′58″S, 42°23′35″W), in January 2013. This lagoon is located between the municipalities of Saquarema and Araruama in Rio de Janeiro State, Brazil (Figure 1).

The lagoon has an area of 2.5 km^2 , with 4.4 km in extension and width varying from 250 to 800 m, with depths varying from 0.2 to 1.7 m, separated from the ocean by a coastal chain 9 m high and 350 m wide, a barrier developed after a strong transgressive period and subject to a semi-arid climate due the occurrence of an upwelling zone (Barbiére 1985). Lagoa Vermelha is under the influence of strong winds and the water column is not stratified (Höhn et al. 1986), being homogeneous in its whole extension. The lagoon was formed during the most recent Quaternary regression and it is located between two quartz rich sandbanks (Coe Netto 1984).

In periods of drought the lagoon experiences a high rate of evaporation, with a 6-m recoil in relation to rainy seasons, leaving the bottom visible, with a cover of algae, gelatinlike and laminated with 2-8 cm in thickness (Santelli 1988). In this same environment flat, laminated gelatinous mats (3–6 cm thick) develop and distribute through the edges of the lagoon up to 30–40 m from the margins (Höhn et al. 1986).

The individual stromatolite analyzed in this work was 20 cm in diameter and 7 cm high. The samples for ¹⁴C dating were prepared and analyzed at the Radiocarbon Laboratory of the Fluminense Federal University (LAC-UFF). The stromatolite was subdivided in 10 arbitrarily defined layers (Figure 2) following its growth pattern, from the bottom (oldest layer) to the top (youngest layer). Thickness of such layers (1.0–1.75 cm) were based on operational conditions only. These samples were treated with hydrogen peroxide in order to remove organic matter. Individual subsamples of approximately 40 mg were chemically treated with HCl and converted to CO₂ by hydrolysis with H₃PO₄. Graphitized samples were measured in a NEC 250 kV single stage accelerator system (SSAMS) (Macario et al. 2013, 2015). Typical currents were 50 μ A¹²C⁻¹ (measured at the low energy Faraday cup). Graphite standard and calcite blanks yielded average ¹⁴C/¹³C ratios of 6×10⁻¹³ and 7×10⁻¹³, respectively. The average machine background was around 50 kyr for the unprocessed graphite, while the average precision ranged from 0.3 to 0.5%. Data analyses were carried on LACAMS software (Castro et al. 2015). Calibration of each estromatolite ¹⁴C age was performed with the OxCal software v4.3 (Bronk Ramsey 2009a) using the Marine13 calibration curve (Reimer et al. 2013) in the



Figure 1 Study region on the coast of Rio de Janeiro State.



Figure 2 The studied stromatolite showing the arbitrarily defined sampling layers.

 2σ range. A chronological growth model (Bronk Ramsey and Lee 2013) was constructed assuming uniform growth in separate sections of the stromatolite. Boundaries were set at layers A04 and A07 relative to mineralogical composition changes, with a general outlier model (Bronk Ramsey 2009b) with 5% prior probability. The local reservoir offset was assumed to be -82 ± 71 ¹⁴C yr as the closest determination available in literature from the paired terrestrial and marine samples of the Manitiba archaeological site (22°55′66″S, 42°29′00″W) dated to 4.2–3.6 ka cal BP (95.4%) in Saquarema (Carvalho et al. 2015). Old carbon incorporation was not considered since there are no carbonate rocks in this region (Jansen et al. 2012).

X-ray diffraction (XRPD) analysis was used to investigate the crystalline structure of the powdered samples. The samples preparation and analysis were undertaken at the Laboratório de Difração de Raios X of the Fluminense Federal University (LDRX – UFF). A Bruker AXS D8 Advance (Cu K α radiation, 40 kV, 40 mA) model was operated in a Bragg–Brentano θ/θ configuration, with the diffraction patterns being collected in a flat geometry with steps of 0.02 degrees and accumulation time of 2.0 s per step using a PSD detector (Bruker AXS LynexEye model). The XRPD data were refined following the Rietveld method with the GSAS-II software (Toby and Von Dreele 2013).

RESULTS

Mineral Composition

Table 1 and Figure 3 show the results of X-ray diffraction of the different operationally defined layers of the stromatolite shown in Figure 2. High magnesium calcite (HMC), represented by (Ca, Mg)CO₃, predominates in most layers. Aragonite was present in all layers, whereas dolomite and quartz were detected in only two of them. No other differences in the mineral composition were found between central layers (A03-A08) and clotted layers (A01-A02, A09-A10).

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Layer	Aragonite (%)	(Ca,Mg)CO ₃ (%)	Dolomite (%)	Quartz (%)
A01	15.05	84.96	0	0
A02	6.64	93.36	0	0
A03	8.4	91.59	0	0
A04	2.94	21.54	75.3	0.23
A05	2.34	97.66	0	0
A06	10.97	88.77	0	0.25
A07	16.71	48.89	34.4	0
A08	20.25	79.75	0	0
A09	23.57	76.44	0	0
A10	9.14	90.86	0	0

Table 1 Mineral composition of each arbitrarily defined layer.

The small amounts of quartz found by XRD probably came from the sand grains attached to or embedded within the mineral matrix. Although Lagoa Vermelha is surrounded by sandbanks, authigenic (Ca, Mg)CO₃ minerals largely predominated, which shows similarity to Precambrian stromatolites. Recent stromatolite accretion is strongly influenced by the incorporation of a large amount of trapped grains (Spadafora et al. 2010).

Growth Rate

Table 2 shows the results for conventional ¹⁴C dates for each layer analyzed as well as calibrated and modeled ages. The model presented in Figure 4 assumes uniform growth in each of three sections. Figure 5 shows a block diagram that represents the computational code used in the growth model on the OxCal software. Boundaries were set at each dolomite increase defining three different growth rates: from A01-A03—section 1 (S1) 0.54 ± 0.08 mm/yr; from A04-A06 —section 2 (S2) 0.29 ± 0.05 mm/yr; from A07-A10—section 3 (S3) 0.093 ± 0.015 mm/yr; with a mean growth rate of 0.19 ± 0.03 mm/yr. Model agreement was 91% with posterior outlier probabilities of less than 5%, except for layer 1, with 13% and 8, with 21%.

DISCUSSION

The gross morphology is characteristic of "biscuit" microbialites and the presence of quartz in the diffractograms indicate the autochthonous origin of the stromatolite. Lamination is evidenced only by color differences and the two upper layers seemed to fuse in a denser region. Growth rate in this region is difficult to evaluate because the natural layering is not well-defined. If color variations are taken as evidence for layering, then each layer would form in 20–30 yr. On the other hand, denser regions show a smaller empty volume, and thus the mass increase partially counterbalances the decrease in the number of natural layers.

Carbonate sedimentation studies conducted by Vasconcelos (1988) in Lagoa Vermelha indicated that the most abundant fractions in top sediments are aragonite and Mg-calcite. According to the authors, Mg-calcite after its deposition can be converted to dolomite that is formed in dryer environmental conditions. Dolomite formation is a result of the coalescence of carbonate nanoglobules around degraded organic matter nuclei (biomineralization) (Spadafora et al. 2010). Several authors have shown that the formation of dolomite is favored when there is high availability of Mg⁺² (van Lith et al. 2002; Dupraz and Visscher 2005; Spadafora et al. 2010). Following van Lith et al (2002) in Lagoa Vermelha, high Mg-calcite is formed before



Figure 3 X-ray diffractograms of each arbitrarily defined layer: (a) samples from A01-A03 layers—section 1 (S1); (b) samples from A04-A06 layers—section 2 (S2); (c) samples from A07-A10 layers—section 3 (S3).

dolomite. This can be confirmed in the present work by the high content of Mg-calcite (Ca, Mg) CO_3 in different layers of the stromatolite. Indeed, many factors are important for dolomite formation such as temperature increase that may contribute to evaporation, resulting in salinity enhancement. Anjos (2004) investigated salinity and $\delta^{18}O$ seasonal variations for Lagoa Vermelha waters and found salinity between 45 and 120, higher than sea water as expected, and $\delta^{18}O$ indicated intense evaporation periods. However, those results do not confirm seasonal variations, showing that they can be due to local climatic events.

Lagoa Vermelha water has a typical seawater Mg/Ca molar ratio of 5 indicating a seawater origin, modified by evaporation and dilution processes (van Lith et al. 2002; Moreira et al. 2004). According to Müller et al. (1972) HMC can be expected when Mg/Ca ratios exceed 2.



Figure 3 (Continued)

Layer	Depth (cm)	Conventional ¹⁴ C age (BP)	Calibrated age 95.4% (cal AD)	Modeled age 95.4% (cal AD)	$\begin{array}{c} \mu \pm \sigma \\ (cal \text{ AD}) \end{array}$	Lab code LACUFF-
A01	9.25	1217 ± 51	930–1290	790–1170	990 ± 90	150059
A02	7.75	1383 ± 69	710–1150	850-1180	1020 ± 80	150060
A03	6.50	1315 ± 55	790–1210	890-1200	1040 ± 70	150061
A04	5.50	1279 ± 52	840-1240	910-1220	1060 ± 70	150062
A05	4.75	1165 ± 65	960-1330	950-1240	1090 ± 70	150063
A06	4.25	1192 ± 53	960-1300	970-1260	1100 ± 70	150064
A07	3.75	1204 ± 53	940-1300	990-1280	1120 ± 70	150065
A08	3.00	1292 ± 51	820-1230	1080-1340	1200 ± 60	150066
A09	2.00	1009 ± 52	1120-1450	1190-1430	1310 ± 60	150067
A10	0.75	791 ± 51	1310–1640	1300–1560	1440 ± 60	150068

Table 2 Results for conventional ^{14}C age, calibrated and modeled ages (in the 2σ range) for each arbitrarily defined layer.



Figure 4 Growth model considering uniform growth between operationally defined layers: from A01-A03 (Section 1), A04-A06 (Section 2), and A07-A10 (Section 3). Envelopes correspond to 1σ and 2σ ranges and dots represent mean values.



Figure 5 Block diagram that represents the computational code used in the growth model considering uniform growth in each of the defined sections.

Moreover, the concomitant occurrence of aragonite and HMC in all layers may reflect different seasonal conditions during the formation of the stromatolite. In Coorong Lagoon, Australia (Botz and Borch 1984), the occurrence of aragonite was related to periods of lower salinity. The hypothesis of dolomite dilution by groundwater inflow into the Lagoa Vermelha has already been addressed by Höhn et al. (1986) and Moreira et al. (1987) interpreting pore-water chemistry and mineral occurrence. However, such hypotheses are not exclusive, they are complementary. The presence of dolomite in layers A04 and A07 endorses some climate change, going through a more arid period, while its absence may be due to greater precipitation and groundwater flow in the region.

Arid conditions in the Late Holocene were also described for fish bones found in archaeological shellmounds (calibrated ¹⁴C ages ranging between 4632 and 3211 cal BP) in Rio das Ostras (RJ) (22°31′40″S, 41°56′22″W) and Saquarema (RJ) (22°55′66″S, 42°29′00″W) (Aguilera et al. 2015). Diagenesis, which depends primarily on climate conditions (Marean 1991), can be recognized from several geochemical alterations that occur at different stages after the burial. The diagenetic imprints in bones observed in Saquarema suggested even drier depositional environmental conditions in comparison to Rio das Ostras showing that Lagoa Vermelha region was also subject to this kind of environmental changes.

Environmental conditions can also be evaluated by the analysis of growth rate. The range of observed values of growth rate were similar to those obtained in other studies. Petryshyn (2012)

estimated the growth rate of sub-fossil stromatolites from alkaline Walker Lake in Nevada varying between 0.07 to 0.39 mm/yr, at the borders and center of the stromatolite, respectively. Paull et al. (1992) estimated stromatolite growth in a coastal hyper-saline lagoon as one natural layer in 21 yr or 0.16 mm/yr. Andersen et al. (2011) estimated the growth of stromatolites from freshwater Lake Untersee (Antarctica) as 1 mm in 40 yr or 0.025 mm/yr. Bahniuk et al. (2013) estimated the growth of a recent sub-fossil stromatolite (2300–200 BP) from the coastal hyper-saline Lagoa Salgada to be about 0.1 mm/yr.

The chronological model shows the growth evolution of each layer and indicates a change in the stromatolite growth rate about 1060 cal AD, reflected in the composition of layer A04 with 75% dolomite. An even more pronounced decrease in growth rate is observed at 1120 cal AD, related to layer A07 with 34% dolomite. The lower growth rates corroborate the scenario of a more arid environment, with higher temperatures and consequently promoting water evaporation and salinity enhancement. The stomatolite then grew until approximately 1440 cal AD with a rate of 0.09 mm/yr.

At that time, a global climatic event took place, the so-called Little Ice Age (LIA). During approximately 1400–1800 AD, non-tropical Northern Hemisphere continents suffered significant cooling, affecting atmospheric circulation and causing episodes of wetter or drier conditions recorded in several parts of the world (Mayewski et al. 2004; Mann et al. 2009). Low-latitude continental areas became more arid as the trade winds strengthened and the Intertropical Convergence Zone (ITCZ) shifted southward (Goni et al. 2009; Gutierrez et al. 2009). A few studies in the southeastern Brazilian coast report strong storm events at 1560–1700 AD (Oliveira et al. 2014; Almeida et al. 2013) and increase in upwelling in the last 700 yr (Mahiques et al. 2005; Souto et al. 2011). The increase in aridity indicated by both mineral composition and decrease in growth rates of the stromatolite of Lagoa Vermelha, leading to its eventual death at about 1440 AD may be a reflection of the local atmospheric changes following LIA.

CONCLUSION

The study of stromatolite growth rate by ¹⁴C dating using AMS associated with mineralogical characterization by X-ray diffraction has allowed the development of a palaeoenvironmental study in the Lagoa Vermelha in the State of Rio de Janeiro, Brazil. The authors were able to correlate possible climate changes that could increase preferential precipitation of specific minerals. Based on the observed results, we conclude that a possible increase in local aridity may have been responsible for the observed increase in dolomite concentration within the stromatolite structure and that LIA could be responsible for the end of stromatolite growth. For the chemical preparation of stromatolites for ¹⁴C-AMS analysis, standard carbonate protocols could be applied, provided organic matter was previously removed with hydrogen peroxide.

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