^{14}C DATING OF ORGANIC RESIDUE AND CARBONATE FROM STROMATOLITES IN ETOSHA PAN, NAMIBIA: ^{14}C RESERVOIR EFFECT, CORRECTION OF PUBLISHED AGES, AND EVIDENCE OF >8-m-DEEP LAKE DURING THE LATE PLEISTOCENE

George A Brook[1] • A Cherkinsky[2] • L Bruce Railsback[3] • Eugene Marais[4] • Martin H T Hipondoka[5]

ABSTRACT. Lacustrine stromatolites are layered accretionary structures formed in shallow water by cyanobacteria. They are a precise indicator of high lake limits and their morphology and structure provide an insight into paleoenvironments of the time. Previous research on lacustrine stromatolites from Etosha Pan in Namibia based on radiocarbon ages of carbonates were close to the limit of the method and did not account for any possible ^{14}C reservoir effect. The ages were used to suggest that the basin was not extensively flooded during the last 40,000 yr. To assess the reservoir effect, the age characteristics of a stromatolite from Poacher's Point were investigated by ^{14}C dating both carbonate and organic residue from samples at different depths in the deposit. The ~15-cm-diameter stromatolite was separated into 12 zones from the center to the edge and block samples were cut from each zone; the carbonate and residual organic residue were dated separately. The carbonate ages ranged from 34,700 to 24,700 ^{14}C yr BP and the organic ages from 15,700 to 2500 ^{14}C yr BP. Ages generally increased with increasing distance from the surface of the deposit. We believe that the organic ages are an accurate estimate of the stromatolite's age, while the much older carbonate ages reflect incorporation of old carbon from limestone bedrock and ancient calcrete introduced by stream and spring flow. Excluding the 2 oldest organic ages (15,700 and 13,600 ^{14}C yr BP), which may reflect contamination by older organic material washed into the lake during flooding, a linear regression relationship between carbonate and organic ages indicates that the reservoir effect on carbonate ranges up to ~24,000 ^{14}C yr BP but decreases slightly as the true age of the deposit increases. This regression relationship was used to correct 2 finite carbonate ages for stromatolites from Pelican Island obtained in the early 1980s, which together with our new organic age for a stromatolite from Andoni Bay, document a >8-m-deep lake in Etosha Pan during the Late Pleistocene, at and prior to ~34,000–26,000 cal yr BP. The organic carbon ages from the Poacher's Point stromatolite suggest prolonged lacustrine conditions during the early to middle Holocene (8000–6600 cal yr BP) but not to the extent seen during the Late Pleistocene.

INTRODUCTION

Stromatolites are laminated organo-sedimentary structures formed by the trapping, binding, and precipitation of minerals by microorganisms. Fossil stromatolites constitute the earliest and most pervasive record of life on Earth and they are still forming in both ocean and freshwater environments today. The stromatolite structure consists of numerous internal columns constructed by cyanobacteria growing in an evaporitic lake. The growth habit of the microbial communities has been imparted upon the carbonate structure, thereby creating a "biogenic fabric," which is a characteristic of this particular bacterial community. Stromatolites still grow today in alkaline and saline lakes where the adverse chemistry of the lake waters suppresses the populations of algae and grazing animals.

Environmental conditions in southern Africa are not conductive to the preservation of organic deposits that are suitable for radiocarbon dating, so many studies have used chronologies based on ^{14}C and U-series dating of calcrete, tufa and lacustrine carbonates. However, recent research has shown that many of these ages are not reliable because at the time of their formation the analyzed carbonates may have included old carbon and after formation they were prone to leaching, recrystallization, and incorporation of younger carbon (Geyh and Eitel 1998). As a result, many interpretations based on carbonate ages are now considered suspect.

[1]Department of Geography, University of Georgia, Athens, Georgia 30602, USA.
[2]Center for Applied Isotope Studies, University of Georgia, Athens, Georgia 30602, USA. Corresponding author. Email: acherkin@uga.edu.
[3]Department of Geology, University of Georgia, Athens, Georgia 30602, USA.
[4]Entomology Centre, National Museum of Namibia, PO Box 1203, Windhoek, Namibia.
[5]Department of Geography, History and Environmental Studies, University of Namibia, PB 13301, Windhoek, Namibia.

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This article uses sample ages on carbonate and organic residue from a stromatolite in Etosha Pan to assess the magnitude of contamination of the carbonate by old carbon. The estimated "reservoir effect" is then used to correct 2 stromatolite carbonate ages for Pelican Island reported by Rust (1984). In addition, an organic age for a stromatolite from ~8 m above the present pan floor at Andoni Bay is reported and the paleoclimatic implications of the results are discussed.

ETOSHA PAN

Etosha Pan occupies the eastern part of the Etosha National Park game reserve. The pan is 80 km north to south and 120 km east to west and has an area of 4760 km^2 (Lindeque and Archibald 1991). Etosha is the end point of an internal drainage system in northern Namibia and southern Angola above the Great Escarpment at elevations near 1080 m asl. Seasonal rainfall varies from 500 mm/yr in the east to ~300 mm/yr in the west. The pan is inundated to very shallow depth during the austral summer wet season, particularly in the west where the Ekuma River enters the depression and then dries out during the austral winter dry season.

Etosha Pan is formed in Kalahari Group rocks/sediments and was formerly the end point of the paleo-Kunene River drainage system before the flow of the Kunene was diverted to the Atlantic Ocean (Miller 2008). The pan floor is covered by greenish-gray, halite-bearing clays of the Etosha Pan Clay Member of the Andoni Formation; the clay is up to 50 m thick (Miller 2008). The Etosha Calcrete Formation dominates the surface geology as it covers the whole of the southern part of Etosha National Park south of the pan and vast areas to the east and west. Miller (2008) describes it as a gigantic groundwater calcrete apron 80 km wide and up to 120 m thick. This calcrete apron was generated by numerous springs in the Otavi carbonates and it continues to be deposited today. The upper sediments of the Kalahari Group may be more than 4 Ma old. Much of the water entering Etosha during the wet season will have come in contact with this old secondary carbonate deposit.

Figure 1 Satellite image of Etosha Pan showing the locations of sites mentioned in the text: 1 = Okondeka; 2 = Poacher's Point; 3 = Southern Andoni Bay; 4 = Pelican Island.

MATERIALS AND METHODS

Two oncoidal stromatolites were studied. EPSO-1 was collected on the western side of the Poacher's Point ridge at ~1084 m asl, about 1–2 m above the present pan surface. The most recent water line shows that when it was collected it was still being washed and rolled at times of shallow flooding of the pan. EPSO-1 is a nearly spherical concretion 19.3–14.5 cm in diameter (Figure 2). In contrast, MART1-14 (Figure 3) was removed from a ~10-m-thick sediment sequence exposed along the southern shore of Andoni Bay at an elevation of ~1094 m asl. The ~28 × 20-cm-diameter oncoid was ~8 m above the present pan floor at ~1086 m asl. The sediment profile included, at the top, 2 m of calcrete overlying ~0.5 m of uncemented sediment containing oncoidal stromatolites ranging from several to ~33 cm in diameter. These stromatolites appeared to be in growth position. Below the stromatolite layer, the sediment face was mantled by sands and clays with occasional stromatolites not in growth position that appeared to have been eroded from the sediment section and slumped downslope. Both the Poacher's Point and Andoni Bay stromatolites are dense and well lithified and the samples we analyzed were mostly (~99%) calcium carbonate.

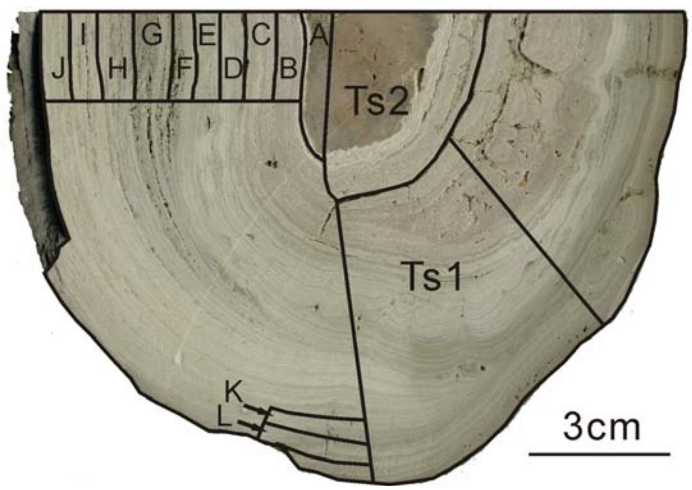

Figure 2 The EPSO-1 oncoid from Poacher's Point showing growth zones and the samples cut for ^{14}C dating (after Brook et al. 2010).

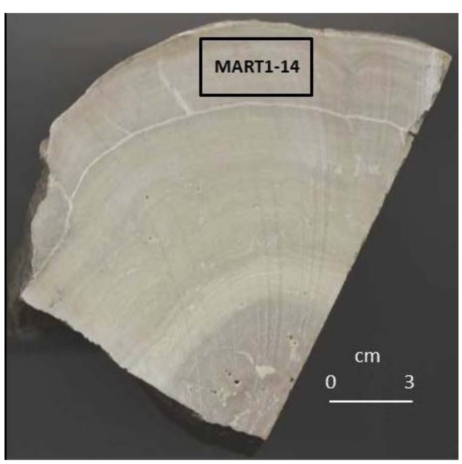

Figure 3 The MART1 oncoid from Andoni Bay showing growth zones and the location of the sample cut for ^{14}C dating of residual organic matter.

Twelve block samples (A-M in Figure 2) were cut from the EPSO-1 oncoid and each was divided into 2 subsamples for dating and stable isotope analysis. The smaller sample of about 0.5 g was used for the carbonate fraction and the larger subsample, about 2–3 g, for extracting and dating the organic residue. A block sample of 2–3 g was cut from the outer 2 cm of the Andoni Bay oncoid; this was used to date the organic residue and for stable carbon isotope studies (Figure 3).

Samples for carbonate age determination were reacted with phosphoric acid at 60 °C for 1 hr to recover CO_2 for graphitization. Samples for organic residue analysis were treated with HCl at room temperature until the reaction completed. The precipitate was collected in a test tube, decanted and treated with fresh 1N HCl at 80 °C for 1 hr. The samples were then rinsed with Milli-Q™ water and dried at 60 °C. The cleaned samples containing organic-mineral compounds were placed in quartz tubes with baked copper oxide. The tubes were evacuated, sealed, and combusted at 900 °C.

The resulting carbon dioxide from both treatments was cryogenically purified from the other reaction products and catalytically converted to graphite. Graphite $^{14}C/^{13}C$ ratios were measured using the compact Pelletron AMS system 1.5SDH-1 with total energy ~1 MeV. (Cherkinsky et al. 2010). Sample ratios were compared to the ratio measured from OXI (NIST SRM 4990b). The sample $^{13}C/^{12}C$ ratios were measured separately using a conventional stable isotope ratio mass spectrometer MAT-252 and were expressed as $\delta^{13}C$ with respect to the PDB standard with an error of <0.1%.

The results of the measurements are reported as conventional ^{14}C ages (Stuiver and Polach 1977) in Table 1 and calibrated in calendar ranges using the calibration program CALIB 6.0 (http://calib.qub.ac.uk/calib/). However, calibrating the ages was not straightforward. Only 8 of the 25 ages could be calibrated using the most relevant calibration curve, the Southern Hemisphere SHCal04 curve of McCormac et al. (2004). The remaining 17 dates were beyond the range of this curve (0–11 cal ka yr BP) and so were calibrated at 2σ standard deviation using the IntCal09 calibration curve based on Northern Hemisphere data (Reimer et al. 2009). The estimated offset between the Northern and Southern Hemisphere is about 40 ± 13 yr (Hogg et. al. 2002), which is significantly less than the calibrated age range.

RESULTS AND DISCUSSION

To estimate the portion of old carbonate derived from the extensive calcrete and limestone deposits surrounding Etosha Pan, we compared the dates from the organic and inorganic fractions. The calibrated ages for the carbonate samples ranged from 40,100 to 29,300 cal yr BP and for organic materials from 19,000 to 2500 cal yr BP (Table 1). In every pair, the carbonate produced a much older age than the organic material. The average difference between the younger organic and the older carbonate age pairs was 23,500 cal yr BP and the variation ranged from 14,100 to 28,800 cal yr BP. This average difference is quite close to the range of ^{14}C ages that Rust (1984) obtained for lacustrine marl (Rust refers to this as chalk) from Etosha Pan, namely from 13,500 to 26,200 cal yr BP. The marl is a sedimentary carbonate that precipitates under suitable conditions from saturated solutions. The ages for the marl suggest that as stromatolites grow they accumulate old carbonate material brought by rivers to the pan. Figures 4 and 5 show that there is a general progression towards younger carbonate and organic ages from the center of the oncoid to its margin with linear regression analysis producing the following relationships:

$$\text{Organic age (cal yr BP)} = 14{,}102 - 1203.8 * \text{Distance (cm)} \quad (R^2 = 0.76,\ n = 10) \tag{1}$$

$$\text{Carbonate age (cal yr BP)} = 40{,}000 - 1264.7 * \text{Distance (cm)} \quad (R^2 = 0.51,\ n = 12) \tag{2}$$

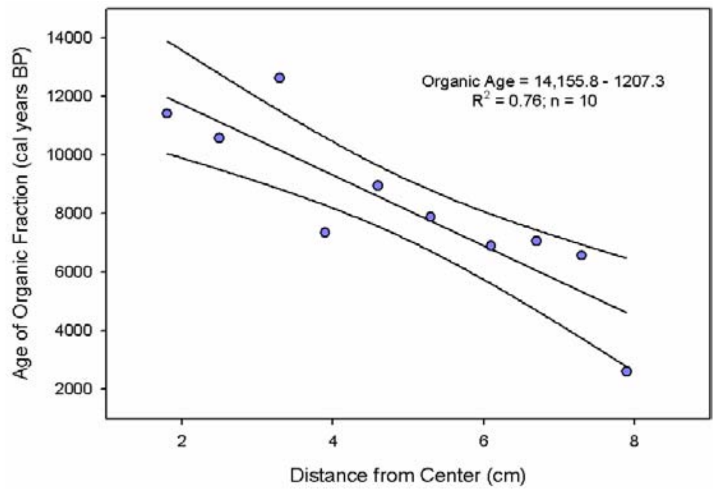

Figure 4 Dependency of the age of the organic fraction on distance from the oncoid center showing 95% confidence limits.

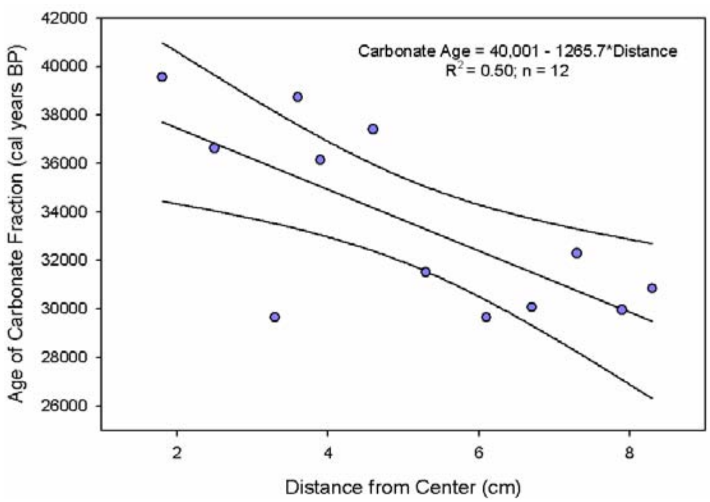

Figure 5 Dependency of the age of the carbonate fraction on distance from the oncoid center showing 95% confidence limits.

Regression Equations 1 and 2 have similar slope coefficients so the regression lines are almost parallel, which could be evidence of a relatively constant old carbon reservoir effect during the Holocene. The value of the effect is unusually large with an average exceeding 20,000 cal yr BP and could be caused by sedimentation of carbonate silts brought by rivers that accumulated on the growing stromatolite surface. In addition to carbonate silts in suspension, it is possible that organic material is also transported to the pan by rivers during flooding of the pan. This organic material would be different from the algal mats of the stromatolite and have a different ^{14}C concentration.

Based on the EPSO-1 age data in Table 1, and excluding samples E and M because they may represent the ages of detrital organic material rather than cyanobacterial mats, linear regression of the remaining 10 carbonate and organic age pairs provides the relationship:

$$\text{Carbonate age } (^{14}\text{C yr BP}) = 23{,}611 + 0.7 * \text{Organic age } (^{14}\text{C yr BP}) \quad (3)$$
$$(R^2 = 0.20, n = 10)$$

Applying Equation 3 to the MART1-14 organic age predicts a carbonate age of 43,827 ^{14}C yr BP for the outside, youngest layers of this stromatolite. This predicted carbonate age is very similar to a series of carbonate ages obtained by Rust (1984) on stromatolites from Poacher's Point and Pelican Island within Etosha Pan (Figure 1). Two stromatolites from Poacher's Point that were collected from the present pan surface produced ages of >42,000 and >41,700 ^{14}C yr BP. In addition, ages of 42,400 ± 1950; 39,300 ± 1470; and >40,000 ^{14}C yr BP were obtained on stromatolites from Pelican Island (referred to as Insel by Rust) that Rust (1984) argues document a lake ~8 m deep based on the elevation from which they were recovered. Rust's ages on stromatolite carbonate had a considerable impact on ideas about the past flooding of Etosha Pan as they suggested that the last time the pan contained an extensive lake was prior to ~40,000 ^{14}C yr BP. In fact, Wilczewski and Martin (1972) assumed that the Pelican Island stromatolites were of Pliocene age.

The predicted carbonate age of MART1-14 (43,827 ^{14}C yr BP) is within statistical uncertainty (see Figure 6) of the 2 finite stromatolite ages obtained by Rust (1984) from Pelican Island (42,400 ± 1950 and 39,300 ± 1470 ^{14}C yr BP). Applying Equation 3 above, the carbonate ages from Pelican Island convert to organic ages of ~26,840 and ~22,410 ^{14}C yr BP, respectively. These ages, and the MART1-14 organic age of 28,880 ± 90 ^{14}C yr BP, clearly record a perennial lake reaching at least 8 m above the present pan floor for an extended period of time at, and prior to, ~29,000–22,000 ^{14}C yr BP, or ~34,000–26,000 cal yr BP.

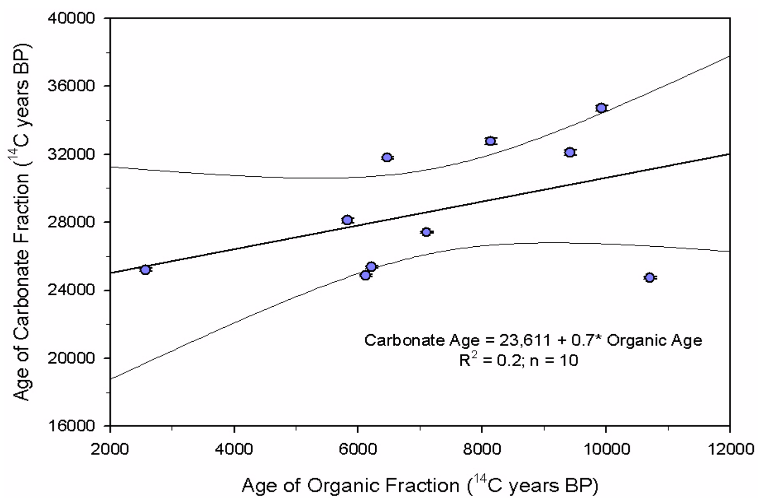

Figure 6 Linear regression between carbonate and organic ages for EPSO-1 showing 95% confidence limits.

So far, there is no evidence to suggest that lake levels reached as high as 8 m above the present pan floor after the interval defined by the Andoni Bay and Pelican Island stromatolites. However, the ages for EPSO-1 appear to form 3 main groups indicating that the pan was flooded more frequently in the periods ~12,700–11,200, 8000–6400, and 2700–2500 cal yr BP (Tables 1 and 2). These periods closely match OSL ages obtained for pan floor and shoreline beach ridge sediments along the western margin of the pan (Figure 1) that record past periods of lake inundation (Brook et al. 2007). The most prolonged flooding appears to have been from 8000–6600 cal yr BP (5 stromatolite ages and a beach ridge OSL age of 6400 ± 1000 cal yr at ~5 m above the present pan floor). Three stromatolite ages in the range 12,700–11,200 cal yr BP correspond to an OSL age of 13,300 ± 2100 cal yr for pan floor sediments deposited at the time the pan flooded. Finally, a stromatolite age of 2700–2500 cal yr BP broadly agrees with beach ridge ages of 5400–2600 and 3100–1100 cal yr for ridges currently ~2.5 m and ~1.0 m above the pan floor, respectively (Table 2).

Table 2 Comparison of beach ridge and pan sediment OSL ages for the western margin of Etosha Pan and stromatolite ^{14}C ages for the eastern margin.

Beach ridge and pan deposits					Stromatolites[a]
Sample ID	Sediment type	Depth (m)	Elevation above pan (m)	OSL age (cal yr)	^{14}C age range (cal yr BP)
OKON-3	Pan floor	1.00	n/a	15,400–11,200	12,700–11,200 (3)
OKDEK-2	Beach ridge	1.00	5	7400–5400	8000–6400 (5)
OKA-2	Beach ridge	1.00	2.5	5400–2600	2700–2500 (1)
OKON-2	Beach ridge	0.50	1.0	3100–1100	12,700–11,200 (3)

[a]The number of ages is given in parentheses.

CONCLUSIONS

The ages we have obtained on organic matter from within the EPSO-1 and MART1 stromatolites would not have been possible without AMS techniques, which allowed the dating of very small samples of carbon. The organic ages appear reliable because in the EPSO-1 deposit they are older at greater depth in the stromatolite and are in correct stratigraphic order. Their reliability is also suggested by $\delta^{13}C$ values that average –22‰, which are typical for algal mats and indicate no or minimal incorporation of limestone/calcrete carbon into the organic residue.

Dating of both the organic and carbonate fractions in the EPSO-1 stromatolite has shown that the carbonate ages are much older than the organic ages and significantly overestimate the timing of past lacustrine events in Etosha Pan because of the incorporation of "dead" carbon from the surrounding calcrete apron and limestone bedrock. Carbonate ages for 12 samples from EPSO-1 ranged from 29,330 to 40,130 cal yr BP, while ages for organic residues from the same samples were much younger, ranging from 2460 to 19,000 cal yr BP. The carbonate-organic age pairs suggest that the carbonate reservoir effect increases the ages of carbonates beyond their true age by up to ~24,000 ^{14}C yr BP, with this value decreasing as the true age of the deposit increases (see Equation 3 above).

The 32,953–34,187 cal yr BP age for MART1-14 is extremely significant as it documents a time when a massive lake occupied Etosha Pan. The MART1 age for this lake, which was more than 8 m deep, is supported by 2 ages in Rust (1984) from Pelican Island. These ages were for stromatolite carbonate and when corrected for the reservoir effect, they provide "true" ages of ~34,000 and 26,000 cal yr BP—very close to the MART1 organic age. The MART1 and Pelican Island stromatolites were recovered from ~8 m above the pan floor attesting to a very deep lake at the time of their formation.

Therefore, it appears that the stromatolites of Etosha Pan are not weathered remnants of Miocene carbonates as suggested by Miller (2008), nor are they fossils inherited from the Pliocene as suggested by Wilczewski and Martin (1972). Instead, they appear to be of Quaternary age and are certain in the future to provide important information on climate changes in northern Namibia during the Late Pleistocene.

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