Reevaluation of Dating Results for Some ^{14}C – AMS Applications on the Basis of the New Calibration Curves Available

K. D. Macario, P. R. S. Gomes, and R. M. Anjos
Instituto de Física, Universidade Federal Fluminense, Av. Litoranea s/n, Campus da Praia Vermelha, Niterói, 24210-340, R.J., Brazil

Received on 31 October, 2007

In this paper we describe briefly some characteristics of the Accelerator Mass Spectrometry (AMS) technique and the need of corrections in the radiocarbon ages by specific calibration curves. Then we discuss previous results of some Brazilian projects where radiocarbon AMS had been applied in order to reevaluate the dates obtained on the basis of the new calibration curves available.

Keywords: Radiocarbon; Dating; Accelerator; Mass spectrometry

I. INTRODUCTION

In recent years new databases for radiocarbon calibration have been published, including the one for samples collected in the Southern Hemisphere [1]. The present work aims to reevaluate previous results from Brazilian projects in which the radiocarbon accelerator mass spectrometry (AMS) technique had been applied, by using these recently available new calibration curves. We also discuss whether and how the new calibration interferes on such results and its interpretation.

Despite the accelerator mass spectrometry technique is not so far fully installed in any Brazilian laboratory, it is certainly disseminated among Brazilian researchers from several fields of science, such as archaeologists, oceanographers, biologists and physicists. Due to the lack of Brazilian AMS facilities, those researchers usually pay a large amount of money to have their samples dated by foreign laboratories. Even more important than that is the usual lack of specialized researchers to collaborate in such essentially multidisciplinary projects. Then, questions such as on sample collection procedures or the correct calibration of the results arise. In this context, this paper objects to review the accelerator mass spectrometry technique, the methods for radiocarbon age calibration and to discuss its applications.

In section 2 we give a very brief description of the main AMS technique characteristics. In section 3 we describe the methods for radiocarbon calibration and its importance. In section 4 we reevaluate some previous results obtained by our group by using the new calibration curves for the Southern Hemisphere, and finally in section 5 we present some conclusions.

II. THE ^{14}C- AMS TECHNIQUE

Long lived rare isotopes, like ^{14}C, are produced in the upper regions of the atmosphere, mainly in the stratosphere, by interaction with neutrons through reactions such as, for example, $^{14}N(n,p)^{14}C$. The neutrons are yielded by cosmic radiation, which consists partially of high energetic protons, mainly originating from the Sun. These nuclides enter the geological cycle and become incorporated into organic materials, ground water and sediments. The half life of ^{14}C is 5730 ± 40 years [2]. So, they decay sufficiently slowly to be used in dating and tracing natural features in the environment. Due to their very long half-lives, the determination of their concentration by measuring the radiation emitted during their decay takes a long time and requires large samples. A much better way to obtain information from these nuclides is by the direct measurement of the undecayed isotopes. As no decay is detected, one does not need to wait thousands of years, in average, for the decay of one atom.

Conventional mass spectrometers can, in principle, be used for determining the relative concentration of the long-lived cosmogenic nuclei, when compared with their stable isotopes. However, there is a major problem in the separation of their isobars, usually with a much larger number of nuclei in the sample than the cosmogenic isotope itself.

The Accelerator Mass Spectrometry (AMS) technique [3,4] is a very powerful method for dating and tracing studies, since it allows the determination of concentrations down to one atom of rare isotope in 10^{15} stable atoms, from samples of a few milligrams. In AMS, usually a Tandem accelerator is used as an electrostatic and magnetic spectrometer, and the determination of extremely low concentrations of rare radioactive isotopes, with sufficient energy to enable the counting and unambiguous identification of each ion, is performed directly, without the need to wait for the radioactive decay, by the use of standard Nuclear Physics detectors. For studies with ^{14}C, the tandem accelerator systems are particularly very useful, since they deal with negative ions extracted from the ion source. The main isobar contaminant, ^{14}N, is not produced as a negative ion, but as $^{14}NH^{-}$, easily separated from ^{14}C by a magnetic field. Furthermore, the main ^{14}C contaminants, the molecules $^{12}CH_2$ and ^{13}CH, are broken apart in the stripper located at the high voltage terminal of the tandem accelerator. With AMS, the measurements last a few minutes, and very small amounts of sample are used. For example, 5 grams of a carbon sample used in the conventional method can be replaced by less than 1 mg when the AMS technique is used. Therefore, archaeological samples do not need to be spoiled, and extremely low radioactive material may be used for biological and medical studies. An ordinary mass spectrometer has a limited sensitivity of 1: 10^9, in long measurement times. With AMS, within a few minutes measurements, a sensitivity better than 1: 10^{15} is achieved, since the typical beam currents are of the order of 10^{-6}- 10^{-9}A.

III. RADIOCARBON AGE CALCULATION AND CALIBRATION

After isotopic ratio $^{14}C/^{12}C$ or $^{14}C/^{13}C$ is measured, the radiocarbon age can be calculated. The ratio of the radioactive isotope over the total carbon must then be corrected for isotopic fractionation, that is the differentiation between isotopes under chemical and biological processes. Such fractionation is corrected by taking into account the measured fractionation between the stable isotopes [5]. This measurement is usually performed by conventional mass spectrometry. Specific standards are used in order to calculate the age of the unknown sample in relation to the year of 1950 and such age is referred to as years before present (BP) [6]. This and other conventions are used to enable the comparison between different measurements at different times [7]. One important thing to have in mind is that the half-life used in radiocarbon dating is the so-called Libby half-life of 5568 years in spite of the accepted half-life of ^{14}C of 5730$\pm$40 years [2]. Such convention will add a systematical error to the calculated date.

Although the Conventional Radiocarbon Age obtained in different laboratories can be compared at any time, the application of radiocarbon dating in archaeology, for example, requires a more accurate age estimate. Not only the known systematical errors introduced in the calculation are a source of uncertainty, but also the very assumption that the isotopic ratio of the atmospheric reservoir of CO_2 remains constant through time is not true. After the ^{14}C is formed through the nuclear reaction of cosmic-rays secondary neutrons with ^{14}N, it immediately reacts with oxygen in the air to form ^{14}C monoxide, which is oxidized to $^{14}CO_2$ by reacting with OH radical. In this processes several factors contribute to the variation in the atmospheric isotopic ratio.

To account for any of such error sources, the Radiocarbon Age has to be calibrated on the basis of an independent dating technique. Therefore, empirical databases of dendrochronologically dated wood samples provide a fine scale set of known age results for comparison. In this technique, the distributions of growth rings in tree trunks are related to its age. Therefore, radiocarbon measurements of such rings reflect the discrepancies of atmospheric isotopic ratio through the years, as each of them was formed in equilibrium with the surrounding atmosphere. The calibration curve is constructed upon such empirical database and the Gaussian distribution obtained for the Conventional Radiocarbon Age is reflected upon such curve. A Bayesian approach is used, generating a probability distribution within a time interval [8]. The calibrated radiocarbon age is usually given in calendar years (AD) and the obtained interval is reported. Moreover, the larger the empirical database gets the curve is more likely to converge.

Based on a comparison between radiocarbon measurements of dendrochronologically calibrated wood from both hemispheres, from the period of 950 to 1850 yr. AD, McComac[9] has shown that the offset between the hemispheres is not constant but varies periodically. For the measurement of Southern Hemisphere samples outside such range, a correction of (41 +/-14) to be applied before calibration was suggested. For being essentially empirical, the calibration database is always increasing but just until recently a specific dataset has been published for the Southern Hemisphere samples [1]. Opposite to the Conventional Radiocarbon Age, which is by definition constant in time, this search for accuracy indicates that calibrated ages information does not exist alone and needs constant revision. But does different datasets or different calibration procedures do mean such a discrepancy in the results? How such corrections affect the interpretation of results? In order to discuss this matter we shall reevaluate some results obtained in archaeological studies performed in Brazil.

For calibration purposes the age range is significant information in order to use the right dataset. While the Southern Hemisphere curve SHCAL04 [1] goes up to 10 Ky, the Northern Hemisphere INTCAL04 dataset [13] goes up to 26 Kyr. BP. Although there is a new coral based calibration curve available up to 50 Kyr. BP [11,12], there is still some disagreement among researches and such curve is not widely accepted yet [26]. In what concerns the Southern Hemisphere, it has been recommended that samples older than 11 Kyr should not be calibrated because of the uncertainties associated with the interhemispheric offset before the Holocene [1].

Another question that arises from such discussion is the great extension of Brazil. Each of the calibration curves will represent a mean for the respective hemisphere, but studies regarding Equatorial locations will be better represented by each of them? An example of such a situation can be obtained in [14-17] where palaeoclimatic studies in the Amazon region are performed. For these studies the Northern Hemisphere dataset was used for calibration.

Even when ^{14}C dating is performed in studies in Center or Southern Brazil, and radiocarbon dating is required, one has to be careful before using the new available Southern Hemisphere dataset [1] for the age calibration. For example, when a marine reservoir of the samples is involved [18], it is more accurate to use calibration curves for this reservoir in the Northern Hemisphere [19], with a correction of ΔR=(0+/-40 years) to account for the regional difference from the average global marine reservoir correction, than the terrestrial reservoir for the Southern Hemisphere [1]. According to Stuiver and Braziunas [19] the measured remaining ^{14}C activity of a sample formed in a specific reservoir will reflect not only its decay but also the reservoir activity. If on the one hand the dissolution of old carbonates in water will decrease the reservoir activity, on the other hand exchange of CO_2 with the atmosphere will restore it. For such reasons the deepness of the site and different oceanic mixing process will contribute to the offset between regional and world ocean ^{14}C ages.

Although the main aim of this paper is to show the importance of radiocarbon calibration and the use of correct calibration curves, it is important to mention that not all the works involving the ^{14}C-AMS technique require calibration, since in several studies, the concentration of ^{14}C is used only as a tracer. When the simple isotopic ratio in the sample is enough information, it should only be corrected for isotopic fractionation and expressed in conventional radiocarbon years in relation to a standard. When the date should be corrected for radioactive decay from the year of origin to 1950, the year a tree ring sample was formed in the case of dendrochronological comparison, the physical half-life is to be used and

this corresponds to the $\Delta^{14}C$ [2]. For an example of this kind of application concerning the isotopic signature of the local waters of an important Brazilian coastal upwelling, refer to [20,21].

IV. REEVALUATION OF SOME PREVIOUS RESULTS

We have investigated the chronology of prehistoric settlements of the central-south Brazilian coast [22-25]. In the southern Brazilian coast there is a high density of shellmounds, intentionally built by prehistoric populations, which can be as high as thirty meters. These shellmounds are dated in general between 6000 and 2000 yr. BP. The material culture recovered in these sites consists essentially of artifacts made from shells and bones of bird, fish, sea and land mammals, including projectile points, ornaments, and other tools and weapons. Thanks to the abundance of fish and shellfish in the estuarine environment, substantial demographic growth was possible. With an abundant food supply all year round, fishers-gatherers enjoyed the benefits of an extremely favorable interaction of elements within their subsistence system. As time went on, population growth decreased the distance between settlements, resulting in the concentration of sites within these circumscribed lagoonal areas.

We dated one charcoal sample from a coastal shellmound of Rio de Janeiro State [22-24], by ^{14}C-AMS at the PRIMELAB, to 7860 ± 80 yr. BP. This was an unexpected result as it would be admissible to assume that the oldest dates would be found among the huge shellmounds of Santa Catarina State, in Southern Brazil. Nevertheless, it is surprising that the oldest dates appear in Rio de Janeiro and São Paulo, in Southeastern Brazil. This demonstrates that the initial settlements occurred in an area that does not coincide with the one in which those cultures reached their highest degree of expression. Therefore, this result compels us to consider two other previously questioned dates, pulling back the traditionally accepted chronology for the settling of the coast by at least two thousand years.

Figure 1 shows the radiocarbon age versus calibrated age for two calibration curves: at the top, from the calibration for the Northern Hemisphere [13], used in our previous and already reported works [22-25]; at the bottom, obtained from the recently available Southern Hemisphere calibration dataset [1]. These graphics are the output of the Oxford University calibration code OxCal v3.10 [10]. They show the Gaussian distribution for the Conventional Radiocarbon Age with its statistical uncertainty, the calibration curve obtained by the respective empirical dataset and the calibration interval obtained for the 2σ range plus the relative probability distribution within such interval. If no calibration curve were available, the radiocarbon dating would lead to the age of 7860 ± 80 yr. BP. Calibration of such date using the Northern Hemisphere dataset with no correction would yield the interval of 9000 to 8450 yr. BP. So, one can see the relative importance of the calibration of the radiocarbon age. Applying the correction suggested by McCormac [9], or the Southern Hemisphere dataset [1], such interval would be from 9000 – 8400 yr. BP, and therefore having no major influence on our results. On the other hand, if we observe the probability distributions within the calibration interval, we can see that for the Southern Hemisphere curve, the highest probability is more concentrated in the recent part of the interval, while for the uncorrected result the probability is more evenly distributed.

We were also involved previously in another research project related with shellmound builders [25], in order to study the period of occupation and sociocultural system of the fishing-collecting groups. Samples from one archaeological site in Buzios, Rio de Janeiro State, were dated at the PRIMELAB. The results, together with other data from other archaeological sites belonging to the same group, reaffirm the long occupation of populations in this region for around 2400 years and lead to the proposal of a new model suggesting a discontinous occupation of these sites, during two distinct periods: $\sim$ 4000-3300 yr. BP and 2000-1500 yr. BP. Moreover, it was possible to show that these sites were not active concomitantly, and that the occupation took place in an intermittent way, with a strong correlation between the periods of occupation and the ones of high sea level. Fig. 2 shows the radiocarbon age versus calibrated age for two calibration curves: on the bottom, obtained from the recently available Southern Hemisphere calibration dataset [1], and at the top, from the calibration for the Northern Hemisphere. If we compare the uncorrected results to those using the Southern Hemisphere dataset we can see once more that little effect will be observed.

Therefore, although there are structural differences between the calibration curves for the two hemispheres and the use of respective datasets is preferable, some results can stay almost unaltered. Concerning the re-analyzed results of the archaeological projects studied, within the age range evaluated, they did not show a strong sensitivity to the new calibration curve for the Southern Hemisphere.

V. SUMMARY AND CONCLUSIONS

After a brief description of some characteristics of the ^{14}C-AMS technique and radiocarbon age calculations, we discussed the need of calibrating the results on the basis of an independent technique such as dendrochronology and the available datasets for such purpose.

Specifically for our projects on archaeological studies, we concluded that, despite the search for accuracy is very important in this field and that small corrections can affect the probability distributions of age estimates, it is not likely that the interpretation of archaeological dating will be threatened by new datasets.

We also discussed the significant information for choosing the right calibration dataset as the age range and the assumption of being in the southern Hemisphere when dealing with Equatorial locations. Finally, we mentioned other situations where the samples are formed in oceanic reservoirs and require the marine dataset for calibration plus a regional correction or when radiocarbon is used as a tracer and no calibration is needed.

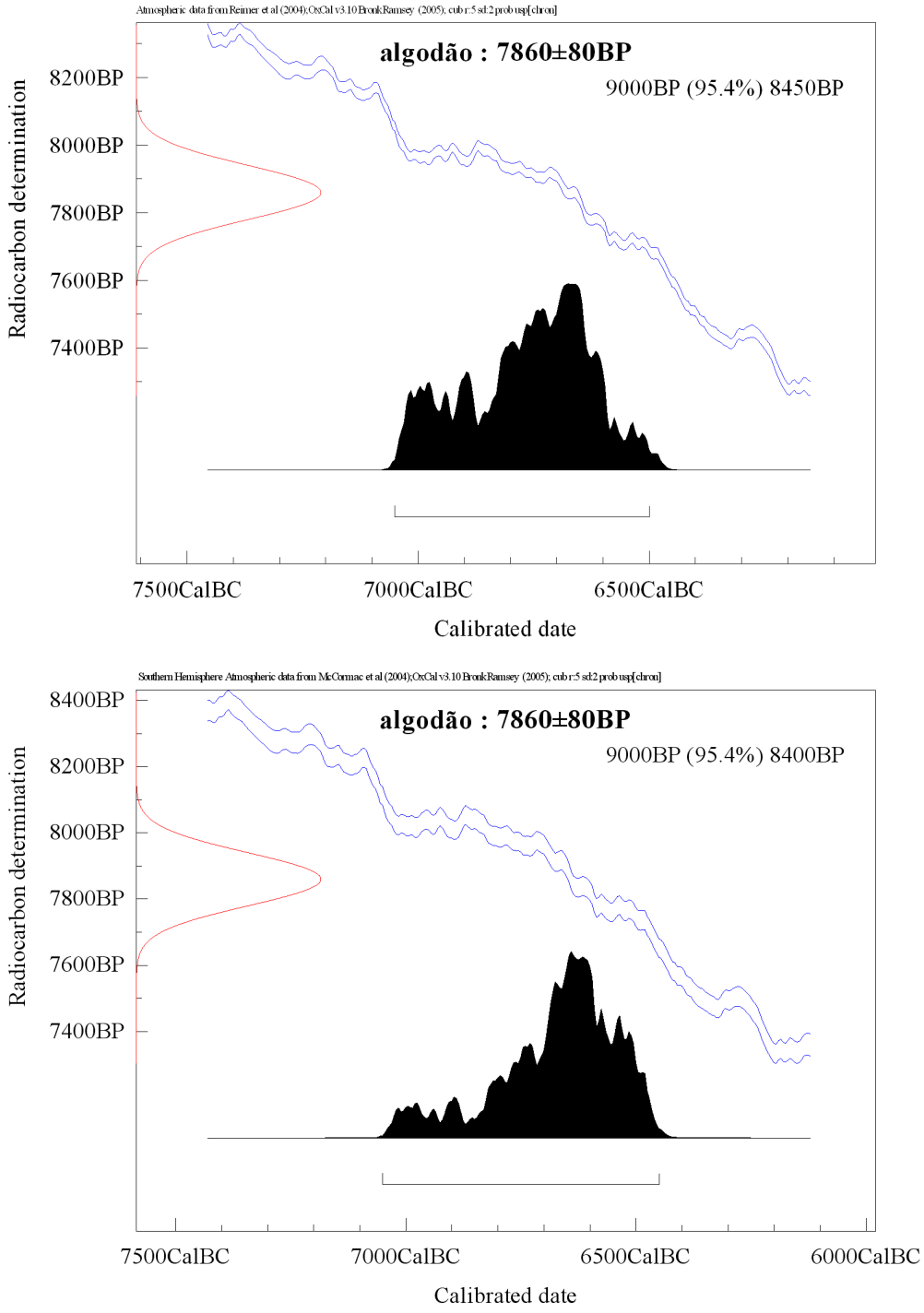
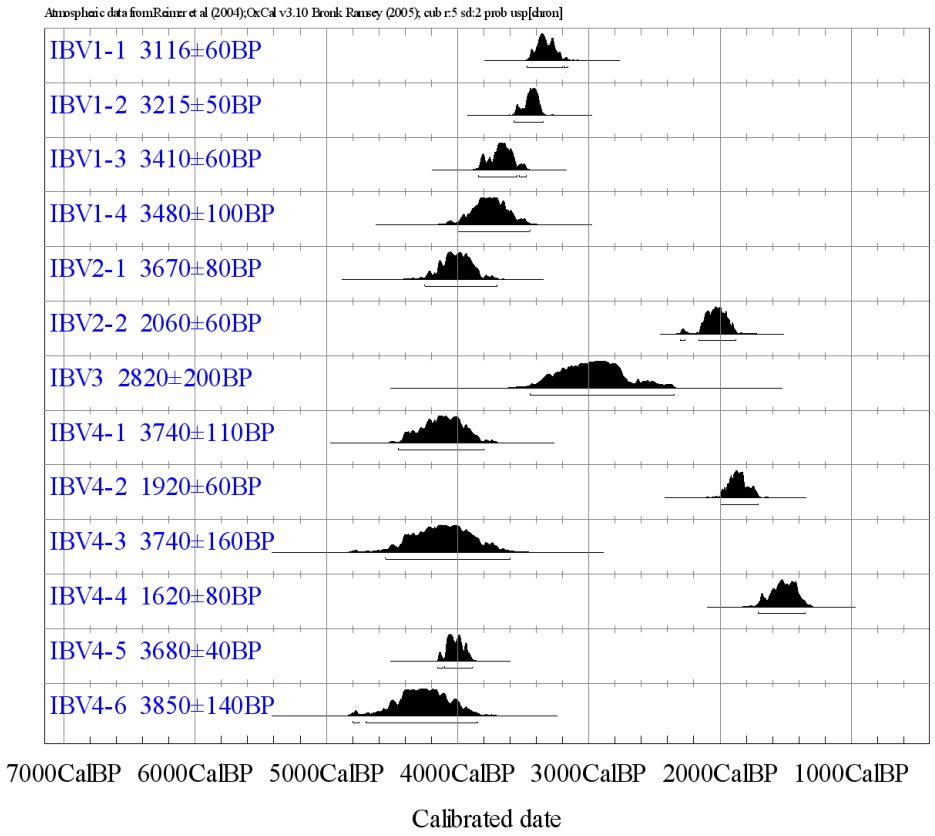


FIG. 1: Output of the Oxford University calibration code OxCal v3.10 [10] for the charcoal sample from the Algodão shellmound. They show the Gaussian distribution for the Conventional Radiocarbon Age with its statistical uncertainty, the calibration curve obtained by the respective empirical dataset and the calibration interval obtained for the 2σ range plus the relative probability distribution within such interval.



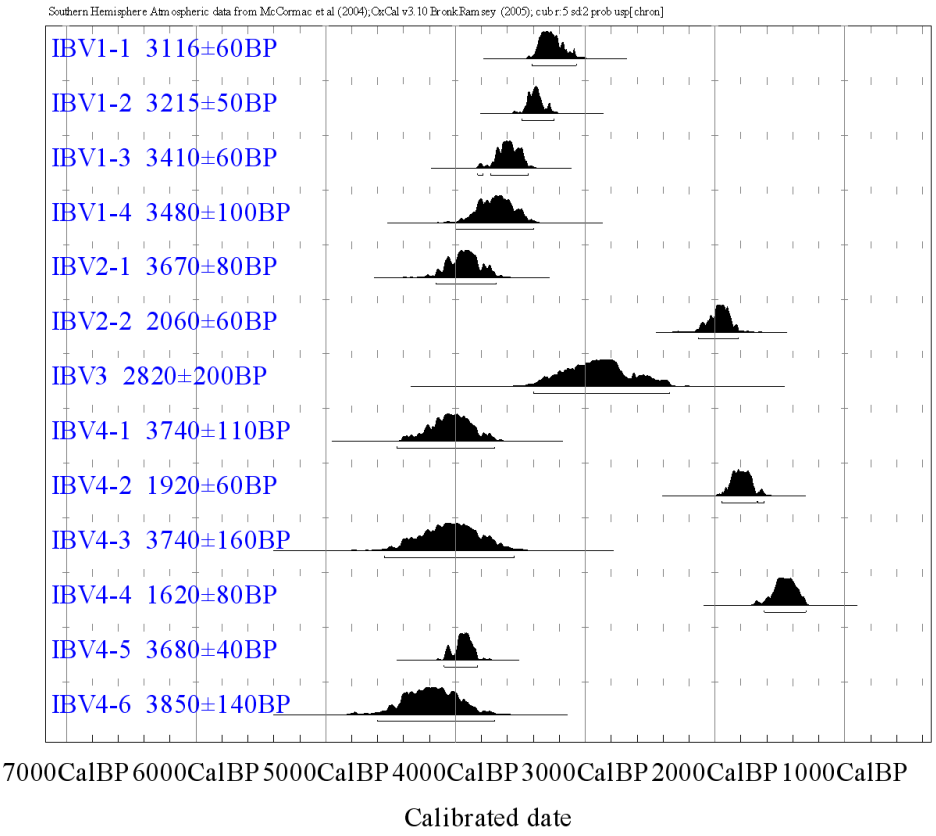


FIG. 2: Output of the Oxford University calibration code OxCal v3.10 [10] for all the available samples from the Ilha da Boa Vista group of shellmounds. They show radiocarbon age versus calibrated age for two calibration curves: on the bottom, obtained from the recently available Southern Hemisphere calibration dataset [1], and at the top, from the calibration for the Northern Hemisphere.

Acknowledgements

The authors would like to thank CNPq and FAPERJ for their partial financial support.

[1] F.G. McCormac, A.G. Hogg, P.G. Blackwell, C.E. Buck, T.F.G. Higham, and P.J. Reimer, Radiocarbon **46,** 1087 (2004).
[2] J. van der Plicht, and A. Hogg, Quaternary Geochronology v 1, **4**, 237 (2006).
[3] L. K. Fifield, Rep. Prog. Phys. **62**, 1223 (1999).
[4] Proccedings of AMS Conferences: Nuclear Instr. Meth. in Phys. Res. B **123** (1997), **172** (2000), **223** (2004), **259**(2007).
[5] H. Craig, The Journal of Geology 2 **62**, 115 (1954).
[6] H. Godwin, Nature **195**, 984 (1962).
[7] H. Godwin, Nature **195**, 943 (1962).
[8] H. Dehling and J. van der Plicht, Radiocarbon **35**, 239 (1993).
[9] F.G. McCormac, P.J. Reimer, A.G. Hogg et al. Radiocarbon **44**, 641 (2002).
[10] C. Bronk Ramsey; Radiocarbon **37**, 425 (1995).
[11] R. G. Fairbanks, R. A. Mortlock, T. Chiu, L. Cao, A. Kaplan, T. P. Guilderson, T. W. Fairbankse, A. L. Bloom, P. M. Grootesg, and M. Nadeau Quaternary Science Reviews **24**, 1781 (2005).
[12] T. Chiu, R.G. Fairbanks, R.A. Mortlockb, and A.L. Bloom, Quaternary Science Reviews **24**, 1797 (2005).
[13] P.J. Reimer et al, Radiocarbon **46**, 1029 (2004).
[14] P.R.S. Gomes et al, Heavy Ion Physics **11**, 485 (2000).
[15] G.M. Santos, P.R.S. Gomes, R.M. Anjos, L.C. Cordeiro, B. C. Turcq, A. Sifeddine, M.L. di Tada, R.G. Cresswell, and L.K. Fifield, Nuclear Instr. Meth. in Phys. Res. B **172**, 761 (2000).
[16] G.M. Santos, R.C. Cordeiro, E.V. Silva Filho, B. Turcq, L.D. Lacerda, L.K. Fifield, P.R.S. Gomes, P.A. Hausladen, A. Sifedinne, and A.L.S. Albuquerque, Radiocarbon **43**, 801 (2001).
[17] J. A Barbosa, R.C. Cordeiro, E.V. Silva, B. Turcq, G.M. Santos, P.R.S. Gomes, A Sifedinne, A L.S. Albuquerque, L. D. Lacerda, P.A Hausladen, S.G. Tims, L.K. Fifield, and V. A Levchenkol, Nuclear Instr. Meth. in Phys. Res. B **223**, 528 (2004).
[18] K.D. Macario, R.M. Anjos, P.R.S. Gomes, A.G. Figueiredo Jr., C.L. de Souza, C.F. Barbosa, M.M. Coimbra, and D. Elmore, Nuclear Instr. Meth. in Phys. Res. B **223**, 535 (2004).
[19] M. Stuiver, T.F. Braziunas, Radiocarbon **35**, 137 (1993).
[20] P.R.S. Gomes, G.M. Santos, K.C. Ferraz, A.N. Marques Jr., R.C. Cordeiro, J.A. Barbosa, and E.V. Silva, Nucl. Phys. **A 734**, E116 (2004).
[21] K.C. Ferraz, A. N. Marques Jr., E.G. Rodriguez, G.M. Santos, and P.R.S. Gomes, Braz. J. Phys. **34**, 732. (2004).
[22] T.A. Lima, K.D. Macario, R.M. Anjos, P.R.S. Gomes, M.M. Coimbra, and D. Elmore, Radiocarbon **44**, 733 (2002).
[23] T.A. Lima, K.D. Macario, R.M. Anjos, P.R.S. Gomes, M.M. Coimbra, and D. Elmore, Braz. J. Phys**. 33**, 276 (2003).
[24] T.A. Lima, K.D. Macario, R.M. Anjos, P.R.S. Gomes, M.M. Coimbra, and D. Elmore, Nuclear Instr. Meth. in Phys. Res. B **223**, 691 (2004).
[25] M. Barbosa, A. Buarque, M.D. Gaspar, K.D. Macario, R.M. Anjos, P.R.S. Gomes, M.M. Coimbra, and D. Elmore, Nuclear Instr. Meth. in Phys. Res. B **223**, 695 (2004).
[26] Correspondence. Quaternary Science Reviews **25**, 855 (2006)