•	•	

# 2 Paleoclimate Studies in Brazil Using Carbon Isotopes in Soils

Luiz C.R. Pessenda<sup>1</sup>, E.P.E. Valencia<sup>2</sup>, R. Aravena<sup>3</sup>, E.C.C. Telles<sup>1</sup> and R. Boulet<sup>4</sup>

<sup>1</sup> Center for Nuclear Energy in Agriculture (CENA), Piracicaba, Brazil

#### Abstract

This chapter presents carbon isotope data of soil organic matter (SOM), collected in natural forest ecosystems in different sites from Brazil. The studied areas are located in Londrina (Southern part of the country), Piracicaba (Southeast), Salitre (Central) and Altamira (Northern). This study is part of the research program on tropical and sub-tropical soils in Brazil, of which the main objective is to use carbon isotopes to provide information on vegetation changes and their relationships with climatic changes during the Holocene. <sup>14</sup>C data of charcoal samples, the humin fraction and soil organic matter (SOM) contents, indicate that the organic matter of this area is at least of Holocene age. <sup>13</sup>C data in SOM indicate that C<sub>4</sub> plants were the dominant vegetation in Londrina and Piracicaba during the early and middle Holocene, while C<sub>3</sub> plants were the dominant vegetation in Altamira and probably a mixture of C<sub>3</sub> and C<sub>4</sub> plants occurred in Salitre during the Holocene.

# Introduction

Paleo-reconstruction of vegetation changes and their relation to climate in tropical and sub-tropical forest is essential for the understanding of the response of these ecosystems to future climatic change. Different approaches that include geomorphological (Ab'Saber, 1977; 1982; Servant et al. 1981; Bigarella and Andrade Lima 1982), biological, botanical (Hafter 1969; Prance 1973; Gentry 1982), palynological (Absy et al. 1991; Ledru 1993) and isotope studies (Pessenda et al. in press a and b; Martinelli et al., in press) have been used to infer past climatic changes in the Amazonia, Central, Southeast and South regions of Brazil.

Paleo-ecological and geomorphological studies suggest the occurrence of severe climatic changes in the South American continent. It has been hypothesized that there were drier periods during the Pleistocene and Holocene than the present, when the tropical forest was replaced by savannah vegetation with predominance of grasses (Van der Hammen, 1974; Absy and Van der Hammen, 1976; Absy,

<sup>&</sup>lt;sup>2</sup> Instituto Boliviano de Ciencia y Tecnologia Nuclear, La Paz, Bolivia

<sup>&</sup>lt;sup>3</sup> University of Waterloo, Waterloo, Ontario, Canada

<sup>&</sup>lt;sup>4</sup> ORSTOM, Institute of Geosciences, NUPEGEL, France

1980; Ab'Saber, 1982; Leyden, 1985; Bush and Colinvaux, 1990; Markgraf 1991). An understanding of the degree to which these changes affected the composition of the soil organic matter (SOM) would improve our ability to understand changes in the future.

The stable carbon isotope composition ( $^{13}$ C/ $^{12}$ C, or  $\delta^{13}$ C) of SOM contains information regarding the presence/absence of C<sub>3</sub> and C<sub>4</sub> plant species in past plant communities, and their relative contribution to community net primary production (Throughton et al., 1974; Stout et al., 1975). This information has been utilized to document vegetation change (Hendy et al., 1972; Dzurec et al., 1985), to infer climate change (Hendy et al., 1972) and to estimate rates of SOM turnover (Cerri et al., 1985).

The  $\delta^{13}$ C values of C<sub>3</sub> plant species range from approximately -32‰ to -20‰ PDB, with a mean of -27‰, while, in contrast, the  $\delta^{13}$ C values of C<sub>4</sub> species range from -17‰ to -9‰, with a mean of -13‰. Thus, C<sub>3</sub> and C<sub>4</sub> plant species have distinct  $\delta^{13}$ C values and differ from each other by approximately 14‰ (Boutton, 1991).

In this chapter changes in the SOM of Brazilian soils and their relationships with past climatic changes are analyzed. The aim of the project developed in the Radiocarbon Laboratory of CENA was to correlate radiocarbon datings to the  $^{13}$ C composition of SOM, with the objective of studying the evolution of local vegetation in the past.  $^{14}$ C dating was used to estimate soil organic matter chronology and  $\delta^{13}$ C was used as an indicator of the vegetation types ( $C_3$  vs.  $C_4$ ) in the local environment.

### **Material and Methods**

The soil samples were collected from natural forests of Londrina, 51°10'W, 23°18'S, Paraná State, in the south of Brazil; Piracicaba, 47°38'W, 22°43'S, São Paulo State, in the southeast; Salitre de Minas or Salitre, 46°46'W, 19°00'S, central Brazil; and Altamira, 3°30'S, 52°58'W, Pará State, in the north (Fig. 1).

The natural forest at Londrina, Piracicaba and Salitre is a Mesophitic semi-deciduous type forest and at Altamira is part of the Amazon forest. The soils of Londrina and Altamira are "Terra Roxa Estruturada", according to the Brazilian soil classification, Alfisol in the American soil classification. The soil sample from Piracicaba is a "Latossolo Vermelho Escuro" (Dark Red Latosol), according to Brazilian soil classification, Oxisol in the American soil classification, and the soil from Salitre is a "Latossolo Vermelho Amarelo" (Yellow Red Latosol), Oxisol in the American soil classification.



Fig. 1: Map showing the sites studied

Soils at all sites were sampled by collecting up to 10 kg of material in 10 cm increments from the surface to 180 cm depth. 1 kg of the sampled material was dried at 60°C to constant weight and root fragments were discarded by hand-picking. Any remaining plant debris was removed by flotation in hydrochloric acid 0.01 M, dried again to constant weight and sieved (0.105 mm for  $^{14}$ C).

The humin fraction was extracted from the 0.210 mm fraction (2.5 kg), using conventional methods (Dabin, 1971; Goh, 1978; Anderson and Paul, 1984): a) acid digestion in hydrochloric acid 0.5 M at 70°C - 80°C for 4 hours and washing with distilled water until pH reaches 3 to 4; b) reaction of the solid residue with at least 30 liters (10 liters per extraction) of sodium pyrophosphate - sodium hydroxide 0.10 M for about 36 hours (12 hours per extraction) and washing with distilled water until pH reaches 3 - 4; c) hydrolysis of residue with 4 liters of hydrochloric acid 3 M at 100°C for 12 hours, followed by washing with distilled water until pH reaches 3 to 4; d) the solid residue was dried at 40°C for 48 hours and sieved (<0.210 mm).

The charcoal samples were hand separated from 10 kg soil samples from Salitre, oven dried at 90°C, weighed and treated using the conventional AAA (acid-alkaline-acid) treatment. From the deepest samples (2.20 m to 3.45 m) charcoal was hand separated from small amounts of soil with the aid of a 5 mm sieve. These samples were used only for <sup>13</sup>C analyses.

The <sup>14</sup>C analyses on charcoal and humin samples were carried out at the Radiocarbon Laboratory of the Center for Nuclear Energy in Agriculture (CENA), using the benzene method and liquid scintillation counting (Pessenda and Camargo, 1991). Benzene samples were counted for at least 48 hours in a low level Packard 1550 liquid scintillation counter. Radiocarbon ages are expressed in years BP and percent modern carbon (pmC) relative to 95% of the activity of oxalic acid standard in 1950 and normalized to a  $\delta^{13}$ C of -25% PDB (Stuiver and Polach, 1977).

The carbon isotopic ratios of SOM were determined by mass spectrometry of  $CO_2$  from sample combustion in an atmosphere of pure oxygen at 900°C. Results were expressed as  $\delta^{13}C$  with respect to PDB standard in the conventional  $\delta$  (‰) notations.

Carbon contents of soil samples were determined in 1 to 5 g of <0.105 mm fraction by combustion in a C,H auto-analyzer and values expressed as weight percent of dry sample.

## **Results and Discussion**

The total organic carbon contents of soils are shown in Fig. 2. The total carbon concentration decreased from the surface to the deeper depths for all soils. The highest concentrations in all soil profiles were observed in Salitre, probably due to the presence of charcoal found in the soil.

The values of  $\delta^{13}$ C in SOM are shown in Fig. 3. The values obtained between the surface and the 40-50 cm interval are representative of C<sub>3</sub> plants, reflecting the current local vegetation (forest) in all soil environments. These values remained almost constant in the case of Altamira, characterizing the predominance of C<sub>3</sub> vegetation during the last 9,810 yrs. BP. In Salitre soil, the values ranged from -26.0 ‰ to -21.0‰ and the isotopic trend observed in these data could be due to isotope fractionation effect, occurring during microbial respiration, resulting in a gradual increase in δ<sup>13</sup>C of SOM with time (Stout et al., 1975; Becker-Heidmann and Scharpenseel, 1992) and/or a change from a mixed C<sub>3</sub> and C<sub>4</sub> vegetation to predominantly C<sub>3</sub> vegetation in the period from 8,790 yrs BP to 1,820 years BP. For Londrina and Piracicaba soils, the values show a significant change from -21.6‰ to -15.0‰, probably indicating predominance of C<sub>4</sub> vegetation in both sites in the periods from 10,800 yrs BP to 3,090 yrs BP and about 6,000 yrs BP to 3,440 yrs BP, respectively. These results suggest that in the case of tropical regions, a) the savannah vegetation was dominated by C<sub>3</sub> grasses; b) woody vegetation instead of grasses dominated the vegetation changes during these

phases; c) the replacement of the forest by savannah vegetation was restricted to small areas.

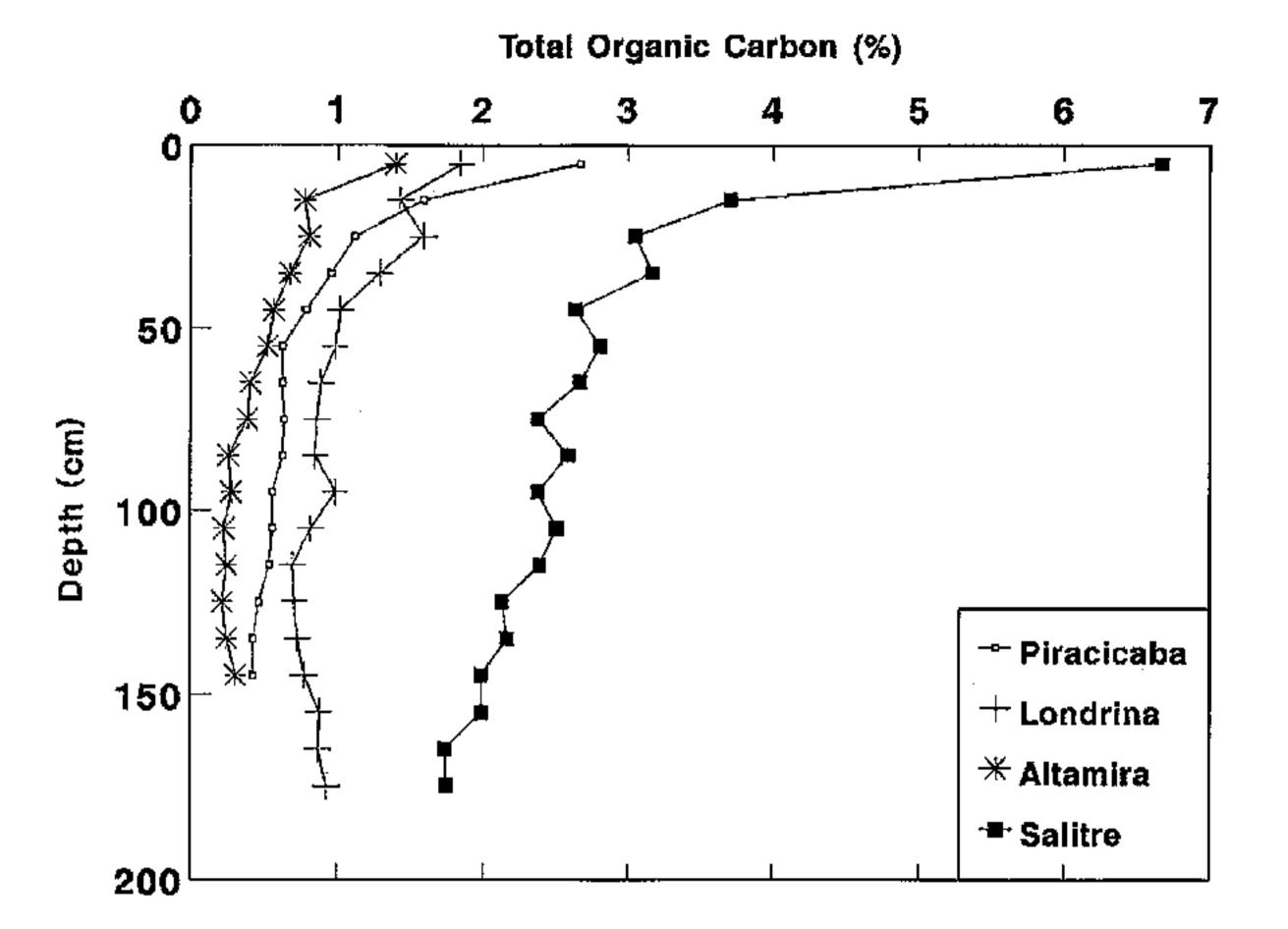


Fig. 2: Total organic carbon of soil profiles

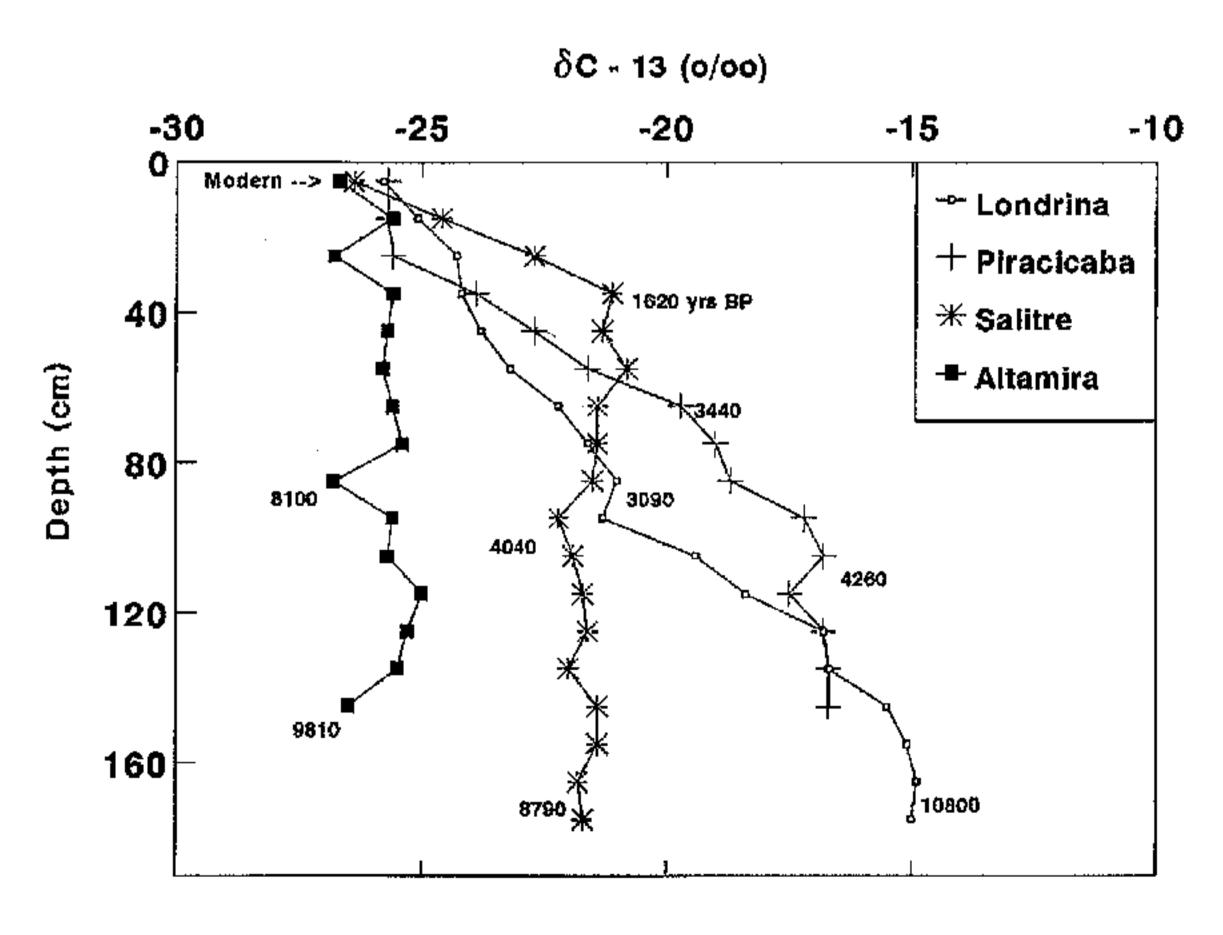


Fig. 3:  $^{14}$ C age and  $\delta^{13}$ C variation as function of soil depth

In Central Brazil, in the Salitre area, Ledru (1993) described changes during the last 32,000 yrs BP based on pollen analyses. She postulated two major periods of forest retreat and predominance of savannah vegetation (grasses), probably associated with very dry climatic conditions. These were from 11,000 to 10,000 yrs BP and 6,000 to 4,500 yrs BP. Dry periods have also been reported in the Central Amazon Basin and other areas of South America during the Holocene (Absy, 1982; Van der Hammen, 1982). The most significant dry phases recorded in these areas and Southern Brazil are 7,500 to 6,000 yrs BP; 4,200 to 3,500 yrs BP; 2,700 to 2,000 yrs BP; 1,500 to 1,200 yrs BP and 700 to 400 yrs BP (Bigarella, 1971; Fairbridge, 1976; Absy et al. 1991).

It seems that the dry phases registered by Ledru (1993) in the Salitre area and by several authors in other regions are in very good agreement with the data obtained in this paper for Central and Southern parts of Brazil, probably indicating that the sub-tropical region was much drier than the tropical region during climate changes in the early and middle Holocene.

Charcoal is present along the entire soil profiles at the three sampling locations in Salitre (Fig. 4). Some peak values are observed at certain soil depths, without any clear correlation between the three locations. The presence of charcoal in this soil is a clear indication that this area has been affected by forest fires, probably during most of its history. The extremely elevated charcoal contents in some soil horizons indicate that these events were more severe during some periods, probably indicating drier conditions. In the upper Rio Negro (Colombia and Venezuela), the presence of charcoal was reported, indicating the occurrence of frequent and wide-spread fires in the Amazon Basin, possibly associated with extremely dry periods and/or human disturbances (Saldarriaga and West, 1986). These events range from 6,000 yrs BP to the present and several events coincide with dry phases recorded during the Holocene (Absy, et al., 1982; Van der Hammen, 1982).

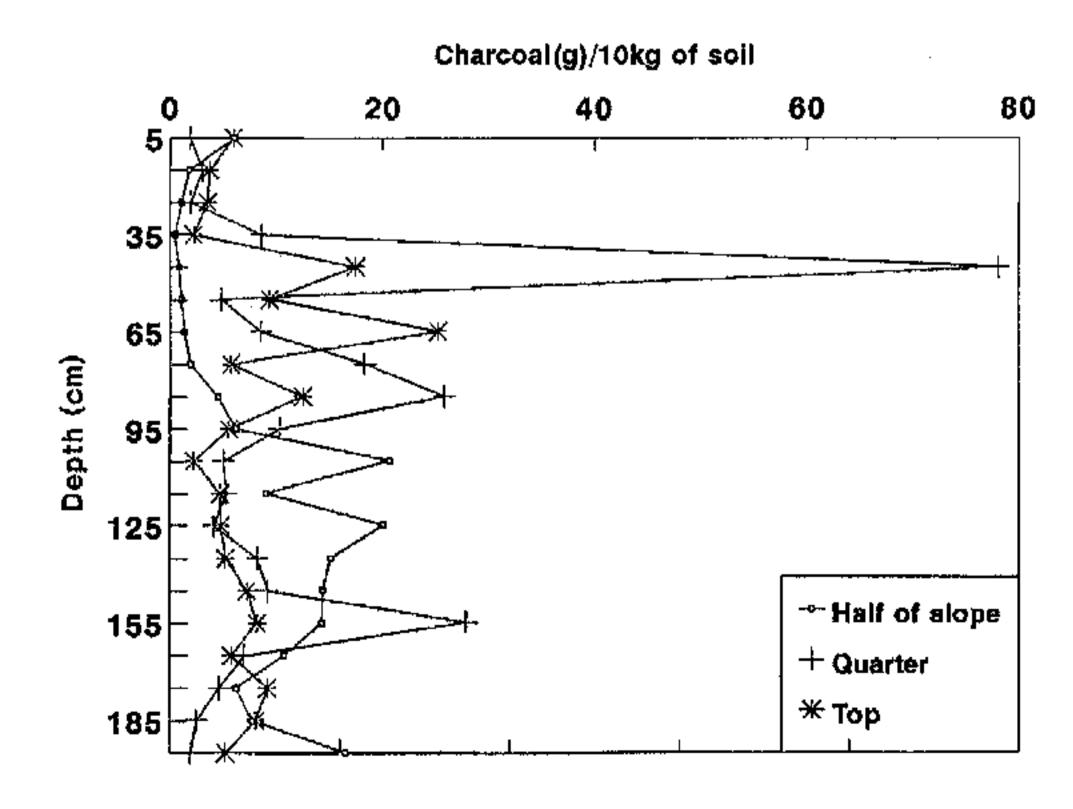


Fig. 4: Charcoal distribution as function of soil depth in Salitre

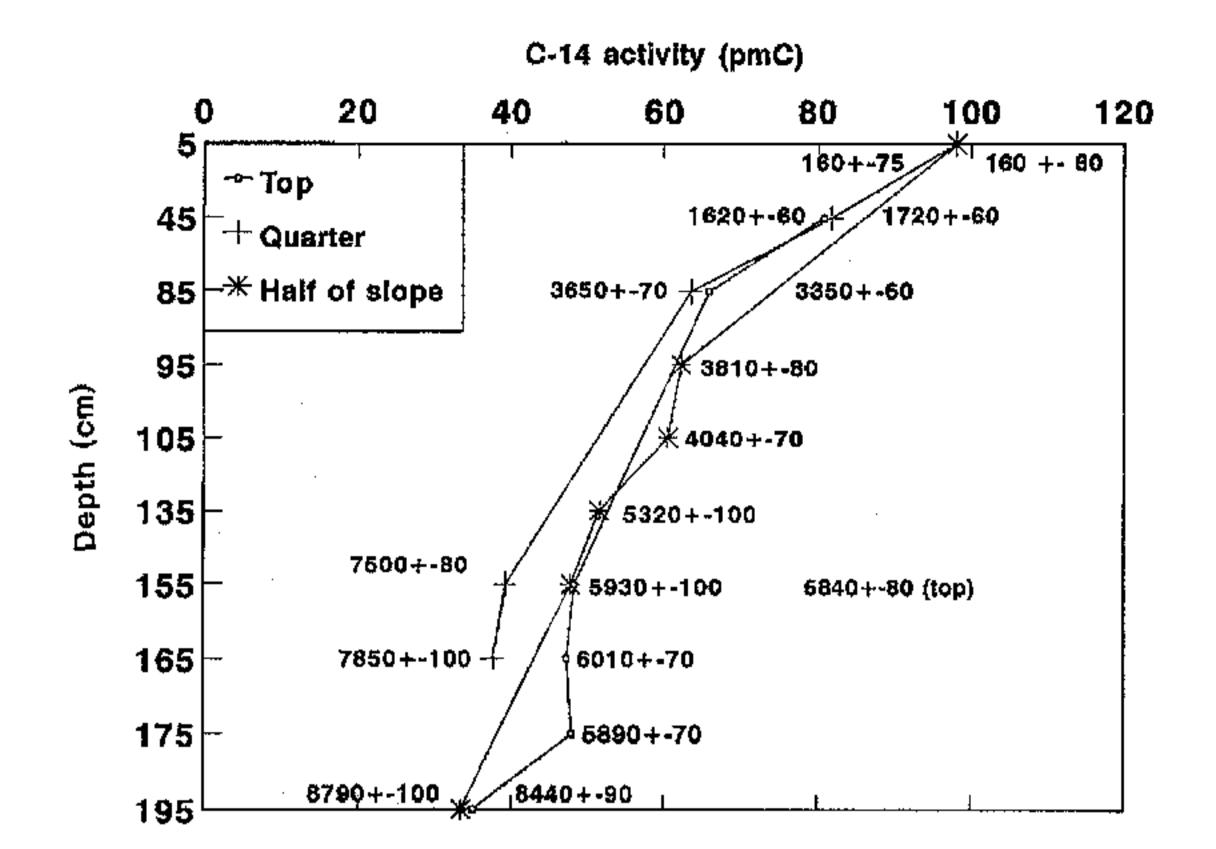


Fig. 5: <sup>14</sup>C dating of charcoal samples from Salitre as function of soil depth

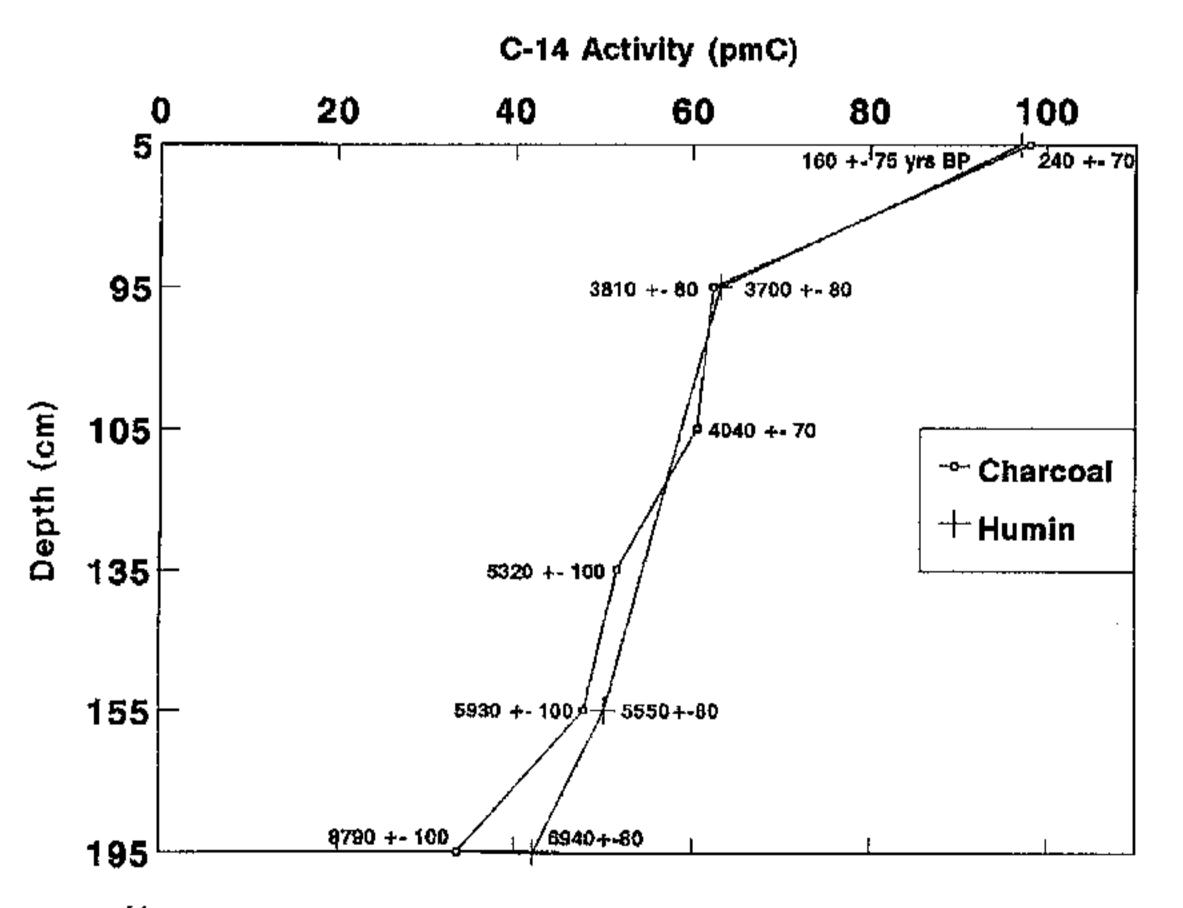


Fig. 6: <sup>14</sup>C dating of charcoal and humin samples in Salitre

Charcoal <sup>14</sup>C ages range from 160 yrs BP close to the soil surface to 8,790 yrs BP at 2.0 m depth (Fig. 5). Considering the age profiles, it is possible to expect that charcoal at the deepest locations should have a radiocarbon age of at least 12,000 yrs BP. These data show that the ages at the three locations were similar in some horizons. However the charcoal samples from the fourth location seem to be older than in the other locations. At the above location, between 150 and 180 cm, the ages were very similar, suggesting a mixing of charcoal at this depth interval.

Figure 6 shows the <sup>14</sup>C dates of charcoal and humin samples. No significant age differences were obtained until a depth of 155 cm, demonstrating that the humin can be a useful fraction to date SOM. At 2.0 m depth, the humin was about 2,000 years younger than the charcoal age, indicating that the input of younger carbon by translocation significantly affected the humin in the deepest parts of the soil profile.

#### Conclusions

14

Carbon isotope data in SOM (humin fraction) collected in soil profiles from Altamira, in the Amazon region, Salitre de Minas, central Brazil, and Piracicaba and Londrina, in the southern region of Brazil, indicate that the organic matter in these soils is at least Holocene in age. The presence of significant amounts of charcoal in the Salitre area suggests that forest fires were a significant process during the Holocene.  $\delta^{13}C$  data in SOM indicate that  $C_3$  plants were the dominant vegetation in the Altamira region and probably a mixture of  $C_3$  and  $C_4$  plants was the dominant vegetation in Salitre during the period 8,790 yrs BP to 1,820 yrs BP. For Piracicaba and Londrina the  $\delta^{13}C$  data indicate a predominance of  $C_4$  plants during the early and middle Holocene, probably indicating that the southern region of Brazil was much drier than the tropical region during climate changes in the past.

# Acknowledgements

We gratefully acknowledge the financial support of FAPESP (São Paulo Foundation for Research), grants nos. 90/3312-0 and 91/1868-1. Most of the laboratory work was done by Maria Valéria L.Cruz, Paulo Ferreira, Cláudio Sérgio Lisi, Gláucia Pessin and Márcio Arruda, to whom the authors are grateful.

## References

- Ab'Saber, A.N. (1977). Espaços ocupados pela expansão dos climas secos na América do Sul, por ocasião dos períodos glaciais quaternários. *Paleoclimas* (São Paulo), 3:1-20.
- Ab'Saber, A.N. (1982). The paleoclimate and paleoecology of Brazilian Amazonia. In Prance, G.T., ed., *Biological Diversification in the Tropics*, New York, Columbia University Press, pp:41-59.
- Absy, M.L., Van der Hammen (1976). Some paleo-ecological data from Rondônia, southern part of Amazonian Basin. *Acta Amazônica*, 10:929-932.
- Absy, M.L. (1980). Dados sobre as mudanças do clima e da vegetação da Amazônia durante o Quaternário. *Acta Amazônica*, 10:929-932.

Absy, M.L. (1982). Quaternary palynological studies in the Amazon basin. In Prance, G.T. (ed.) Biological Diversification in the Tropics, New York, Columbia University Press, pp:67-73.

- Absy, M.L., Cleef, A., Fournier, M., Martin, L., Servant, M., Sifeddine, A., Ferreira da Silva, M., Soubies, F., Suguio, K., Turcq, B., Van der Hammen, T. (1991). Mise en évidence de quatre phases d'ouverture de la forêt dense dans le sud-est de l'Amazonie au cours des 60.000 dernières années. Première comparaison avec d'autres régions tropicales. C.R. Acad Sci Paris, t. 312, Sér II 312:673-678
- Anderson, D.W., Paul, E.A. (1984). Organo-mineral complexes and their study by radiocarbon dating. Soil Science Society American Journal, 48:298-301.
- Becker-Heidmann, P., Scharpenseel, H.W. (1992). The use of natural <sup>14</sup>C and <sup>13</sup>C in soils for studies on global climate change. In Long, A. and Kra, R.S. (eds.), *Proceedings of the 14th International* <sup>14</sup>C Conference. radiocarbon, 31(3):535-540.
- Bigarella, J.J. (1971). Variações climáticas no Quaternário Superior do Brasil e sua datação radiométrica pelo método do carbono 14. Instituto de Geografia Universidade de São Paulo. *Paleoclimas*, 1:1-22.
- Bigarella, J.J., Andrade-Lima, D. (1982). Paleoenvironmental changes in Brazil. In: Prance GT (ed) Biological Diversification in the Tropics. Columbia Univ. Press, New York, pp:27-40.
- Boutton, T.W. (1991). Stable carbon isotope ratios of natural materials. II. Atmospheric, terrestrial, marine and freshwater environments. In Coleman, D.C. and Fry, B. (eds.), *Carbon Isotope Techniques*, New York, Academic Press, pp:173-185.
- Bush, M., Colinvaux, P.A. (1990). A pollen record of a complete glacial cycle from lowland Panama. J Vegetat Sci, 1:105-118.
- Cerri, C.C., Feller, C., Balesdent, J., Victoria, R., Plenecassagne, A. (1985). Application du traçage isotopique naturel en <sup>13</sup>C, a l'étude de la dinamique de la matière organique dans les sols. *C.R. Acad. Sci.*, Paris, 300, Série II, 9:423-428.
- Dabin, B. (1971). Etude d'une méthode d'extraction de la matière humique du sol. Science du Sol, 1:47-63.
- Dzurec, R.S., Boutton, T.W., Caldwell, M.M., Smith, B.N. (1985). Carbon isotope ratios of soil organic matter and their use in assessing community composition changes in Curlew Valley, Utah. *Oecologia*, 66:17-24.
- Fairbridge, R.W. (1976). Shellfish-eating preceramic Indians in coastal Brazil. Science, 191: 353-359.
- Gentry, A.H. (1982). Phytogeography patterns as evidence for a Chocó refuge. In Prance GT (ed) Biological Diversification in the Tropics. Columbia Univ. Press, New York, pp:112-135.
- Goh, K.M., Molloy, B.P.J. (1978) Radiocarbon dating of paleosols using organic matter components. J. Soil Sci, 29(4):567-573.
- Haffer, J. (1969). Speciation in Amazonian forest birds. Science 165: 131-137.
- Hendy, C.H. 1972, Rafter, T.A., MacIntoshi, N.W.G. (1972). The formation of carbonate nodules in the soils of the Darling Downs, Queensland, Australia and the dating of the Talgai cranium. In Rafter, T.A. and Grant-Taylor, T. (eds.), *Proceedings 8th International Conference*, Lower Hutt, New Zealand, Wellington, Royal Society of New Zealand, pp:D106-D126.
- Ledru, M.P. (1993). Late quaternary environmental and climatic changes in central Brazil. Quaternary Research, 39:90-98.
- Leyden, B.W. (1985) Late quaternary aridity and Holocene moisture fluctuations in the Lake Valencia basin, Venezuela. *Ecology*, 66:1279-1295.
- Markgraf, V. (1991). Younger Dryas in southern South America. Boreas, 20:63-69.
- Martinelli, L., Pessenda, L.C.R., Valencia, E.P.E., Camargo, P.B., Telles, E.C.C., Cerri, C.C., Victória, R.L., Aravena, R., Richey, J., Trumbore, S (1997). Carbon -13 and carbon-14 depth

Paleoclimate in Brazil

- variation in soil profiles of sub-tropical and tropical regions of Brazil and relations with climate changes during the Quaternary. *Oecologia*. (in press)
- Pessenda, L.C.R., Camargo, P.B. (1991). Datação radiocarbônica de amostras de interesse arqueológico e geológico por espectrometria de cintilação líquida de baixo nível de radiação de fundo. *Química Nova*, 14(2):98-103.
- Pessenda, L.C.R., Valencia, E.P.E., Camargo, P.B., Telles, E.C.C., Martinelli, L.A., Cerri, C.C., Aravena, R., Rozanski, K. (in press a). Radiocarbon measurements in Brazilian soils developed on basic rocks. *Radiocarbon*, in press.
- Pessenda, L.C.R., Aravena, R., Melfi, A.J., Telles, E.C.C., Boulet, R., Valencia, E.P.E., Tomazello, M. (in press b). The use of carbon isotopes (<sup>13</sup>C, <sup>14</sup>C) in soil to evaluate vegetation changes during the Holocene in central Brazil. *Radiocarbon*, in press.
- Prance, G.T. (1973). Phytogeographic support for the theory of Pleistocene forest refuges in the Amazon basin, based on evidence from distribution patterns in Caryocaraceae, Chrysbonaceae, Dichapetalaceae and Lecythidaceae. *Acta Amazonica*, 3(3):5-28.
- Saldarriaga, J.G., West, P. (1986). Holocene fires in the northern Amazon basin. Quaternary Research, 26:358-366.
- Servant, M., Fontes, J.C., Rieu, M., Saliége, X. (1981). Phases climatiques arides holocènes dans le sud-ouest de l'Amazonie (Bolivie). C.R. Acad. Sci, II, 292:1295-1297.
- Stout, J.D., Rafter, T.A., Throughton, J.H. (1975). The possible significance of isotopic ratios in paleoecology. *In*: Suggate, R.P. and Cresswell, M.M. (eds). *Quaternary Studies*. Wellington, Royal Society of New Zealand, 279-286.
- Stuiver, M., Polach, H. A. (1977) Discussion: Reporting <sup>14</sup>C data. Radiocarbon, 19:355-363.
- Throughton, J.H., Stout, J.D., Rafter, T. (1974). Long-term stability of plant communities. Carnegie Institute of Washington Yearbook, 73:838-845.
- Van der Hammen, T. (1974). The Pleistocene changes of vegetation and climate in tropical South-America. *J.Biogeogr.*, 1:3-26.
- Van der Hammen, T. (1982). Paleoecology of tropical South America. In Prance G.T. (ed.). Biological Diversification in the Tropics. New York, Columbia, Univ. Press, pp:60-65

#### **Editors**

Prof. Dr. Julio C. Wasserman
Laboratoire de Chimie Bio-Inorganique et Environnement
CNRS – EP 132, Centre Helioparc
2, av. du Président Angot, F-64000 Pau, France

Prof. Dr. Emmanoel V. Silva-Filho Dept. de Geoquímica – UFF Outeiro de São-João Batista s/n° Centro, Niterói, RJ, 24020-150, Brazil

Prof. Dr. Roberto Villas-Boas Centro de Tecnologia Mineral, CETEM/CNPq Rua 4, quadra D, Cidade Universitária – Ilha do Fundão Rio de Janeiro, RJ, 21941-590, Brazil

"For all Lecture Notes in Earth Sciences published till now please see final pages of the book"

Cataloging-in-Publication data applied for

#### Die Deutsche Bibliothek - CIP-Einheitsaufnahme

Environmental geochemistry in the tropics / Julio C. Wasserman ... (ed.). - Berlin; Heidelberg; New York; Barcelona; Budapest; Hong Kong; London; Milan; Santa Clara; Singapore; Paris; Tokyo: Springer, 1998

(Lecture notes in earth sciences; 72)
ISBN 3-540-63730-3

ISSN 0930-0317 ISBN 3-540-63730-3 Springer-Verlag Berlin Heidelberg New York

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, re-use of illustrations, recitation, broadcasting, reproduction on microfilms or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer-Verlag. Violations are liable for prosecution under the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1998 Printed in Germany

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: Camera ready by author

SPIN: 10656748

32/3142-543210 - Printed on acid-free paper

