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Chronological studies of tree-rings from the Amazon Basin using thick target PIXE and proton backscattering analysis

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Abstract

A tree-core sample (*Aspidosperma obscurinervium*, popular name: "pequiá marfim") about 161 years old (cut in 1990), from the Ducke Reserve at the Amazon Basin, Manaus, Brazil was analyzed by PIXE (Particle Induced X-ray Emission) and proton backscattering in 136 different spots along its life. Twenty-two elements plus the density of the wood were measured (C, O, H, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Co, Rb, W and Pb). Average C, O, and H results (49.77% ± 0.15%, 44.29% ± 0.14% and 5.95% ± 0.12%, respectively) compare well with literature values for the biomass in the Amazon region. The variability of trace elements along the tree rings showed important features that could be caused by modifications in the environment during the life of the tree. The well behaved variability of some trace elements (like K, P, Mn, Ca, etc.) seems to reflect the physiological response of the tree to external changes in the environment. The concentration of K varied from about 4 up to 2000 ppm in a given period of the life of the tree. The same period also shows important changes in the bulk composition and structure of the rings (e.g. C and density series). Multivariate statistical methods (cluster and factor analyses) were used for data interpretation, helping in the separation of periods of important transformations in the tree. The elemental time series is compared with historical records of regional development and with some global events that could possibly affect the tree. The period of maximum variation in the elemental concentrations appears to be related to the Brazilian rubber boom (1859–1912), responsible for several transformations in the Amazon region. In particular in the Manaus region, large development has occurred in the beginning of the 20th century, which are reflected in the results of this tree-core analysis. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Instrumental meteorological records all over the world date at most from about 200 years ago in very limited regions. For the study of anthropogenic alterations in the environment and climate change it is essential to have good characterizations of the past climate and environment. Wigley [1] discusses several methods for paleo-climatic studies and its temporal resolution. Hansson [2] discusses the analyses of ice cores from polar regions for the study of variations in temperature, precipitation, and chemical composition of

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atmospheric aerosols up to hundreds of thousands of years ago. Tree-rings are a useful tool for recovering climatic and environmental alterations in the scale from years to thousands of years. Variations in the chemistry and physical structure of the tree-rings can be associated with variations in the environment and climate around the tree [3–7].

During the last century, intense activities due to the modification of land use and tenure, mining activities and biomass burning are changing the Amazon Basin environment significantly [8,9]. A precise characterization of these environmental changes is difficult due the shortage of instrumental historical records of climatic and environmental variations in the region. When existent, these records are poor and fairly recent. Tree-rings with hundreds (or even thousands) of years available in the Amazon region [10] can give historical information about environmental and climatic variations along the life of the tree.

Due to its sensitivity, spatial resolution, multielementarity and feasibility, simultaneous PIXE (Particle Induced X-ray Emission) and proton backscattering analyses of wood can provide satisfactory historical records of the elemental composition of the tree rings [3–6,11–15]. Due to the possibility of dating, time series of the composition of tree rings can be directly associated with historical events along the life of the tree. Two mechanisms can be pointed as indicators of environmental changes around the tree: direct contamination of the wood via uptake by the tree (from soil, water or atmosphere) of "toxic" elements via roots, leaves and stem and metabolic changes in concentrations of key trace elements for the tree, in response to environmental changes [7,16].

2. Methodology

Amazon trees are usually composed of very hard wood, which makes it difficult, if not impossible, to extract tree cores using the regular manual tools. For this study, a small sample from a tree that had been cut for other purposes was used. This sample was acclimatized for several days in a low relative humidity environment and was cut according to the indication in Fig. 1, for density measurements using gamma rays. Density measurements were performed at "Centro de Energia Nuclear na Agricultura" (CENA-University of São Paulo) each 0.2 mm along the wood stick. Commonly, trees from the Amazon Basin do not present visible formation of rings due to relative regular climate conditions along the year. For these cases, the density analysis can be a useful technique for identifying the structure of the rings. A fast Fourier transform band-pass filter was used to analyze the density series of the wood. The extreme low and high frequencies were filtered to elucidate the ring structure, providing an estimate of the age of the tree. After the density measurement, the inner part of the sample was cut in a thin (~1 mm × 1 cm × 284.6 mm) stick, adequate for fitting the PIXE chamber (Fig. 1). The sample was submitted to vacuum inside the PIXE chamber and analyzed each about 2 mm in 136 dots along the life of the tree. A slit beam collimator 1.5 × 5.0 mm and a computer controlled stepping motor system were used to define the irradiation geometry and the precise positioning of the sample.

PIXE and proton backscattering analyses were performed at the "Laboratório de Análise de Materiais por Feixes Iônicos" (LAMFI) at the Institute of Physics of the University of São Paulo. Both analyses were performed simultaneously using a 2.4 MeV protons beam from a Pelletron Tandem Accelerator NEC 5SDH. PIXE was used to measure trace elements above Mg and proton backscattering was used to determine the

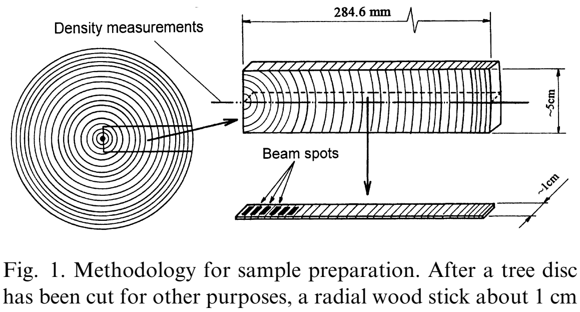

Fig. 1. Methodology for sample preparation. After a tree disc has been cut for other purposes, a radial wood stick about 1 cm thick is cut for density measurements. After that, a thin slice of the center part of the wood stick (about 1 mm thick) is taken for the elemental ion beam analysis.

composition of the organic matrix of the wood in each spot. The backscattering spectrum was able to discriminate well C and O above minimum detection limit (MDL) for each analyzed spot. N is supposedly present in the sample with concentrations below MDL, and H is present in the sample but cannot be observed directly in proton backscattering spectra due to its low atomic mass. Assuming that the composition of the wood was basically C, O, and H, an analytical calculation was used to simulate the backscattering spectrum as a function of the ratio C/H and O/H. This calculation resulted in the relative concentration of C, O, and H in each analyzed spot [17]. This technique was validated for C, O, N and H using several NIST reference materials and plastic foils with well known bulk composition.

Charging effects were eliminated using a thin grounded gold foil (~45 μg/cm^2) supported by a carbon self-sustained film (~15 μg/cm^2) about 2 cm in front of the sample. The integrated charge of the beam was obtained measuring the forward scattering of protons in the gold foil. This methodology was cross calibrated with the faraday cup of the PIXE chamber for thin film samples showing average differences of about 2.5% for a large range of integrated charge values. The thick target quantification of the PIXE analysis was performed using a combination between the code THICK (part of the package PIXAN [18]), thin target quantitative calibration with several MicroMatter standards, and matrix determination by proton backscattering. The composition of the matrix for each irradiated spot was used for calculations of the stopping power and X-ray self-absorption in the sample. The methodology was evaluated and validated using NIST standards for biological samples showing good results for most of the measured elements.

Factor analysis was used to analyze the data variability and group similar elements. Cluster analyses from the point of view of the variables (or elements) were used as a tool to group elements according to their distance from each other. A hierarchical cluster analysis from the point of view of the cases was also applied in order to identify regions of the tree with similar elemental composition.

3. Results

Based on the time series of the density of the wood, the age of the tree was estimated as 161 ± 17 years. Table 1 shows the average elemental concentrations of trace elements measured by PIXE and the number of spots measured above the MDL for each element. Table 2 shows the average concentration of the organic matrix measured by proton backscattering spectrometry and compares the results for C, O and H with results from the literature for the regional biomass and wood samples [19–21]. Fig. 2 shows the time series for some of the measured elements plus the density of the wood as a function of the estimated date for each spot. Some elements such as Pb and Al that could possibly be associated with environmental contamination were measured only in few regions of the tree with concentrations above MDL. Following the variation of these elements, several changes in the concentration of other elements occur showing a very smooth and well-defined

Table 1
Average concentrations of trace elements measured in the tree-rings by thick target PIXE[a]

Elements	# Spots > MDL	Average (ppm)	STD
Al	9	376	254
Si	134	138	85.6
P	33	28.0	31.1
S	134	183	32.1
Cl	91	14.1	21.3
K	47	257	504
Ca	134	397	115
Ti	52	1.55	1.27
Cr	6	0.655	0.357
Mn	134	4.18	2.51
Fe	133	2.79	3.24
Co	69	0.531	0.217
Ni	93	0.707	0.440
Cu	134	2.22	0.843
Zn	134	162	163
Rb	9	3.25	1.92
Sr	101	3.40	1.66
W	92	3.26	2.18
Pb	4	3.91	2.88

[a] The average values correspond to results from spots above the minimum detection limit (MDL). STD is the standard deviation of each element.

Table 2
Average concentrations of C, O and H compared to compositions of the Amazon forest biomass [19,20] and composition of carbon for trunk material of several tree species from the Amazon region [21]. In this work, the errors presented for the average values of C, O and H are the standard deviation of the average $(\mathrm{STD}/\sqrt{\#\mathrm{spots}})$, whereas the criteria of error estimates from Ref. [17] is not indicated

Elements	This work (%)	Biomass [19] C6H9O4 (%)	Measured biomass (%) [20]	Trunk composition (%) [21]
C	49.77 ± 0.15	49.7	53.8 ± 1.8	48.6
O	44.29 ± 0.14	44.1	39.1 ± 2.3	–
H	5.95 ± 0.12	6.2	5.9 ± 0.1	–
N	–	–	1.6 ± 0.7	–

pattern. For some elements (like K, Mn, Ca, Zn, etc.) this behavior was attributed to metabolic response of the tree to variations in the environment. For instance, variations in K concentration, are extremely intense (from below 4 up to 2000 ppm) suggesting they are not only proportional to external variations in the K concentration in the environment, but they could be an amplification of external perturbations undergone by the tree. Such a variation in the chemical composition of the wood is easily detected by PIXE and can be used as an indicator of modifications in the environment around the tree.

Cluster and factor analyses were applied to help the interpretation of the time series. Using factor analysis in the series with no or very few missing values, it was possible to identify four factors. The first one related to C and Zn, the second one related to other biologically important elements, S, Ca and Mn, the third one related to Fe, Si and Cu and the fourth one related to the density of the wood. The oxygen series provided negative factor loading in factors 1, 3 and 4, and factor loading zero in the factor 2. Cluster analysis applied from the point of view of the elemental composition provided similar results to the factor analysis. Extending the cluster analysis to elements with missing values, it provided complementary results relating W to the factor 1; K, P, Sr, Cl and O to the factor 2; Co, Ni and Ti to the factor 3; and H to factor 4. Table 3 shows results of the combination cluster plus factor analyses indicating elements with similar variability.

A cluster analysis was performed also from the point of view of the cases in order to group together periods of the time series with similar behavior or elemental composition. Results of this cluster analysis are presented in Fig. 2, indicating the presence of six different clusters. These results plus a complementary visual analysis of the time series suggest a division of the time series in seven regions (or periods), as indicated in Fig. 2. Despite the relative low concentration, the Mn time series shows well-shaped and distinct patterns in each phase of the life of the tree. These phases also correspond to some of the regions identified by the cluster analysis. It is important to notice the correlation between changes in the concentration of elements measured by different techniques like K, Mn, Si by PIXE, C by backscattering spectrometry, and density by gamma absorption. Significant changes in the C bulk composition and structures of the tree rings are associated with changes in the trace elements composition (e.g.: good correlation between C and Si).

3.1. Discussion of the elemental time series

The elemental time series presented in Fig. 2 are divided into seven regions as a result of the multivariate statistical analyses and visual interpretation of the graphs. Region (1) shows a regular behavior for most of the elements and a constant decrease of the density of the wood. The separation between region (1) and (2) is well marked by the series of C, Si, H, S and density. Region (2) also shows a regular behavior for most of the elements but with different values as compared to region (1). The beginning of region (3) is indicated by relatively high concentrations of Al, Zn and Pb (Al and Pb are below MDL for most of the sample). Density increases significantly in this region,

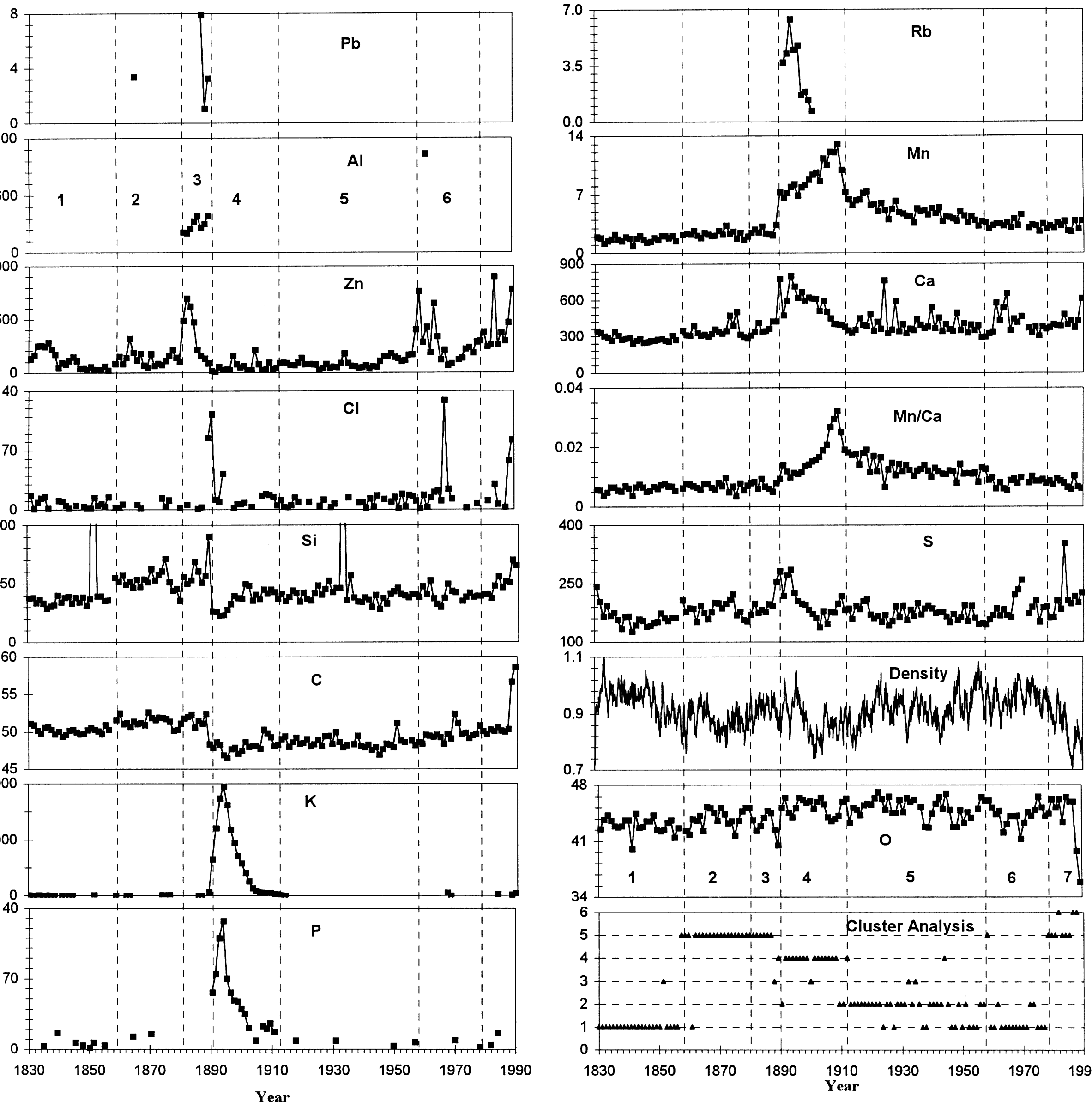

Fig. 2. Time series of elements measured by PIXE and proton backscattering analyses as a function of the estimated date. The time series of density is showed with higher resolution than the elemental time series in order to show more details in the structure of the wood. The seven periods identified by cluster analysis plus comparisons (see text) are indicated and numbered in the figure. The results of the cluster analysis from the point of view of the cases are also presented in the figure, showing the cluster number as a function of the date of the spot. Units are ppm for the trace elements, % for bulk material (C and O), and g/cm^3 for density.

Table 3
Elements with similar variability grouped with combined results from cluster and factor analyses

Group 1	Group 2	Group 3	Group 4
C	S	Fe	Density
Zn	Ca	Si	H
Si	Mn	Cu	
W	K	Co	
	P	Ni	
	Sr	Ti	
	Cl		
	O		

and Zn concentration shows a very smooth behavior. The relatively high concentrations of Al and Pb may be attributed to environmental contamination. The high variation of Zn can be related to responses of the plant's metabolism to these external factors. The end of region (3) appears to be a gate for a series of events in region (4). Region (4) is marked by enormous variations in several key elements of the tree: K, P, Mn, Ca, S, Si, Cl and C, each one with a distinct pattern (except for C and Si). Right in the interface between regions (3) and (4) there is a sharp transient variation in Cl, followed by relatively long term variations in other elements. Most elements show very smooth, well-formed, and distinct variations along region (4). This behavior suggests the presence of processes biologically controlled by the tree metabolism, possibly responding to external factors. The concentration of K, for instance, varied from less than 4 up to 2000 ppm, and then back to 4 ppm, along 23 measured spots, with smooth variations, followed by P and Rb. The ratio Mn/Ca, suggested in the literature as an indicator of soil acidification [5,6,12,14], shows an intense increase along most of region (4), with an important decrease in the last three points. Region (5) appears to be a period when most of the elements are going back to its concentrations in periods (1) and (2), supposedly the undisturbed behavior of the tree. The transition between regions (5) and (6) is smooth for most of the elements, which can be observed in the cluster analysis (Fig. 2) for clusters 1 and 2. The density of points attributed to cluster 2 are gradually changing to cluster 1. Region (6) shows variations in several elements. Again, a very high concentration of A1 correlates with high concentrations of Zn followed by a sharp and intense oscillation in Cl. In opposition to region (4), there was no significant variation in K, P, Rb and Mn, but there was some variation in Ca and S. In the cluster analysis, region (6) showed similarities with region (1). Finally, region (7) is similar to regions (2) and (3) based in the results of the cluster analysis, but there is an important increase in the concentration of several elements (e.g. Cl, Zn, S and W), and a drop in the density of the wood.

3.2. Global and local chronological events

Several local (change in land use and occupation, biomass burning, etc.) and global events (volcano eruptions, changes in radiation patterns, global climate changes, etc.) could be responsible for chemical and physical variations in the structure of tree rings. A major eruption of a volcano for instance, due to its large emissions of aerosol particles to the atmosphere can change significantly the spectrum of solar radiation reaching the ground, can cause temperature variations at the surface, and affect the atmospheric chemistry in the tropics. As examples, we can point some events which could potentially have affected the regional environment during the life of the tree:

(a) 1815 – Eruption of the Tambora volcano.
(b) 1827 – Beginning of the Brazilian rubber boom.
○ Strong occupation in the Amazon region.
○ Search for unexplored regions.
(c) 1850–1910 – Golden phase of the rubber boom in Brazil: period of easy enrichment at Amazon due to the rubber boom.
(d) 1866 – Emperor's decree open the Amazon for foreigners' ships.
(e) 1876 – Vapor ships coming from the Ocean starts to go to Manaus.
(f) 1883 – Eruption of the Krakatoa volcano (Indonesia).
(g) 1901 – Starts the construction of the Port of Manaus.
(h) 1911–1926 – Period of great drought and biomass burning in Amazon.

(i) 1912 – Begin the crash of the rubber boom in Brazil.

(j) 1912–1920 – Brazil looses the international monopoly of rubber.

(k) 1967 – Installation of a free port zone in Manaus.

(l) 1979 – Installation of waste storage area nearby the Ducke Reservation.

Comparing these events with the measured elemental time series, the period of greatest variation in the elemental time series of the tree is among 1859–1912. The same period is related to the Brazilian rubber boom, responsible for many transformations into the Amazon Region due to strong occupation and regional development. However, there is no straight and conclusive association between these events and the variations in the time series. These events are not presented here as causal factors driving the time series, but they are examples of potential factors that could influence the tree rings behavior. Also, a more detailed survey is needed in order to understand and quantify other potential factors affecting the composition and structure of tree-rings in the Amazon region, as well as the application of other techniques is needed to validate the dendrochronology of Amazon trees.

4. Conclusion

Several important variations in the elemental time series were identified along the life of the tree. The metabolic response of the tree environmental changes produced very intense signals on the time series suggesting an amplification effect that can be used to identify important events of environmental contamination or changes in general. Toxic elements even if below detection limits must produce great alterations in the metabolism of the tree that could be easily observed as variations in the concentration of some trace elements in the tree rings.

The complementarity of PIXE, proton backscattering, and density techniques showed to be very important for this work. This combination allowed a good quantification of the matrix elements (further applied for thick target PIXE corrections), plus an increase of the number of measured variables with significant importance for the data interpretation. Results showed that PIXE and proton backscattering are compatible with the analysis of tree rings from the Amazon Basin in terms of sensibility and spatial resolution, constituting a promising tool for such studies.

Further work is needed in order to correlate the variations in the composition and structure of the tree rings with environmental and climate changes in the Amazon region. Also, better methodologies for dendrochronology need to be developed for tropical trees in order to provide a better understanding of the variations in the chemical composition of the rings.

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