CHEMICAL STUDY OF SEDIMENTS FROM SOLIMÕES AND NEGRO RIVERS BY INAA

José O. dos Santos[1], Casimiro S. Munita[2] and Emílio A. A. Soares[3]

[1] Coordenação de Cursos Técnicos e Superiores - Instituto Federal de Educação, Ciência e Tecnologia de Sergipe
Av. Lourival Baptista, s/n
79000-000 Lagarto, SE
osmansantos@ig.com.br

[2] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
camunita@ipen.br

[3] Departamento de Geociências – Universidade Federal do Amazonas (UFAM)
Av. Gal. Rodrigo O. J. Ramos, 300
69077-000 Manaus, AM
easores@ufam.edu.br

ABSTRACT

The events of the last 70,000 yrs of the history of the Solimões-Amazon river system are recorded in the fluvial terraces at region of confluence of the Negro and Solimões rivers, and are markers of changes in the landscape of the Amazon region and it can be observed by analyzing the sedimentary deposits quaternary in Amazon fluvial system. The aim of this work was to contribute with the characterization sedimentological - stratigraphic of Pleistocene succession of the confluence zone of the Negro and Solimões rivers by means of elemental chemical analysis. To provenance study, 24 elements were determined by Instrumental Neutron Activation Analysis from sediment samples collected at confluence of Negro and Solimões rivers and the results were interpreted using cluster and linear discriminant analysis, which classification to priori were samples previously defined according to Pleistocene stratigraphic units individualized at study area. According to discriminant analysis, one can infer that samples from the basin of the Solimões River and Paraná do Ariaú grabens (GPA) are not significantly different, but there was a clear separation of sediments from Negro and GPA groups. It was also obtained that samples from highest and lowest terraces that the of the Solimões river and Paraná do Ariaú are different, suggesting that it is a process that reflects the influence of chemical weathering on the uppermost terrace deposits. Thus, this work contributes to determine the contribution of the sediments deposited by the Solimões and Negro rivers in the filling of tectonic depressions and in the variations of degree of weathering between younger and older units, and provides additional subsidies to build the geological evolution of the area.

Keywords: INAA, LDA, Sediments, Solimões-Amazon River.

1. INTRODUCTION

The Amazon system is the largest and most complex terrestrial ecosystem, and its formation is correlated by dynamics of the Amazonas River system [1-2]. The main changes in the landscape of the Amazon region, which has been shown on the pattern of sedimentation,

relief and in the distribution of current biodiversity, have contributions from Andean tectonics and climate change that occurred in the Cenozoic. These transitions in the landscape can be observed through of the analysis of the sedimentary deposits of the Amazon basin, since they are results of migration and overlapping of different river systems from the Cretaceous [3].

In order to develop an evolutionary sedimentary-tectono model to Pleistocene period to the confluence of the rivers Negro and Solimões, it is running a multidisciplinary project to stratigraphic-sedimentological characterization of the Pleistocene succession at region of confluence of the rivers Negro and Solimões, located at western of the Amazon Basin. It was carried out Mapping of sedimentary units of Cretaceous and Pleistocene, paleoenvironmental reconstruction of the sedimentary deposits and Pleistocene depositional events was characterized by sedimentological criteria and morfostratigraphics, supported by methods from the Physical and Chemical Sciences [4]. In particular, the analysis of trace elements of sediments samples to geochemical study of sediments, it can contributed mainly to determine the contribution of sediment load deposited from Negro and Solimões rivers in filling of tectonic depressions and changes in the weathering degree between younger and older units, and thus have additional subsidies to build the geological evolution of the area.

The geochemistry of trace elements has been extensively investigated during last years because of their importance to study of provenance and petrogenical and geochemical problems. Trace elements, in particular rare earth elements, form a coherent group with similar chemical proprieties, which is important to reveal chemical processes in geological systems, also providing a characteristics fingerprint of different mineral [5]. Studies of fluvial sediments have become a major approach to reconstruction of paleoclimates, chronological determination and evaluating the sedimentation aspects and geological events. Since the difference in chemical composition elementary of geological samples are small, the analytical technique employed have sufficiently accurate and precise, and allows giving sensitive and reliable results, in the wide range of very low concentration [6].

Here, we presented results of Instrumental Neutron Activation Analysis (INAA) to study the chemical composition of sediments collected in fluvial deposits at the confluence of Negro and Solimões rivers (Figure 1). In this paper, the chemical compositional study has set the foundation for understanding the last phase of sedimentation in Amazon basin by studying the evolution of fluvial dynamics over the last 70,000 years BP. The determination of trace elements has been determined by INAA because of its sensitivity and capability for multi-elemental non-destructive analysis to address the quantitative aspects of trace elements contents in geological samples [5].

2. METHODOLOGY

2.1. Sample Collection

The confluence of Negro and Solimões rivers results in the formation of the Amazon River downstream from the city of Manaus, Brazil (Figure 1). The Negro river, with basin area of 686,810 km^2, drains the western slopes of the Guyana shield and joins Solimões River. The Solimões River have a drainage area of 2,150,000 km^2, delivers what sediment-rich waters, dammed from Andes located in the west of basin [7].

Evidence of the Quaternary tectonic and sedimentary history of Solimões-Amazon river system is registered in fluvial deposits found in the confluence zone of Negro and Solimões Rivers [3]. Extensional tectonics originated tectonic depression that have controlled the Pleistocene sedimentation influenced by Solimões (Paraná do Ariaú – GPA and Lago do Miriti – GLM grabens) and Negro river dynamics. The Pleistocene units occur in three levels of terraces. The Negro river always exhibited a straight style, confined in basement Cretaceous and Miocene rocks and with restricted alluvial plain, whereas the fluvial pattern of Solimões River has changed during the Holocene.

For chemical compositional characterization of sediments from confluence zone of Negro (Cachoeira do Castanho Grabens – GCC and Cacau do Pirera Grabens – GCP), Paraná do Ariaú Grabens (GPA) and Solimões rivers, samples of sediments deposited by fluvial system were collected at high points of terrace (Figure 1), storage into plastic bags, where the water contents are about 2-3% and where they did not remain immersed during long periods times.
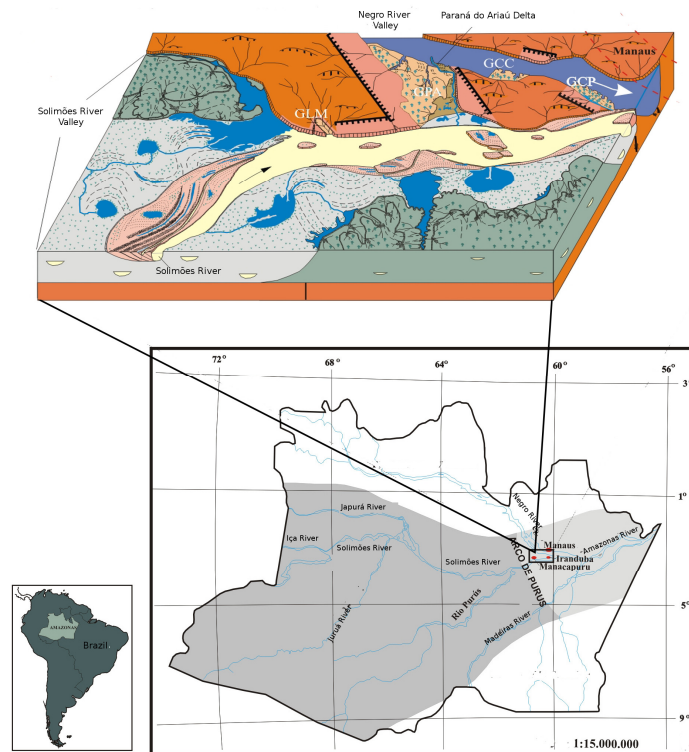

Figure 1. Location of studies sites.

2.2. Sample Preparation

Sediments samples were ground in an agate mortar until a granulometry of 100-200 mesh was achieved and quarted for the chemical determination by instrumental neutron activation

analysis (INAA). Finally, the powered samples were dried in an oven at 105°C for 24 hrs and stored in desiccators. Different authors have considered that there is no significant volatilization from the elements studies in this work when heated in this temperature [8, 9].

Constituent Elements in Coal Fly Ash - NIST-SRM-1633b, were used as standards in all analysis. The standard reference material Brick Clay - NIST-SRM-679 was used to check the analytical quality of the results. The standards and the samples were dried in an oven at 105°C, the standards for 4 hrs and samples for 24 hrs and stored in desiccators until weighing.

2.3. Irradiation

About 100 mg of sediments samples, and NIST-SRM-1633b were weighed in polyethylene bags and wrapped in aluminum foil. Groups of 8 ceramic samples and two reference materials were packed in aluminum foil and irradiated in the swimming pool research reactor, IEA-R1m (IPEN/CNEN – SP) at a thermal neutron flux at about 5 x 10^{12} n·cm^{-2}·s^{-1} for 8hrs.

2.4. Gamma Spectrometry

Two measurement series were carried out using Ge (hyperpure) detector, model GX 1925 from Canberra, with a resolution of 1.90 keV at the 1332.49 keV gamma peaks of ^{60}Co, with S-100 MCA of Canberra with 8192 channels. As, K, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days cooling time and Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, and Zn after 25-30 days. Gamma ray spectra analysis was carried out using the software Genie 2000 NAA Procedure from Canberra.

2.5. Statistical Interpretation

One of the most widely used multivariate procedures to data interpretation in earth sciences is discriminant analysis, which is commonly used to provenance study and can be used for establishing a baseline for geological provenance studies [10]. Mathematically, the discrimination of samples is determined using the linear combination of variables that provides the maximum difference between two or more predetermined groups [11].

In this paper, Linear Discriminant Analysis (LDA) was applied to INAA results to determine the level of chemical variability between the characterized samples and differentiate between the sedimentary deposits. LDA is a multivariate method which produces a data reduction enables the consideration of extensive variables that result from multi-element chemical characterization such as INAA. In order that the LDA is a technique that can be used for pattern recognition under supervision, so requires a priori classification. Here, it was assumed that samples collected from each sedimentary deposit was originated at that site collection (Paraná do Ariaú – GPA; Rio Negro; Rio Solimões), which established a priori compositional groups. Stepwise Discriminant Analysis also was used to selected chemical elements most useful to differentiate the groups of samples [12].

3. RESULTS AND DISCUSSION

To evaluate the analytical process and to establish the chemical elements which can be used in the data interpretation, the elemental concentrations for reference material Brick Clay - NIST-SRM-679 were statistically compared with the data found in our laboratory. The precision of several elements (La, Th, Sc, Fe, Eu, Ce, Zn, Hf, and Co) was better than 5%. Some elements presented a RSD (Relative Standard Deviation) of less than 10% (Nd, Rb, Sm, Ba, Sb, Ta, and Tb) and are similar to those from the literature [13].

Elements that have low precision can reduce the discriminating effects of other well measured elements. In this study all the elements with precision of less than 10% were considered for interpretation of the results (Na, Lu, Yb, La, Th, Cr, Cs, Sc, Ce, Fe, Eu, Zn, Co, Ta, U and Hf). The Zn presented RSD better than 10% but was excluded from the data set because its determination suffers strong gamma ray interferences of ^{46}Sc and ^{182}Ta. The K and Sb were better than 10%, however they were excluded because they presented 15% of missing values.

The results were transformed to $\log_{10}$ to compensate for the large magnitude difference between the measured elements at the trace level and the larger ones. One reason for this is the belief that elements from geochemical studies have a natural lognormal distribution, and that data normalization is desirable [14].

In order to confirm compositional groups, LDA was used to sample groups previously defined according to the individualized Pleistocene stratigraphic units in the confluence zone, related floodplains of the Negro and Solimões rivers and tectonic depressions. Figure 2 presents a bivariate plot of discriminant functions showing some overlap between samples from Solimões River and GPA, suggesting similarities of these samples according to chemical composition. However, in Figure 3 can be observed a clear separation between samples from Negro river and GPA. Thus, this results suggest that the overlap observed in Figure 2 can be indicative of the strong influence of sediments from Solimões River in the filling in GPA, since its formation, while the separation between groups in Figure 3 can be interpreted that the sedimentary input from Negro in GPA is insignificant.
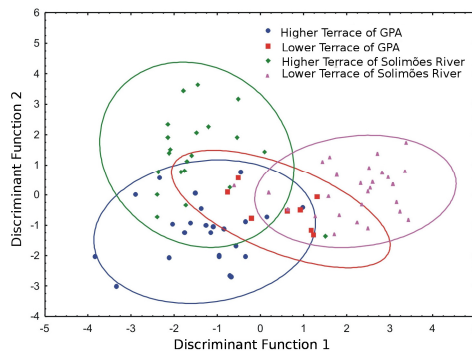

Figure 2. Linear discriminant analysis of sediments samples from GPA and Solimões. Ellipses represent a 95% confidence level
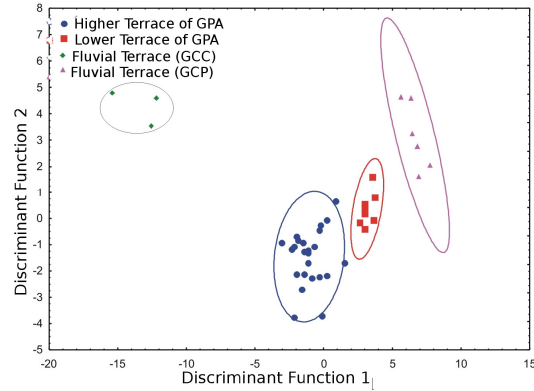
Figure 3. Linear discriminant analysis of sediments samples from GPA and Negro. Ellipses represent a 95% confidence level

Figure 4 and Figure 5 show a clear separation between samples from the higher and lower terraces of Solimões River and the Parana Ariaú, respectively. This individualization probably reflects effects of chemical weathering on the deposits of the uppermost terraces which present reddish and mottled appearance due to mineralogical and chemical transformations. Stepwise discriminant analysis established that the discriminatory elements for the studied groups were Na, As, Fe, Ce, K, Sc, Cr, Yb, Hf, Cs, Sm and U, whose average values are given in Table 1.
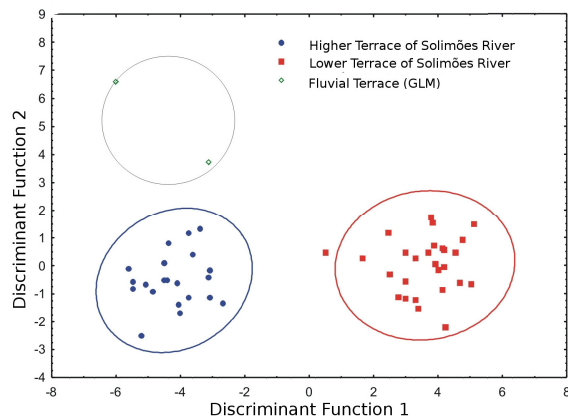

Figure 4. Linear discriminant analysis of sediments samples from GPA and higher terraces of Solimões. Ellipses represent a 95% confidence level
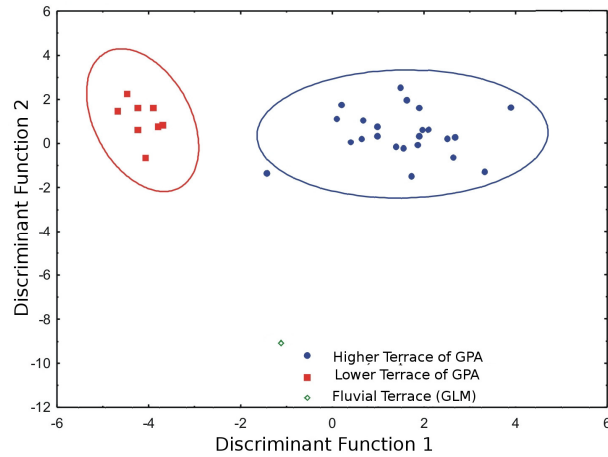
Figure 5. **Linear discriminant analysis of sediments samples from GPA and lower terraces of Solimões. Ellipses represent a 95% confidence level**

Table 1. Average concentration values and corresponding spreads (=standard deviation) of GPA, Negro river and Solimões river, in µg/g, unless indicated otherwise.

Element	GPA		Negro River		Solimões River	
	Upper terrace	**Lower terrace**	**GCP**	**GCC**	**Upper terrace**	**Lower terrace**
As	4,1±1,2	4,4±2,4	4,3±1,6	3,6±1,9	4,8±2,0	7±4
Ba	190±94	375±183	283±133	512±408	254±118	549±254
Ce	84±51	90±40	105±42	70±6	122±42	88±14
Co	3,9±2,6	9±11	8±5	3,3±1,5	8±4	12±4
Cr	79±18	69±14	80±7	62±20	68±18	72±11
Cs	8±5	8,2±2,8	8,1±1,4	4,7±2,5	8,6±2,6	8,6±2,3
Eu	1,4±1,1	1,5±1,0	1,7±0,8	0,93±0,05	2,1±1,2	1,5±0,3
Fe%	3,7±2,0	3,2±1,2	4,1±0,7	3,4±2,0	2,7±0,8	4,0±1,3
Hf	11±4	10±4	9±3	16±6	10±4	8±4
K%	0,72±0,33	1,4±0,5	1,08±0,08	0,9±0,4	1,6±0,6	1,8±0,5
La	45±24	45±18	57±22	36,3±1,4	58±21	46±8
Lu	0,58±0,17	0,55±0,14	0,58±0,17	0,47±0,06	0,70±0,20	0,54±0,12
Na%	0,09±0,05	0,27±0,26	0,08±0,01	0,06±0,02	0,19±0,21	0,6±0,4
Nd	34±15	51±23	56±23	23,3±1,4	58±35	38±11
Rb	51±33	81±33	71±13	35±19	91±36	105±27
Sb	1,5±0,8	1,1±0,5	0,78±0,15	0,55±0,05	1,1±0,4	1,1±0,3
Sc	15±4	16±4	18,6±2,1	14±4	17±3	17±4
Sm	6±3	9±6	28±48	7±6	10±7	10±7
Ta	1,8±0,7	1,7±0,4	1,81±0,12	1,5±0,4	8±10	3±5
Tb	1,1±0,7	1,1±0,5	1,3±0,6	0,73±0,25	1,3±0,8	0,86±0,28
Th	15±3	14,5±2,7	16±2	13±3	15,0±2,1	15±3
U	4,9±1,2	4,6±1,4	5±2	4,5±0,5	3,8±1,0	4,5±1,7
Yb	3,6±1,1	3,8±0,8	4,0±0,5	3,0±0,4	4,6±1,4	3,5±0,6
Zn	51±31	77±48	86±45	51±29	80±39	112±39

4. CONCLUSIONS

The INAA of sedimentary deposits from the confluence zone of Negro and Solimões Rivers was successful in identifying distinct compositional groups. According to statistical interpretation to results INAA it was possible infer that the elemental chemical composition of samples from Solimões River and GPA are not significantly different and samples from Negro river and GPA are distinct, which indicate the strong influence of sediment supply from Solimões River in the filling of GPA. We obtained samples from higher and lower terraces of Solimões River have different chemical composition, which leads us to infer that this reflects the influence of chemical weathering on the deposits of uppermost terraces, since they have distinct coloration due mineralogical and chemical transformation. The results provided information about the fluvial dynamic of confluence zone of Negro and Solimões Rivers contributing with subsidies to reconstruction of the geological evolution history of Amazon basin.

REFERENCES

1. J. L. Guyot, J. M. Jouanneau, L. Soares, G. R. Boaventura, N. Maillet, C. Lagane, "Clay mineral composition of river sediments in the Amazon Basin", *Catena*, **71**, pp.340-356 (2007).
2. J. L. Gaillardet, B. Dupré, C. J. Allègre, P. Négrel, "Chemical and physical denudation in the Amazon River Basin, *Chemical Geology*, **142**, pp.141-173 (1997).
3. E. A. A. Soares, S. H. Tatumi, C. Riccomini, "OSL age determinations of Pleistocene fluvial deposits in Central Amazonia", *Anais da Academia Brasileira de Ciências*, **82(3)**, pp.691-699 (2010).
4. Soares, E. A. A. 2007. Depósitos pleistocenos da região de confluência dos rios Negro e Solimões, porção oeste da Bacia do Amazonas. Tese (Doutorado) – Instituto de Geociências, Universidade de São Paulo, São Paulo. 205 p.
5. R. Ravisankar, E. Manikandan, M. Dheenathayalu, B. Rao, N. P. Seshadreesan, K. G. M. Nair, "Determination and distribution of rare earth elements in beach rock samples using instrumental neutron activation analysis", *Nuclear Instruments and Methods in Physics Research B*, **251**, pp.496-500 (2006).
6. M. A. Phedorin, V. A. Bobrov, E. L. Goldberg, J. Navez, K. V. Zolotaryov, M. A. Grachev, "SR-XRA as method of choice in the search of signals of changing palaeoclimates in the sediments of Lake BaiKal, compared to INAA and ICP-MS", *Nuclear Instruments and Methods in Physics Research A*, **448**, pp.394-399 (2000).
7. A. Laraque, J. L. Guyot, N. Filizola, "Mixing processes in the Amazon River at confluences of the Negro and Solimões Rivers, Encontro das Águas, Manaus, Brazil", *Hidrological Processes*, **23**, pp.3131-3140 (2009).
8. J. A. Cogswell, H. Neff, M. D. Glascock, "The effect of firing temperature on the elemental characterization of pottery", *Journal of Archaeological Science*, **23**, pp. 283-287 (1996).

9. A. Schwedt, H. Mommsen, " On the influence of drying and firing of clay on the formation of trace element concentration profiles within pottery", *Archaeometry¸* **49**, pp 495-509 (2007).

10. R. B. Schultz, "Geochemical relationships of Late Paleozoic carbon-rich shales of the Midcontinent, USA: a compendium of results advocating changeable geochemical conditions", *Chemical Geology*, **206**, pp.347-372 (2004).

11. R. A. Johnson, D. W. Wichern, *Applied Multivariate Statistical Analysis*, Trentice Hall, New Jersey & USA (1992).

12. C. S. Munita, L. P. Barroso, P. M. S. Oliveira, "Stopping rule for variable selection using stepwise discriminant analysis", *Journal of Radionalytical and Nuclear Chemistry*, **269**, pp.335-338 (2006).

13. C. S. Munita, R. P. Paiva, M. A. Alves, P. M. S. Oliveira, E. F. Momose, "Contribution of Neutron Activation Analysis to Archaeological Studies", *Journal of Microprobe Techniques*, **18**, pp.381-387 (2000).

14. C. Reimann, P. Filzmoser, "Normal and lognormal data distribution in geochemistry: death of myth. Consequences for the statistical treatment of geochemical and environmental data", *Earth and Environmental Science*, **39 (9)**, pp.1101-1014 (1999).