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Provenance studies in Amazon basin by means of chemical composition obtained by INAA

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Abstract This study determines the provenance of the 106 sediments samples deposited by the Solimões and Negro rivers in the tectonic depressions in Manaus, Amazon state, Brazil. Twenty-four chemical elements in the sediment samples collected before the confluence of Negro and Solimões rivers have been determined using instrumental neutron activation analysis, INAA. It is inferred from the multivariate statistical methods that samples from the basin of the Solimões river and tectonic depression 1 (the most significant of the region) are not significantly different. These results indicate the contribution this river in the sedimentary fill during the evolution in the Quaternary.

Keywords Geochemistry · INAA · Amazon basin · Mahalanobis distance

Introduction

The Amazon system has the largest and most complex terrestrial ecosystem and its formation correlates with the dynamics of the Amazonas river system [1, 2]. The main changes in the landscape of the Amazon region, which depends 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 era. These transitions in the landscape can be observed through the analysis of the sedimentary deposits of the Amazon basin, since they result from the migration and overlapping of different river systems since the Cretaceous period [3].

In order to develop an evolutionary sedimentary-tectonic model on the Pleistocene and Holocene periods to the confluence of the rivers Negro and Solimões, a multidisciplinary project has been carried out on the stratigraphic-sedimentological characterization of the Pleistocene-Holocene succession of the region of confluence of both rivers, located at western of the Amazon basin. In this region, most of the Quaternary deposits are confined to four tectonic depressions (informally named 1, 2, 3 and 4) (Fig. 1). The most significant is the depression 1 that encompasses two levels of river terraces developed by the Ariau river, whose dinamics and fill sediments may have been influenced by the Negro and Solimões rivers. The sedimentation in the depressions 2 and 3 was affected by the Rio Negro as depression 4 by the Solimões river. The oldest terrace is of reddish color displaying features of pedogenesis and an age of 65,000 years before Present (BP). The younger terrace is of gray color and has an age of 9000 years BP [3, 4]. Depressions 2 and 3 contain sediments deposited by the Negro river and exhibit an age around 45,000 years BP. Depression 4 contains sediments of the Solimões river and they were not dated.

The study of trace elements has been investigated during last years because of their importance to study of provenance, geological and petrogenical problems [5, 6]. The geochemistry analysis by means of trace elements, in particular rare earth elements, are important to reveal chemical processes in geological systems and also for providing

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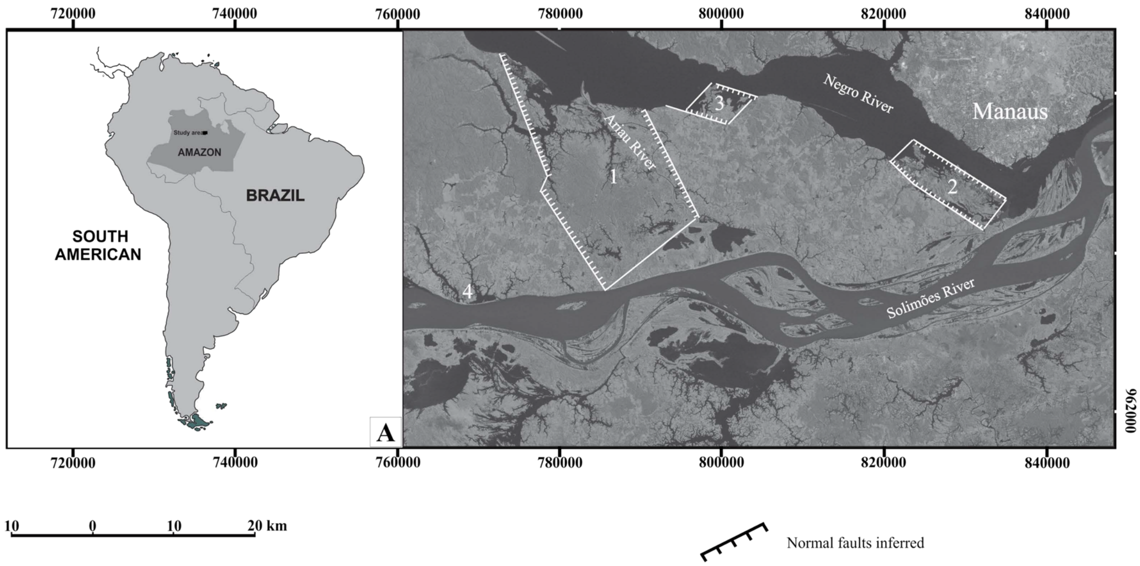

Fig. 1 Map of South America highlighting, the Amazonas State and workplace (*black rectangle*). Confluence of the Negro and Solimões rivers area illustrating the tectonic depressions *1*, *2*, *3* and *4* and its structural limits

characteristic fingerprint of different minerals [7]. The results it may contribute to the geological studies in the area.

Since the differences in chemical composition between the samples are small, the analytical technique used must be accurate, precise and should be able to give sensitive and reliable results in the wide range of low concentrations [8]. Among the various techniques INAA employing γ-ray spectrometry seems to be the most suitable analytical technique because it does not require mineralization of samples and allows the determination of several elements simultaneously with high sensitivity, accuracy and precision. Moreover, sample preparation is relatively easy and fast.

The aim of this paper was to study the As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb, and Zn contents in quaternary sediments collected in fluvial deposits at the confluence of Negro and Solimões rivers, Manaus city, Northern of Brazil, for understanding the last phase of sedimentation and the evolution of fluvial dynamics over the last 70,000 years BP. The dataset was studied by means of multivariate statistical methods like discriminant analysis and robust Mahalanobis distance to identify the compositional groups [9, 10].

Experimental

Sample collection

The confluence of Negro and Solimões rivers results in the formation of the Amazon River downstream from the city of Manaus, Brazil (Fig. 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 [11]. In this work, the sediments were collected in outcrops of fluvial terraces (upper and lower) near to surface (Fig. 1), storage into plastic bags, where the water contents are about 2–3 % and where they did not remain immersed during long period times.

Sample preparation and standard

Sediments samples were ground in an agate mortar until a granulometry of 100–00 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 h and stored in desiccators [12, 13].

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 be means of *Z* score, and particulary its precision by means of relative standard deviation (RSD). The standards and the samples were dried in an oven at 105 °C, the standards for 4 h and samples for 24 h and stored in desiccators until weighing.

Irradiation

About 100 mg of sediments samples, and NIST–SRM-1633b were weighed in polyethylene bags and wrapped in aluminum foil. Groups of 8 sediments samples and two reference materials were packed in aluminum foil and irradiated in the swimming pool research reactor, IEA-R1 (IPEN–CNEN/SP) at a thermal neutron flux at about 5×10^{12} n cm^{-2} s^{-1} for 8 h.

Gamma spectrometry

Two measurement series were carried out using Ge (hyperpure) detector, model G× 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.

Statistical treatment

The first stage in statistical interpretation of geochemical data is to describe the ranges of concentrations of the elements and to get an identification of the presence of outliers, which are observations that appear to be inconsistent with the rest of the data. The outlier detection in multivariate space is one important task in statistical interpretation of geochemical data, since outlying samples can contain a lot of valuable information about data set and its presence can interfere in statistical interpretation of data, especially in provenance studies [14]. Generally, atypical samples in a geological data set does not need to be especially high (or low) in relation to all values of a variable, and thus attempts to identify these samples with classical univariate methods commonly fail. In order to resolve this difficulty, several methods to identify outlier on multidimensional data set have been proposed based on covariance matrix and mean vector, such as the methods which use Mahalanobis distance [15]. This statistical method often uses classical Mahalanobis distance (MD) to detect if an observation is far from the center of the data distribution and if MD calculated is higher than the critical value the sample is candidate to be outlier.

The classical Mahalanobis distance estimator (MD) between the points $\overline{X}_i$ and $\overline{X}$ is defined by Eq. (1), where $\overline{X}_i$ is the ith observation from a p-dimensional data set, with p equal to number of variable, S is a covariance matrix and is a $\overline{X}$ mean vector.

$$\mathrm{MD}_i = \sqrt{\left(X_i - \overline{\mathrm{X}}\right)^T S^{-1}\left(X_i - \overline{\mathrm{X}}\right)} \quad (1)$$

To a data set with normal distribution, MD has a χ^2_p distribution and observations with a large distance, in general $\mathrm{MD}^2 > \chi^2_{p,0.975}$, are indicated as outliers [16]. However, masking effects decrease the MD of an outlier. On the other hand, swamping effects increase the MD of non-outlying observation [15]. This way, the MD needs to be estimated by a robust procedure in order to provide reliable measurements because the Mahalanobis distance is very sensitive to the presence of outliers.

In this context, the minimum covariance determinant estimator (MCD) is frequently used as robust estimator for location and covariance, where MCD is determined by a subset of observation of size k, generally $k \approx 0.75n$ (n is a number of samples), which minimizes the determinant of the sample covariance matrix [17]. The choice of k determines the robustness of the estimator. Using robust estimators of location and scatter in Eq. (1) results in so-called robust distances (RDs) and if $\mathrm{RD}^2 > \chi^2_{p,0.975}$ the sample can be declared as a candidate outlier [18].

In this work, for outliers detection by RD analysis, the "*mvoutlier*" and "*chemometrics*" packages running under R environment were used [19–21]. It was constructed graphics with classical Mahalanobis distance of data against the robust Mahalanobis distance called dd-plot, which can be used to detect outlier [22]. In addition, the first principal components against the second principal component was plotted from data set using different symbols according to RD, and four ellipses were drawn, on which Mahalanobis distances are constant corresponding to 25, 50, 75 % and adjusted quantile of the Chi square distribution. In this last plot, samples that have a RD higher than criteria were defined outliers. Graphics for each geochemical group which are indicated in Fig. 1 (tectonic depressions 1, 2, 3 and 4) were generated, showing MD and RD versus the observation numbers, where samples with distance higher than cutoff are considered as a potential outlier [22].

After outlier detection, 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. 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 [23]. LDA is a multivariate method which produces a data reduction and enables the consideration of extensive variables that result from multi-element chemical characterization such as INAA. For LDA technique can be used for pattern recognition under supervision, when a priori classification is required. Here, it was assumed that the samples collected from each sedimentary deposit was originated at the collection site (tectonic depression 1, 2, 3 and 4), which established a priori compositional groups [24, 25].

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 of reference material Brick Clay—NIST–SRM-679 were statistically compared with the data found in our laboratory according to *Z* score. The standard difference or *Z* score values obtained for certified elements in this reference materials were $|Z_{score}| < 2$, indicating that our results are satisfactory [26]. The RSD, which is correlated with the precision of dataset, of several elements (La, Th, Sc, Fe, Eu, Ce, Zn, Hf, and Co) was better than 5 %. Some elements presented a RSD of less than 10 % (Nd, Rb, Sm, Ba, Sb, Ta, and Tb) and are similar to those from the literature [27].

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). 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 [9].

Using the RD estimator, based on minimum covariance determinant ($k = 0.75n$), we can find 14 points that are unusually far away from location and call those points outlying in our data set. The dd-plot from Negro river (depression 2 and 3) group is shown in Fig. 2, where we can identify five outliers. Similar graphics were made from others groups and we could detect four samples in depression 1 and five in Solimões area (depression 4). Figure 2 shows that the data set are not contaminated because all points found are near the cutoff line and it is possible also to see that five (5) samples in Negro river group, where RDs is above cutoff line.

The RDs were computed and four inner ellipses (Fig. 3) are shown for 0.25, 0.5, 0.75 and adjusted quantiles of $\sqrt{\chi^2_{24;0.975}}$, where observations between 0.25 and 0.5 tolerance ellipses are shown by a larger dot and the most distance non-outlier are plotted as a small plus. Finally, multivariate outliers that are outside the outer tolerance ellipse are represented by a large plus [19]. Considering this criterion, five samples are shown to Negro river (Fig. 3), four for depression 1 and five for Solimões river.

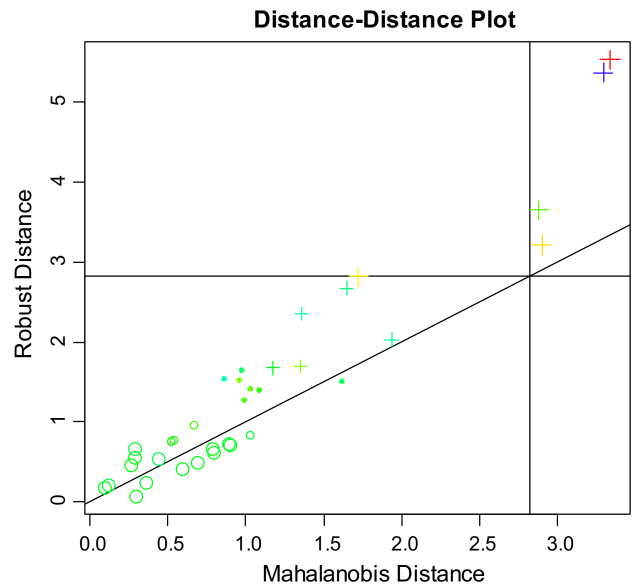

Fig. 2 dd-plot to Negro river. Samples far from *cutoff line* can be considered an outlier

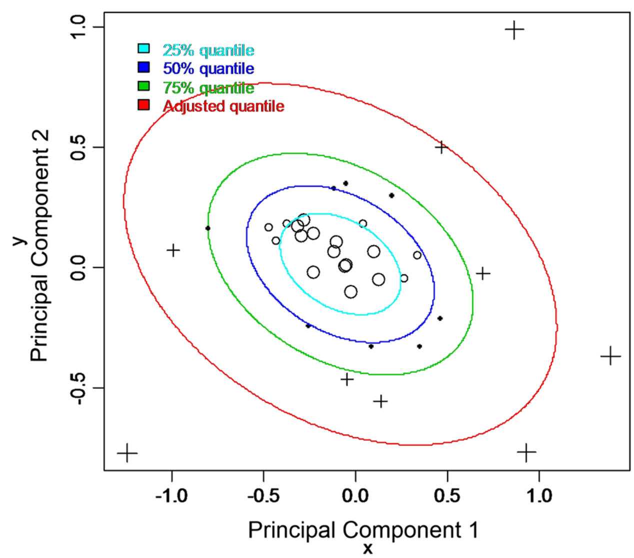

Fig. 3 The groups are tolerance ellipses defined for Chi squared quantiles 0.25, 0.5, 0.75 and adjustable quantile to Negro river (RN) samples

To confirm the samples which considered outlier suspects, the Fig. 4 shows that using RDs estimator several outliers have been identified which were not considered discrepant by means of MDs.

In order to confirm compositional groups, LDA was used to sample groups previously defined according to the individualized Pleistocene and Holocene stratigraphic units in the confluence zone, related floodplains of the Negro (depression 2 and 3) and Solimões rivers (depression 4) and depression 1. Figure 5 presents a bivariate plot of

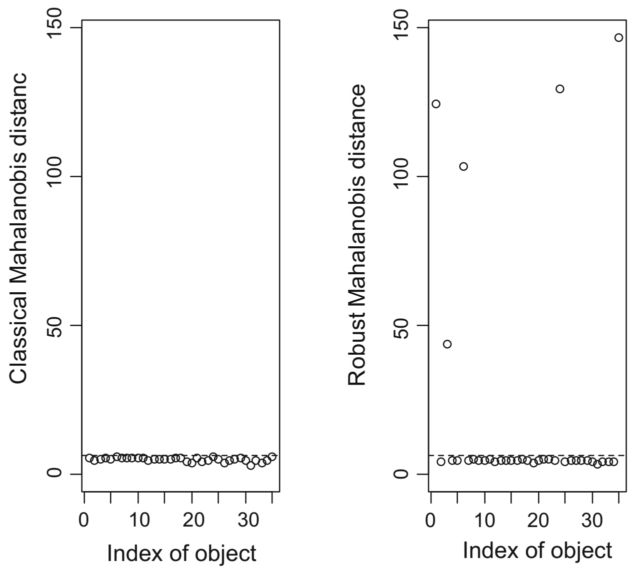

Fig. 4 Plots show the MDs (*left*) and RDs (*right*) of Negro river samples versus the object number. The *horizontal line* represents cutoff line (5 samples above cutoff line to RDs)

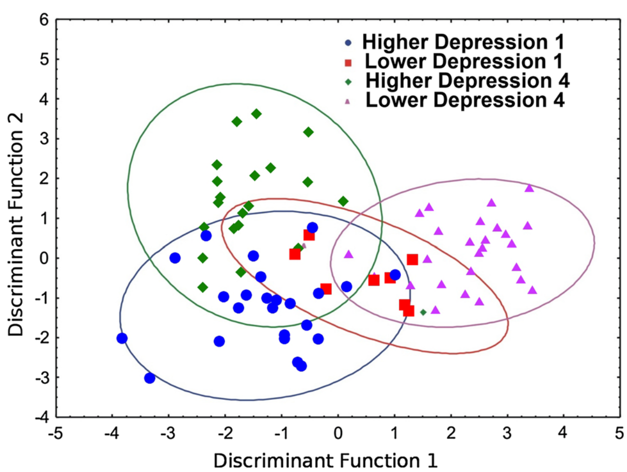

Fig. 5 Linear discriminant analysis of sediments samples from depression 1 and Solimões river (depression 4). Ellipses represent a 95 % confidence level

discriminant functions showing some overlap between samples from Solimões river and depression 1, suggesting similarities of these samples according to chemical composition. However, Fig. 6 shows a clear separation between samples from Negro river and depression 1. Thus, these results suggest that the overlap observed in Fig. 5 can be indicative of the strong influence of sediments from Solimões river (depression 4) in the filling of depression 1, since its formation. The separation between groups in Fig. 6 shows that the sedimentary input from Negro in depression 1 is insignificant.

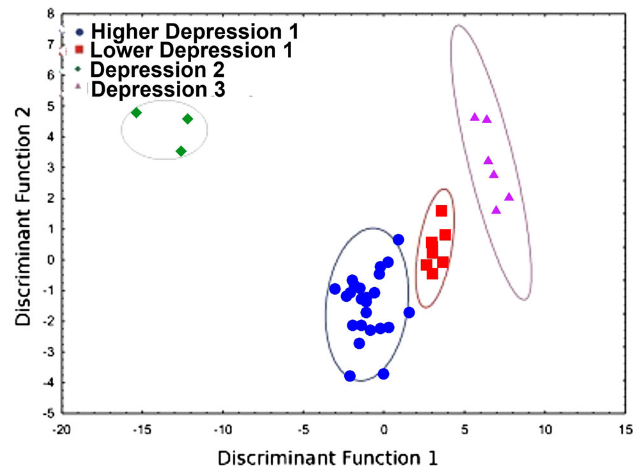

Fig. 6 Linear discriminant analysis of sediments samples from depression 1 and Negro river (depressions 2 and 3). Ellipses represent a 95 % confidence level

Table 1 Average concentration values and corresponding spreads (=standard deviation) of depression 1, depression 2 and 3 (Negro river) and depression 4 (Solimões rivers), in μg/g, unless otherwise indicated

Element	Depression 1 (Ariaú—$n = 32$)	Depression 2 and 3 (Negro—$n = 28$)	Depression 4 (Solimões—$n = 46$)
As	4.26 ± 2.21	4.02 ± 1.02	5.83 ± 3.71
Ba	303.93 ± 164.95	452.56 ± 188.80	473.50 ± 234.25
Ce	87.33 ± 36.95	91.61 ± 24.98	95.51 ± 26.43
Co	7.26 ± 9.93	6.71 ± 2.83	10.28 ± 4.77
Cr	72.30 ± 14. 35	67.33 ± 13.54	71.69 ± 10.53
Cs	8.39 ± 3.08	5.81 ± 1.72	10.44 ± 12.30
Eu	1.26 ± 0.83	1.26 ± 0.49	1.72 ± 0.65
Fe %	3.33 ± 1.36	2.64 ± 1.23	3.58 ± 1.21
Hf	11.23 ± 4.06	13.70 ± 4.88	8.27 ± 3.01
K %	1.19 ± 0.54	0.96 ± 0.22	1.72 ± 0.50
La	43.90 ± 17.58	53.69 ± 12.75	49.91 ± 13.81
Lu	0.55 ± 0.13	0.58 ± 0.12	0.59 ± 0.16
Na %	0.23 ± 0.24	0.07 ± 0.02	0.44 ± 0.37
Nd	43.91 ± 19.80	41.76 ± 16.50	50.26 ± 34.09
Rb	74.61 ± . 30.90	61.04 ± 17.62	95.70 ± 33.36
Sb	1.26 ± 0.60	0.73 ± 0.09	1.03 ± 0.36
Sc	15.18 ± 3.23	15.03 ± 3.01	17.27 ± 3.27
Sm	7.94 ± 5.15	11.51 ± 23.21	9.53 ± 7.15
Ta	1.76 ± 0.51	2.12 ± 0.63	5.52 ± 8.32
Tb	1.04 ± 0.40	0.87 ± 0.41	1.00 ± 0.47
Th	14.75 ± 2.47	17.09 ± 2.79	14.67 ± 2.67
U	4.73 ± 1.36	4.81 ± 1.14	4.27 ± 1.51
Yb	3.67 ± 0.84	3.52 ± 0.59	3.86 ± 0.95
Zn	65.51 ± 44.25	71.21 ± 25.73	102.16 ± 36.42

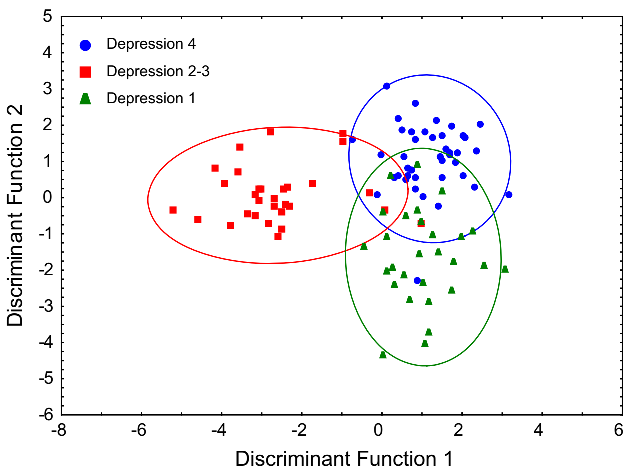

Fig. 7 Linear discriminant analysis of sediments samples from depression 1, Solimões (depression 4) and Negro (depressions 2 and 3). Ellipses represent a 95 % confidence level

This individualization probably reflects effects related to different sources of sedimentary material transported by rivers Negro and Solimões and the chemical weathering on the deposits of the 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 7 presents a bivariate plot of discriminant functions showing some overlap between samples from Solimões river and depression 1, suggesting similarities of these samples according to chemical composition. However, a separation between samples from Negro river and depression 1 can be seen in Fig. 7. Thus, these results are indicative of the strong influence of sediments from Solimões river in the filling of depression 1, since its formation. The separation between groups Negro river and depression 1 groups can be interpreted as being insignificant the sedimentary input from Negro river to depression 1, which is in accordance with the conclusions from the analysis of Figs. 5 and 6.

Conclusions

The INAA of sedimentary deposits from the confluence zone of Negro and Solimões rivers was successful in identifying distinct compositional groups. The results showed that the robust Mahalanobis distance estimator by minimum covariance determinant was able to detect atypical samples that the classical Mahalanobis distance has not been able to identify. According to statistical interpretation to INAA results it was possible to infer that the elemental chemical composition of samples from Solimões river and depression 1 are not significantly different and samples from Negro river and depression 1 are distinct, which indicate the strong influence of sediment supply from Solimões river in the filling of Depression 1. This indicates that the tectonic depression Depression 1 was not the path to the old course of the Negro river during the Late Pleistocene and Holocene. Samples from the higher and lower terraces of Solimões (depressions 1 and 4) and Negro (depressions 2 and 3) rivers have different chemical composition, which leads us to infer that this reflects the influence of chemical weathering and pedogenesis on the deposits of uppermost terraces, since they have distinct coloration (reddish) due mineralogical and chemical transformation. The results provided information about the Quaternary fluvial dynamics of confluence zone of Negro and Solimões rivers contributing with subsidies to reconstruction of the geological evolution history of this portion of Amazon basin.

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