# Chemical analyses of the Quaternary fluvial terraces at Careiro-Castanho and Autazes, central Amazonia

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## Abstract

Three quaternary fluvial plains, formed by the Solimões and Amazonas Rivers, are present in the region of Careiro-Castanho and Autazes, south of the city of Manaus, Central Amazonia. They are divided in upper (TS), intermediate (TI) and lower terrace (TInf). Their distribution is asymmetric, covering the Cretaceous-Miocene geological units in continuous stripes of more than 200 kilometers in length. In this work, 70 samples from the three terraces were analyzed using instrumental neutron activation analysis, INAA, to determine the concentrations of Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Sc, Sm, Th, U and Yb. The data set was interpreted using two multivariate statistical methods: cluster analysis and discriminant analysis. The study showed that the samples form three different groups including the samples TS, TI and TInf. Chemical and mineralogical transformation of the TS deposits show more weathering influence when compared to TI and TInf.

## 1. Introduction

In the Careiro-Castanho and Autazes region, south of the city of Manaus, there are three fluvial Quaternary terraces levels, with asymmetric spatial distribution, developed over Cretaceous-Miocene units. This basement occurs in an elongated range NE-SW direction, approximately 180 kilometers long and 15 kilometers wide, supported by lateritic iron crusts. The three fluvial terraces levels extending more than 130 kilometers by south to north and around 220 kilometers in east-west direction, composing the active and inactive alluvial plains of the Solimões-Amazonas fluvial system of the study area. Generally, the terraces are situated between 10 and 50 meters high, presenting point bars morphology with low drainage density, characterized by rare secondary plain channels in addition to many lakes with different sizes and shapes. These deposits are mainly constituted by sand and mud (silt and clay) in different proportions, forming the point bars bearing inclined heterolithic stratifications (IHS) pairs. The TS deposits places mainly the south-central part of the study area, extending over 100 kilometers and presenting a reddish color, while the TI and TInf deposits occurs as thin elongated stripes with 30 kilometers maximum wide extension, presenting gray color and being rich in organic matter. In central Amazonia region, the differentiation of these fluvial terraces levels has been mainly based in geomorphological aspects, so that it has been generalized lumped in the Quaternary geological units “impeded flood plain” and “older scroll dominad plain” from Latrubesse & Franzinelli (2002), Q3 and Q4 from Rossetti *et al.* (2004) and N3ta, N4apa and N4a from CPRM (2008). Confirming the developed studies in the alluvial plains of the Solimões-Amazonas fluvial system, southern Manaus, the fluvial terraces were chemically separated in three distinct groups based in 70 samples analysis whose concentrations of Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Sc, Sm, Th, U and Yb were determined by INAA. The TS samples formed a very distinct group, whereas the TI and TInf samples showed some overlapping, what suggests a close chemistry composition, so, it might be lumped in a unique group. This separation probably reflects the weathering larger influence over the TS deposits that presents reddish color and mottled aspect due to chemical and mineralogical transformations.

## 2. Geological setting

The study area is located over the Solimões-Amazonas alluvial plains, around the Careiro-Castanho e Autazes region, southern Manaus. In this region three quaternary fluvial terraces levels overlapping siliciclastic rocks (sandstones, claystones and conglomerates) of ‘Alter do Chão’ (Cretaceous) and ‘Novo Remanso’ (Miocene) formations were descripted by Soares *et al.* (2010). This basement show hills sustained by lateritic crusts situated between 50 and 60 meters high. The quaternary deposits are constituted of three asymmetric fluvial terraces, named TS, TI and Tinf. In this study, layed out as parallels strips to the current Solimões-Amazonas channel, whose ages vary between 1300 and 65200 years BP (Before Present).

The TS is disposed between altitudes of 30 and 50 meters, being the main unit in the south-central part of the study area and presenting a smooth hills relief, presenting large trees and exposing a thin soil layer on top. It occurs far from the current channel of the Solimões-Amazonas fluvial system compounding its inactive alluvial plain and shows pinkish to reddish colors, with massive and mottled aspect characterized by ferruginous red and yellow spots, being composed of mud with subordinate sandy layers forming IHS pairs.

The TI and TInf are disposed between 10 and 40 high, presenting a plain relief, just as lateral accretion lines. They are covered by small vegetation and occur as elongated strips with 30 kilometers maximum wide extension, periodically flooded, compounding the active alluvial plain of the Solimões-Amazonas fluvial system. The TI shows brownish-gray color and is mainly constituted of massive mud presenting incipient pedogenesis features. On the other hand, the TInf shows light-gray color, with total absence of pedogenesis features, being composed by sand and mud intercalations in different proportions forming IHS pairs.

The studied fluvial terraces with point bars bearing IHS indicate an active meandering fluvial style to the Solimões-Amazonas system during the period between 1300 to 65200 years BP, different from the current anastomosed style. The fluvial channels lateral migration, a common feature of meandering style, provided the migration of whole Solimões-Amazonas fluvial system for more than 130 kilometers northward. It allowed a broad fluvial terrace deposits development, which were abandoned afterwards and exposed to weathering processes, pedogenesis and vegetal colonization.

## 3. Methods

### 3.1 Sampling

The geological and geomorphological data were obtained through the remote sensors products integration: four mosaicked scenes from the visible band RGB composition of Landsat-5 images – TM sensor, thirteen mosaicked scenes of the L band, HH polarization, six meters spatial resolution from Synthetic Aperture Radar (SAR) images, obtained by the sensor SAR99-B, both products given by the ‘Sistema de Proteção da Amazônia’ (CENSIPAM) and, in addition, four mosaicked scenes of Shuttle Radar Topography Mission (SRTM) data from National Aeronautics and Space Administration (NASA) obtained in 2000. The geological samples chemically and sedimentary analyzed were collected between 1 to 3 meters from the top of several outcrops on the fluvial terraces three levels (Figure 1).

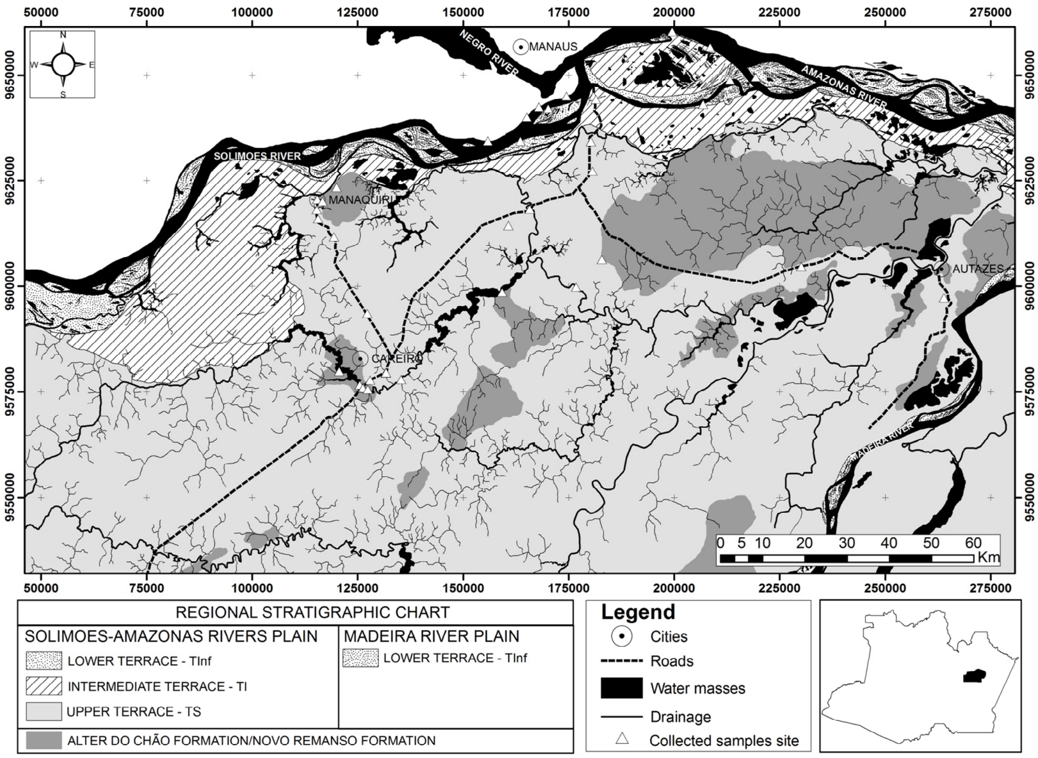

Figure 1. Geological setting and location of studied sites.

3.2 Analytical procedures

The samples were dried during 24 h in an oven at 105$^{o}$C, and then crushed manually in an agate mortar with a pestle, until an appropriate fine granulometry was obtained, in order to pass through a 100 mesh sieve. This procedure makes the material more homogeneous and adequate for trace analysis. The silicon contamination from agate mortars is not a serious problem since this element was not determined.

About 100 mg of sediment samples, NIST-SRM-1633b and IAEA Soil-7 were weighed in polyethylene bags. Groups of 8 samples and one of each reference material were packed in aluminium foil and irradiated in the swimming pool research reactor, IEA-R1m, at IPEN-CNEN/SP with a thermal neutron flux of about $1.5 \times 10^{12}$ n $\cdot$ cm$^{-2}$ $\cdot$ s$^{-1}$ for 8 h. Two measurement series were carried out using Ge (hyperpure) detector, model GX 2519 from Canberra, resolution of 1.90 keV at the 1332.49 keV gamma peak of $^{60}$Co, with S-100 MCA of Canberra with 8192 channels. K, La, Lu, Na, U, and Yb were measured after 7 days and Co, Cr, Cs, Eu, Fe, Sc, Ta, Tb, Th, and Zn after 25-30 days. Gamma-ray spectrum analysis and concentrations calculation were carried out using the Genie-2000 Neutron Activation Analysis Processing Procedure software from Canberra. Constituent Elements in Coal Fly Ash (NIST-SRM-1633b) was used as standard and IAEA-Soil-7, Trace Elements in Soil, was used as check samples in all analyzes. Those materials were dried in an oven at 105°C for 24 h and stored in desiccator until weighing Hazenfratz et al. (2012).

### 3.3 Statistical treatment of data

In order to elucidate the major variations in the concentrations of the data set obtained by INAA, it is indispensable to employ multivariate statistical methods that consider the correlation between elemental concentrations, as well as absolute concentrations to study the upper (TS), intermediate (TI) and lower terrace (TInf). The methods employed were cluster and discriminant analysis. To perform the cluster analysis the Ward's method and the squared Euclidean distances were used to calculate dissimilarities between samples.

## 4. Results and discussion

One of the basic premises for the use of a chemical compositional analysis of geological samples is that the samples can be differentiated if the analytical technique has a good sensitivity, precision, and accuracy for the analyte of interest. If an element is not measured with good precision, it may affect the other well-measured elements and the discriminant effect tends to be reduced. Small differences in elemental concentrations can be used to form groups of similar composition. So, the precision of the analytical technique in geological studies using trace elements is a key point in chemical differentiation in geological studies. In this study the precision of the method was studied using the reference material IAEA Soil – 7 Trace Elements in Soil. A comparison between the results obtained and the certified values was realized. The precision was expressed as relative standard deviation, RSD. The elements with RSD less than 10% were used in the data interpretation.

All possible interferences occurring in gamma-ray spectrometry were considered and checked. A possible source of error in the determination of REE elements is the presence of significant amounts of fissible nuclides ($^{235}$U and $^{233}$U). As it is well known, REE nuclides, especially among the light REE elements (La to Sm), are produced both by activation and by fission. In this work no interferences were expected in the samples because of the very low uranium fission in the determination of La and Ce. This interference is negligible when the uranium concentration does not exceed 5 ppm Glascock (1992). Although Ta and Zn had RSD less than 10%, they were not included in the data set because their concentrations can be affected as a consequence of a strong γ-ray interference of $^{65}$Zn and $^{182}$Ta with γ-ray energy in 1115.4 keV and 1121.2 keV, respectively. Using those criteria, the elements Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Sc, Sm, Th, U, and Yb were used in the subsequent data analysis. None of the elements considered presented missing values. In total, 70 samples were analyzed. Range, mean and standard deviation are presented in Table 1.

Table 1. Range, mean and standard deviation for all samples in μg/g, unless indicated.

| *Element* | *Range* | *Mean ± SD** |
|---|---|---|
| Co | 1.37 - 33.50 | 10.29 ± 7.63 |
| Cr | 20.30 - 111.00 | 66.43 ± 16.92 |
| Cs | 1.30 - 21.50 | 8.60 ± 3.65 |
| Eu | 0.29 - 3.10 | 1.56 ± 0.56 |
| Fe,% | 0.05 - 10.00 | 3.78 ± 1.64 |
| Hf | 3.90 - 24.06 | 9.72 ± 3.52 |
| La | 19.49 - 77.50 | 46.35 ± 12.22 |
| Lu | 0.20 - 1.30 | 0.63 ± 0.18 |
| Na,% | 0.04 - 1.22 | 0.47 ± 0.41 |
| Sc | 5.10 - 24.30 | 15.13 ± 4.00 |
| Sm | 2.79 - 21.80 | 7.68 ± 2.89 |
| Th | 4.90 - 37.70 | 14.66 ± 5.10 |
| U | 1.79 - 6.80 | 3.68 ± 1.07 |
| Yb | 2.06 - 7.24 | 3.81 ± 0.90 |

* Mean and standard deviation of 70 individual samples

Initially, the results were transformed to $\log_{10}$ to compensate for the large differences of magnitudes between the measured elements in trace level and macro ones. The $\log_{10}$ transformation of data before a multivariate statistical method is common. One reason for this is that many elements tend to have a natural log-normal distribution, and the normality of the data is desirable. Another reason is that a logarithmic transformation tends to stabilize the variance of the variables and would thus give them approximately equal weight to the variables with minor variance, such as the trace elements. So the data set were studied by means of cluster analysis in order to study the similarities among samples.

In the resulting dendrogram showed in Figure 2, the cluster analysis is used in the initial inspection of the data because it is a fast and efficient technique for evaluating relationships between large number of samples, using distance measures between them.

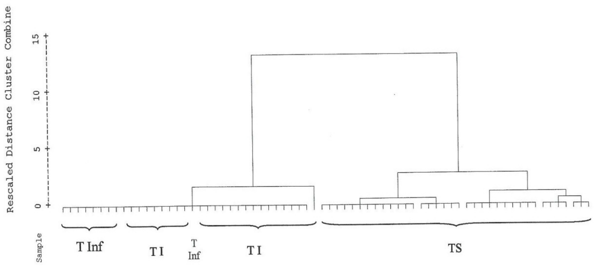

Figure 2. Dendrogram of the 70 samples, where TS, TI and TInf are upper, intermediate and low terrace, respectively.

So, dendrograms may accurately represent the differences between within-group members, but greatly distort the differences between groups. Thus, the effectiveness of dendrograms as a means of faithfully illustrating differences between groups is questionable. Dendrograms can be used as an initial step in the identification of groups, but they are inadequate as a quantitative measure to differentiate between groups.

Keeping this in mind, the Figure 2 shows the clusters containing the samples from upper (TS), intermediate (TI) and low (TInf) terraces. The cluster with the samples from TI and TInf form only one cluster very well separated from the samples from the upper terrace (TS). The TI and TInf samples showed some overlapping that suggests a close elemental composition, so it were lumped in a unique group.

In order to confirm the last assumption the data were submitted to discriminant analysis. Discriminant analysis was used to isolate those samples which could most effectively reveal the differences between clusters and establish a discriminant function for this purpose. The plot obtained by canonical discriminant functions is presented in Figure 3. The plots show the three groups of the samples TS, TI and TInf very clear.

At is can be seen, the results show that the samples of each terrace form a very tight chemically homogeneous group, showing a high degree of elemental similarity inside them.

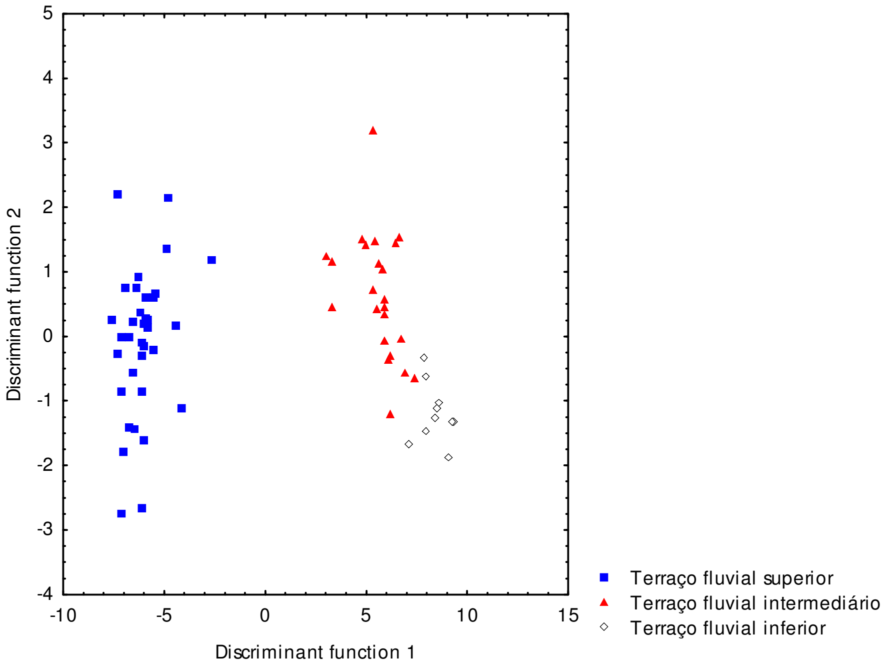

Figure 3. Discriminant function 1 vs discriminant function 2 for the 70 samples.

On the other hand, when the data set of each terrace are studied using cluster analysis, 9 samples from TI proved to be different from the group, form part of samples from TInf. However, when the data set are studied by discriminant analysis, they become similar to the other samples of each terrace. This means that the difference that occurs is not very important and when the data set is studied using a statistical method which considers the correlation structure between the chemical elements, like discriminate analysis, it is possible to see the three groups of samples. This assumption is confirmed using the element ratios. Taylor and McLennan (1995) suggest that certain trace element ratios in fine grained sediments are especially sensitive to provenance. In Table 4 some ratios for the three fluvial terraces are presented.

Table 4. Element ratios for TS, TI and TInf terraces.

| | TS (n=36) | TI (n = 25) | TInf (n = 9) |
|---|---|---|---|
| Th/Sc | 1.07 | 0.87 | 0.90 |
| Th/U | 3.59 | 4.73 | 3.91 |
| Cr/Th | 4.38 | 4.61 | 5.00 |
| Lu/Hf | 0.06 | 0.65 | 0.07 |

In Figure 3, it is possible to see three well defined groups that represent the fluvial terraces (TS, TI and TInf). Their chemical differences probably reflect the weathering major influence over the TS deposits than the TI and TInf units, considering its reddish color and mottled aspect due to mineralogical and chemical transformations. Nevertheless, the weathering performance during the TS development on Pleistocene was not so intense to consume the instable minerals as feldspar and interlayered clay minerals.

## 5. Conclusion

The discriminant analysis suggested two distinct groups in the Solimões-Amazonas fluvial system, based on the Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Sc, Sm, Th, U and Yb. One group is formed by the TS samples, and the other by the TI and Tinf samples. The weathering processes that acted during the fluvial terraces development reflect the more evident chemical differences in the TS deposits relative to the TI and TInf deposits. On the other hand, the absence of an evident separation between the samples of TI and TInf terraces might be correlated to an weak remobilization of elements during the weathering process act in Holocene.

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