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# Geochemical stream sediment signatures from Precambrian terrains of Uruguay

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## RESUMO

Dados geoquímicos do cristalino Uruguaio coletados nos anos de 1980 foram recuperados pela Direção Nacional de Mineração e Geologia do Uruguai (DINAMIGE) em 2020 envolvendo 32.000 amostras de solos e sedimentos de corrente analisadas para 22 elementos químicos (Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, P, Pb, Sb, Sn, V, W, Y and Zn) por meio de espectrometria de emissão atômica por plasma de corrente direta. Parte desses dados, 6755 amostras, ou seja, aproximadamente 21% do total, foram processadas por métodos estatísticos multivariados e procedimentos de sistemas de informação geográfica (SIG) objetivando a caracterização das anomalias geoquímicas derivadas de processos ambientais e geológicos. Inicialmente as amostras foram classificadas como background e anomalias/outliers, por critério multivariado. Os dados gerais e dos diferentes conjuntos foram processados por métodos estatísticos e SIG individualmente. Os resultados foram apresentados considerando as unidades originais ou em ocasiões considerando os dados transformados de maneira a homogeneizar a variabilidade. Foram definidas nove assinaturas geoquímicas relacionas com os domínios geológicos. Três delas envolvem unidades de baixo contraste com enriquecimento moderado em Ba, Co, Cu ou Mn. As restantes seis assinaturas geoquímicas relacionaram-se com unidades geológicas específicas e apresentaram assinaturas multivariadas. Foram definidas sete assinaturas relacionadas com anomalias três delas de origem litológico, duas superficiais e as outras mistas, incluindo a possibilidade de depósitos de sulfetos.

**Palavras-chave:** Anomalia, ambiente, elementos traço, prospecção, teor de fundo

## ABSTRACT

Geochemical data of Uruguayan crystalline terrains collected in the 80's were recovered by the National Mining and Geology Directorate of Uruguay (DINAMIGE) in 2020 involving 32,000 soil and stream sediment samples analyzed for 22 elements (Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, P, Pb, Sb, Sn, V, W, Y and Zn) by direct current plasma spectrometry. A set of 6755 samples of these data, more or less 21% of the total, were processed by multivariate statistical methods and geographic information system (GIS) procedures aiming characterization of geochemical signatures derived from environmental and geological processes. Samples were classified as background or anomalies/outliers at the beginning. The general data and the different sets were processed by statistical methods and GIS individually. The results considered the original units or sometimes, the transformed data for uniformity of variability. Nine geochemical signatures related to the geological domains were defined; three of them involved low contrast units with moderate enrichment in Ba, Co, Cu or Mn. The remaining six geochemical signatures were related to specific geological units and presented multivariate signatures. Seven signatures related to anomalies were defined, three of them of lithological origin, two superficial and the others mixed, including the possibility of sulphide deposits.

**Keywords:** Anomaly, background, environment, exploration, outliers, trace-elements.

## 1. INTRODUCTION

Uruguayan territory has 177,000 km$^2$, 3.4 million people (2020) and significant agricultural vocation with 11.2 million heads of cattle (2016), production of more than 4 million tons of cereals or beans and 329 thousand tons of fruits and growth forestry industry (2018). Mining activities for metal minerals were practically absent in Uruguay, nevertheless, a geochemical exploration program was developed during the 80s in the crystalline terrains, ranging about 25,000 km$^2$, with geochemical studies and geological mapping in 1:50,000 scale, in cooperation with BRGM, France. Geochemical results were published in inedited reports, some doctorate thesis (MIDOT, 1984; FILIPPINI-ALBA, 1998) and isolated articles (FILIPPINI-ALBA; OLIVEIRA, 1997; FILIPPINI-ALBA *et al.*, 1998; FILIPPINI-ALBA *et al.*, 2001).

Surprisingly, the UNESCO's global geochemical database (DARNLEY *et al.*, 1995), which attempted to integrate several regional geochemical surveys on a single global basis, did not take into consideration the regional geochemical data of Uruguay. Then, the National Mining and Geology Directorate of Uruguay (DINAMIGE) decided to recover in 2020 the old regional geochemical data including multi-element analyses of almost 32,000 samples*. On the other hand, the world began to worry about environmental science and geomedicine at the same time (THORNTON, 1990), when the concept of "geochemical background" returned to scene.

Reimann and Garrett (2005) used data from two subcontinental-scale geochemical mapping projects to demonstrate that trying to define 'a background' for a large area is complex, because background may change from area to area within a region and between regions. Therefore, the authors mentioned difficulties to define background levels in environmental context, especially for soils, which preclude eco-toxicological research.

A significant concept in that sense was appointed by Darnley *et al.* (1995): During the past four decades many millions of km$^2$ have been explored with geochemical mapping and several degrees of thoroughness, and hence many mineral deposits were discovered. The biological applications of geochemical mapping began in the 1920s from research into the trace element composition of soils. As geochemical maps covering large areas became available, a variety of biochemical phenomena have been recognized through empirical associations between trace element and morbidity patterns in plants and animals. More recently, as the variability of the natural geochemical background has become better known, it has been recognized that in order to identify and quantify anthropogenic pollution it is necessary to have a map of the natural background.

Galuszka and Migaszewski (2011) indicated that the concept of geochemical background in environmental sciences has emerged in the early 21st century, when many review articles on this thematic problem have been published, emphasizing differences with the concept used in exploration geochemistry, when the source of the anomaly was negligible and the elements considered in each case were usually different. Historically, the first attempts to assess the geochemical background were based on average values of elements concentration in crustal rocks (Clarke values) or on concentration of elements in fine-grained clastic sedimentary deposits (the average shale value).

The univariate statistical methods for defining anomalies were ostensibly used in geochemical exploration with gradually replacement by multivariate and spatial data analysis methods (HOWARTH, 1983). This suggests a transformation of the concept of geochemical background, evolving from a constant value to the concept of variability as a function of geographic position. The use of multivariate regression (ROQUIN and ZEEGERS, 1987), robust statistic (DI ZHOU, 1987) and multivariate outliers (GARRETT, 1989) represent this transition.

Reimann and Caritat (2017) appointed that the geochemical background must be evaluated in various scales, so they considered maps covering 81% of the Australian territory. A similar approach was developed in Europe by Demetriades *et al*. (2018). Both studies showed clearly geochemical spots of As, Cu, Ni, Pb and V varying from 0.01 or 0.1 ppm to some hundreds or thousands of ppm considering continental, national or local scales and the complexity associated to different aspects of geochemical prospecting. Licht (2020) remarked the diversity associated to sampling media, granulometry, solubilization, analytical methods and data processing methods in the

* Data were sent to the author as informal way.

perspective of geochemical background. Geochemistry of stream sediments and soils from Vale do Ribeira, Sao Paulo state, Brazil, were compared (FILIPPINI-ALBA *et al.*, 2008). Anomalies of Cu in stream sediments confirmed 62% of the cases of soils affected by lithological or mineral anomalies. Geochemical reply of soils was depth-dependent. Local nature of background was also suggested for the Andes Mountain Range, Peru (SANTOS-FRANCÉS *et al*., 2017).

If the previous text was summarized, Exploration Geochemistry and Environmental Geochemistry are closely disciplines focusing on processes related to the surface of the Earth. However the former considered mineral anomalies and the latter anomalies related to toxic or potentially toxic substances in the environment. The sources of the anomalies appear as important in both cases. Regression models of pathfinders contents as a function of Fe, Mn and organic matter (SELINUS, 1983; ROQUIN; ZEEGERS, 1987) or factors related to multivariate associations (FILIPPINI-ALBA *et al.*, 2001) were considered to represent lithological and superficial processes in exploration geochemistry in the way that residuals could be related to mineralization. Bowie and Thornton (1985) have mentioned soils contaminated with Ni due to the occurrences of mafic rocks, and As, Cd, Cu, Pb and Zn related to mineralization, inducing toxic levels in crops and cattle. These anomalies would be processed in different way for each discipline. Anomalies derived from superficial processes and lithological anomalies would be classified as “false anomalies” in geochemical exploration. However, they can be equivalent to anomalies derived from social-economic activities, occurring contamination or pollution in the environment, so “true anomalies” in the environmental geochemistry perspective.

Some geochemical prospectors migrated to environmental applications in the 80s when concerns about nature have increased; exploration geochemistry programs reduced and developed countries transferred their mining companies abroad. Some concepts derived from exploration geochemistry continued to be used in the environmental perspective; however, some processes were updated or improved, for instance, partial extraction, bioavailability and speciation. The term "threshold" was dropped, giving way to the "guidelines".

Here, geochemical prospection data and the digital geological map of a portion of the Uruguayan Precambrian terrains were processed by statistical methods and modeling in GIS, with the objective of understanding the nature of the geochemical signatures related to the background and the anomalies, in the way that suggestions about the sources of anomalies could be appointed, that is, if their origin is related to the environment, lithology or potential mineral deposits. Data processing was applied as different way, if the unpublished reports of the old regional geochemical program were considered.

## 1.1 GEOLOGY OF THE STUDY AREA

Uruguay is divided in two similar halves by the Negro river, a tributary of the Uruguay river (west frontier), running roughly east to west (Fig. 1). Precambrian terrains dominate the southern half, with the Rio de la Plata craton (RPC) in about central position and the Dom Feliciano belt (DFB) running towards northeast in the east sector.

Rapela *et al.* (2011) appointed the RPC as the oldest and southernmost core of South America. DFB includes the following sequences: (i) basement inliers of Archaen to Mesoproterozoic ages; (ii) schist belt composed of pre-collisional Neoproterozoic metavolcanic and metasedimentary sequences at greenschist-to-lower amphibolite grade and (iii) a Neoproterozoic calc-alkaline granitoids belt.

The study area is located in the east border of the RPC including west part of DFB (Table 1).

## 2. DATA SOURCES, SAMPLING, ANALYTICAL METHODS AND DATA PROCESSING

The study area included 6755 samples of soils and sediments in about 6,000 km² (Fig. 1) collected in the period 1979-1984. The average sampling density was of 1.1 samples/km$^2$. Four kinds of geological materials were collected: 1276 alluvial soils, 42 autochthonous soils, 5378 overbank sediments and 59 stream bed sediments, but only overbank sediments were considered in this study as explained in the next sections.

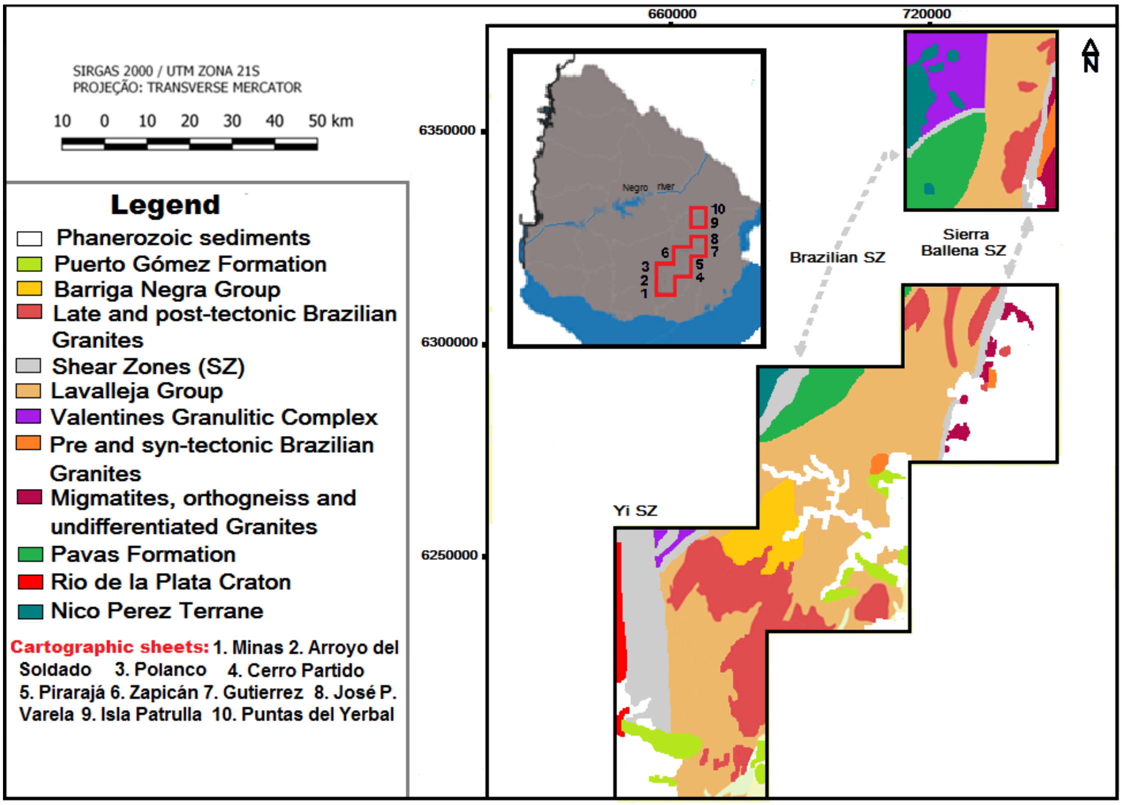


**Figure 1**

Geology of the study area based on DINAMIGE (1985) and Preciozzi *et al.* (1985) with contributions of Midot (1984), Hartmann *et al*. (2001), Oyhantçabal *et al.* (2011) and Masquelin *et al*. (2017).

**Table 1** - Description of the geological domains in the study area based on Geological map of Uruguay (DINAMIGE, 1985; PRECIOZZI *et al.*, 1985) with contributions of Midot (1984), Hartmann *et al.* (2001), Oyhantçabal *et al.* (2011) and Masquelin *et al.* (2017).

| Code | Geologic Domain | P/E | Description |
|---|---|---|---|
| HOS | Holocene Sediments | Ho | Lime-clayey sediments |
| DOL | Dolores Formation | Ple | Lodolites and fine sandstones |
| LIB | Libertad Formation | Ple | Mud-rocks without bedding, bronw-gray to green |
| PUE | Paso del Puerto Formation | Pli | Fine to conglomeradic sandstones |
| PGO | Puerto Gomez Formation | Ju | Tholeiitic basalts and andesites |
| BNG | Barriga Negra Group | C-N | A discordant ruditic-pelitic-volcanic assemblage. |
| LAG | Post-late-tectonic Brazilian | Neo | Biotite-anphibolic granites, sometimes two micas, leucoigranites |
| BRZ | Brazilian shear zones | Neo | Various cataclasites and migmatites |
| YIZ | Sarandi del Yi Shear Zone | Neo | Milonites and granites |
| SBZ | Sierra Ballena Shear Zone | Neo | Various milonites |
| GLA | Lavalleja Group | Neo | Schist Belt composed by deformed volcanic rocks and sedimentary rocks. |
| VAL | Valentines-Rivera Granulitic Complex | Meso | Gneisses, amphiboltes, quarzites, proxenites, migmatites and granites. |
| SYG | Pre-syn-tectonic Brazilian | Pal | Calc-alcaline granites and granodiorites. |
| MOG | Granite-gneiss Complex | Pal | Migmatites, Orthognaiss and Undifferentiated Granites |
| PAV | Pavas Block | Pal | Amphibolite-facies metamorphic rocks made up of mafic orthogneisses with bulk tonalite–trondhjemite–granodiorite protolith composition. |
| RPC | Rio de la Plata Craton | A-P | Acid and basic orthogneiss and granitoids. |
| NPT | Ninco Perez Terrane | A-P | Alkali-calcic, hornblend - biotite, basic and oriented granites and metagranites, medium to coarse or porfiritic texture. |

P/E= Period/Epoch; Ho= Holocene; Ple= Pleistocene; Pli= Pliocene; Ju= Jurassic; C-N= Cambriam-Neoproterozoic; Neo= Neoproterozoic; Meso= Mesoproterozoic; Pal= Paleoproterozoic; A-P = Archean – Paleoproterozoic.

The samples were dried in room heated to 45 °C, manually disaggregated in agate mortar and sieved to 80 mesh. Then, they were analyzed by emission atomic spectrometry by direct current plasma (VALENTE; SCHRENK, 1970) for the following 22 elements: Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, P, Pb, Sb, Sn, V, W, Y and Zn. Digestion was conducted in two stages, *i.e.*, attack with $HClO_4$ at 140°C at first and insertion of hot HCl-HF at 80°C in the sequence.

Samples related to Arroyo del Soldado, Cerro Partido, Minas and Polanco (Fig. 1), 1:50,000 sheets of National Cartographic Program, Uruguay, were analyzed in BRGM (France) during training stage (1979 – 1983). The other cartographic sheets were analyzed by DINAMIGE (Uruguay) with similar instruments and methods. Treinta y Tres cartographic sheet, between sheets 8 and 9 (Fig. 1), were not included due to partial absence of data. Geochemical data were sent to the author as part of an informal technical cooperation.

Filippini-Alba (1998) classified data analytical precision of Uruguayan data according to two groups, by means of variance analysis with analytical replicates and sampling replicates: (1) Ag, As, B, Be, Cd, Mo, Nb, Sb, Sn and W; (2) Ba, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Y and Zn. The elements of Group (1) had several samples with contents lesser than the respective detection level and analytical error greater than 15%. The elements of Group (2) had adequate variance and analytical error lesser than 10%. Sampling error was high for some elements of both groups probably due to cross-sampling towards the stream.

Elements of group 2 and Gamma radiometry (Rɣ) were selected for statistical data processing and GIS modelling. Data processing involved univariate statistics, histograms, dispersion graphics, analysis of variance (ANOVA) and cluster analysis with SPSS®. Join procedure and map calculator were applied in the GIS ArcGIS®.

## 3. RESULTS

### 3.1. PRE-TREATMENT OF DATA

Data were normalized by the respective mean of each group defined by the sampling material for variance homogeneity. However, in all cases, inclusive when only the alluvial soils and the overbank sediments were considered, ANOVA was significant. Therefore, only the overbank sediments were considered for further treatment of data. The sum of values of the twelve elements of group 2 and Gamma radiometry (Rɣ) transformed in percentage of the each mean, named SU#, was used for classifying the geochemical samples as background values and "anomalies" by means of threshold 1540, a value very near the 80% percentile. Histograms of SU# pre and post-cutting are presented as Fig. 2. The post-histogram showed reduced variance and deformation, but distribution was truncated due to the cutting process.

Therefore, two data files were elaborated, the "background file" (4296 samples) and the "outliers file" (1082 samples). The "background file" was overlaid on the digital geologic map (DINAMIGE, 1985) and the attribute tables of each layer were joined at ArcGIS®. Hence, the geological codes were assigned to each sample of the "background file". Geological units with less than 30 samples and undefined cases were discarded, deriving in a final "background file" with 4250 samples. The "outliers file" was processed based on K-means cluster analysis (SPSS®).

### 3.2 UNIVARIATE STATISTICAL METHODS AND CORRELATIONS

The statistics of the total samples of overbank sediments show the occurrence of anomalous values (extreme maximums), fact confirmed by the medians lesser than the means in most cases, high values of standard deviation when compared to the mean and by the skewness and kurtosis values, deriving on deformed distribution frequencies if compared to the Gaussian distribution (Table 2).

Histograms of the variables were classified in three groups: (1) Ni-type; (2) ɣ-Radiometry type and, (3) Zn-type (Fig. 3). The Ni-type histogram represents a much-distorted distribution of frequencies, especially for low values, due to the influence of de detection limits. Cr and Pb showed the same behavior. The ɣ-Radiometry type histogram is deformed, especially in the central part, with alternation of classes of low and high frequency. Co imitates this behavior. The use of logarithmic scale did not resolve deformation for neither type (1), nor type (2) histograms. The Zn-type histogram showed an almost log-normal behavior along with Ba, Cu, Fe, Mn, P, V and Y.

A positive correlation Cr-Ni generally occurs for stream sediments geochemistry from Uruguay (FILIPPINI-ALBA *et al.*, 2001), as the respective dispersion diagram showed (Fig. 4). Outliers appear in all diagrams with univariate characteristics. The trend to several subpopulations was highlighted for Ba-P, Ba-Pb, Fe-Mn and V-Cu.

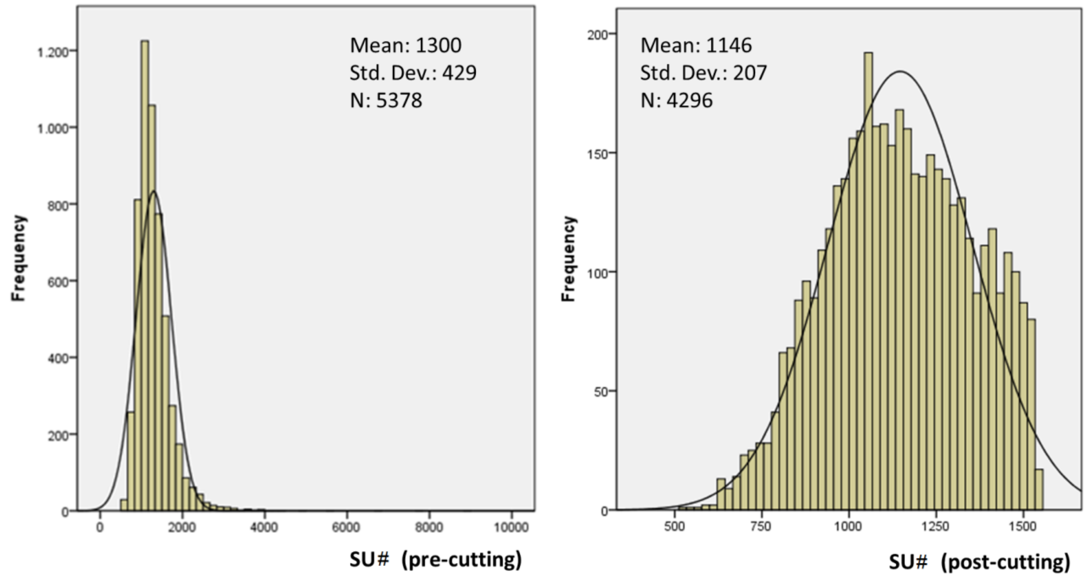


**Figure 2**
SU# histograms before and afterwards cutting process.

**Table 2** - Basic statistics for overbank sediments samples included in this study.

| Variable | N | Minimum | Maximum | Mean | Median | SD | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|
| Fe, % | 5378 | 1 | 17 | 4 | 3,5 | 2 | 1,3 | 3 |
| Mn, ppm | 5378 | 74 | 15610 | 1035 | 817 | 792 | 6 | 72 |
| Ba, ppm | 5378 | 139 | 5240 | 598 | 538 | 235 | 3 | 34 |
| Co, ppm | 5378 | 5 | 953 | 16 | 12 | 15 | 49 | 3095 |
| Cr, ppm | 5378 | 10 | 1980 | 52 | 32 | 64 | 11 | 225 |
| Cu, ppm | 5378 | 10 | 532 | 23 | 19 | 15 | 11 | 298 |
| Ni, ppm | 5378 | 10 | 940 | 27 | 16 | 31 | 10 | 197 |
| P, ppm | 5378 | 65 | 4014 | 346 | 280 | 211 | 5 | 46 |
| Pb, ppm | 5378 | 10 | 331 | 19 | 16 | 10 | 8 | 169 |
| V, ppm | 5378 | 10 | 413 | 68 | 59 | 27 | 3 | 22 |
| Y, ppm | 5378 | 5 | 155 | 27 | 21 | 15 | 3 | 13 |
| Zn, ppm | 5378 | 10 | 359 | 68 | 58 | 25 | 2 | 7 |
| pH | 4068 | 5.0 | 8.5 | 6.4 | 6.5 | 0.6 | 0.2 | 0.1 |
| Rɣ, cps | 5378 | 30 | 400 | 88 | 80 | 29 | 2 | 11 |

## 3.3 GEOLOGICAL DOMAINS SIGNATURES

Geochemical variance was affected by the geological domains (lithology in Fig. 5). The variable SU# was used as outlier discriminator, which explains the low presence of outliers (circles and asterisks) in the respective diagram. The individual variables showed a more complex behavior with occurrence of more quantity of outliers.

The Kruskal–Wallis non-parametric statistical test was used as evidence of the significance of the influence of lithology. Anyway, the test is only valid for extreme groups (Table 3).

**Table 3** - Results of Kruskal-Wallis non-parametric test, 16 degrees of freedom, significance of 0,01% in all cases (Statistic).

| Variable | Statistic | Extreme mean ranks | |
|---|---|---|---|
| Ba | 401 | 1186 (RPC) | 3046 (NPT), 3280 (BRZ) |
| Co | 334 | 1224 (PUE) | 2738 (RPC), 2870 (YIZ) |
| Cr | 832 | 340 (PUE) | 3748 (PAV) |
| Cu | 641 | 725 (PUE) | 850 (SIG), 853 (MOG) |
| Fe | 460 | 338 (PUE), 525 (DOL) | 2731 (PAV), 2743 (VAL) |
| Mn | 138 | 1671 (LAG) | 2457 (MOG) |
| Ni | 797 | 620 (PUE) | 3626 (PAV) |
| P | 331 | 716 (PUE) | 2647 (BRZ), 2916 (NPT) |
| Pb | 757 | 1018 (PAV), 1299 (DOL) | 2948 (YIZ), 2982 (LAG) |
| Rγ | 494 | 1111 (RPC) | 2877 (LAG), 3103 (NPT) |
| V | 488 | 994 (PUE) | 3006 (PAV) |
| Y | 651 | 671 (PUE), 676 (DOL) | 2836 (PAV), 2877 (BRZ) |
| Zn | 285 | 688 (DOL) | 2640 (NPT), 2661 (PAV) |
| SU# | 485 | 351 (PUE) | 2701 (BRZ), 2825 (NPT) |

Therefore, as a verification of the test results, the means of the groups related to each geological domain were organized by increasing values of the sum of the variables transformed as percentage of the means (SU#). The minimum values, intermediate-high values and maximum values were indicated as gray colored, underlined and bold numbers respectively (Table 4). Dolores Formation (DOL), Libertad Formation (LIB) and Paso del Puerto Formation (PUE), all of them of sedimentary origin, showed low means for several variables. The Holocenic sediments were classified together; however, its SU# variable was something larger with intermediate values of Mn (Table 3). The Granite-Gneis Complex (MOG) and the Sierra Ballena shear zone (SBZ) showed Mn-enrichment and intermediate Ba. The latter repeated for the Pre-Syn-tectonic Brazilian Granites (SYG), with impoverishment of Co and Ni for MOG and SYG. Puerto Gomez Formation (PGO), Barriga Negra Group (BNG) and Lavalleja Group (GLA) are at least slightly enriched in Cu, and the Sarandi del Yi shear zone (YIZ) and the Post-Late-tectonic Brazilian Granites (LAG) are Pb-enriched, which would be able to explain the Cu-Pb mineral occurrences hosted. In that sense, the signature Cr+Fe+V+(Ni) appears suitable for The Valentines Rivera Granulitic Complex (VAL) that hosts an Fe-deposit. The Brazilian shear zone (BRZ) has a differentiated geochemical pattern in relation to the nearby rocks, the Nico Perez Terrain (NPT) and the Pavas Formation (PAV).

The previous facts were summarized based on the geological map defining nine different geochemical signatures (Fig. 6). Some geological units were joined by proximity and geological origin, as DOL, LIB, PUE and HOS; MOG, SBZ and SYG or BNG, PGO, RPC and GLA.

## 3.4. ANOMALOUS SIGNATURES

Cluster analysis was developed on non-transformed data considering the “outliers file”. Twelve groups were recommended but only seven were consistent. Therefore, five groups showed extremes values for some element including only six samples. ANOVA test was significant for all the variables. The maximun values and intermediate values were indicated by comparison for each variable (Table 5).

Each anomalous group showed specific characteristic, based on signature, content of the associated elements and spatial relation to geological units (Table 6). The spatial relation was never uniform, therefore, the anomalous groups appeared related to same geological units depending on its geographical location. Phosphates, Mn-nodules and sulphides (Pb and Zn) were interpreted based on the high contents of P, Mn and base metals respectively. A3 signature appears associated to LAG signature (Fig. 6). A4 and A11 signatures suggest secondarily a primary value related to mafic-ultramafic rocks respectively. PAV signature (Fig. 6) confirms the last proposition.

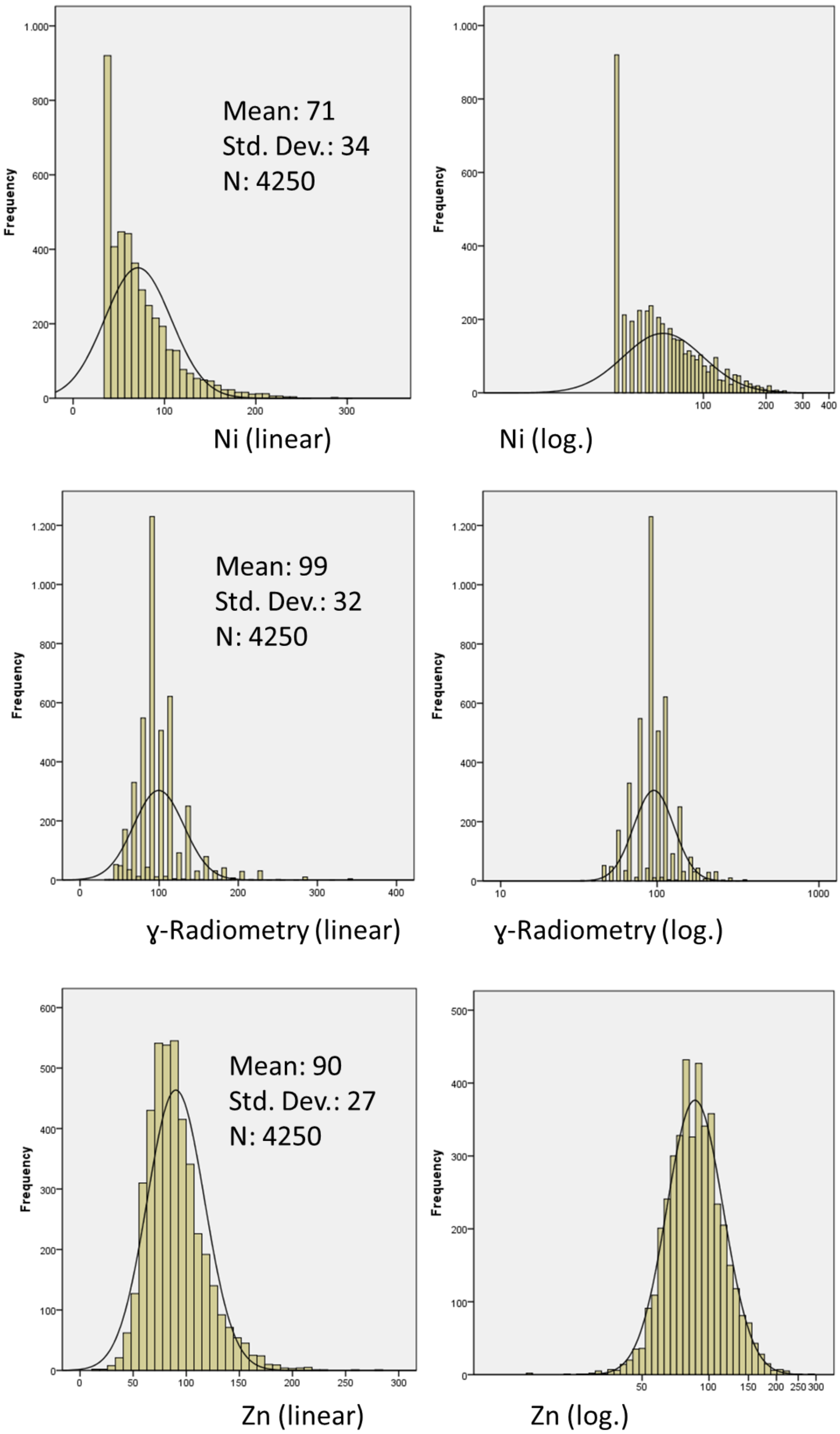


**Figure 3**

Histograms of Ni, ɣ-Radiometry and Zn in linear and log-scale models. Data were expressed as percentages of means.

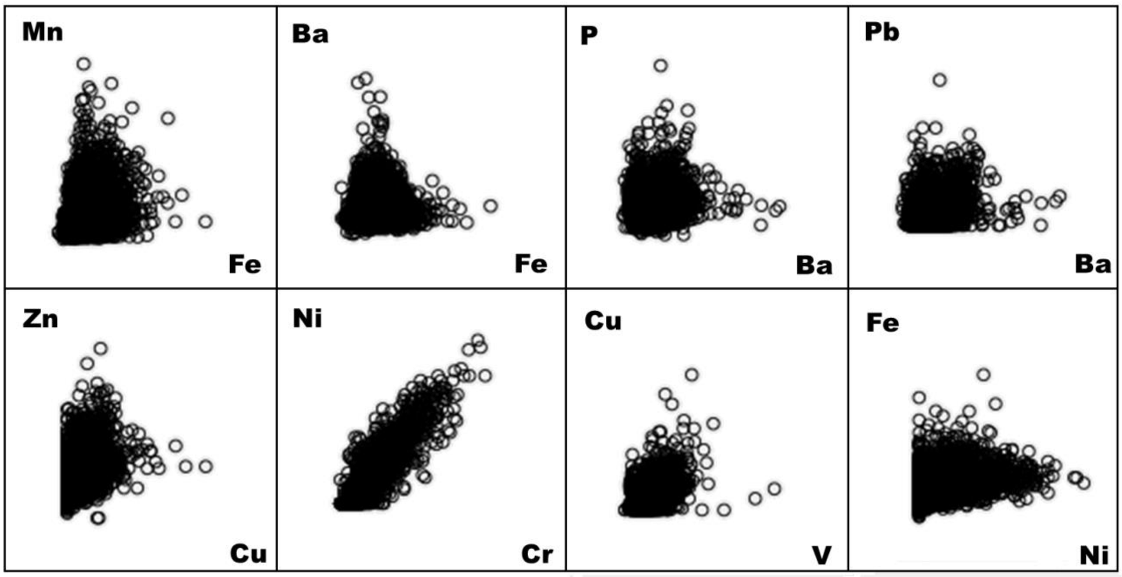


**Figure 4**
Dispersion diagrams for data transformed as percentage of the means.

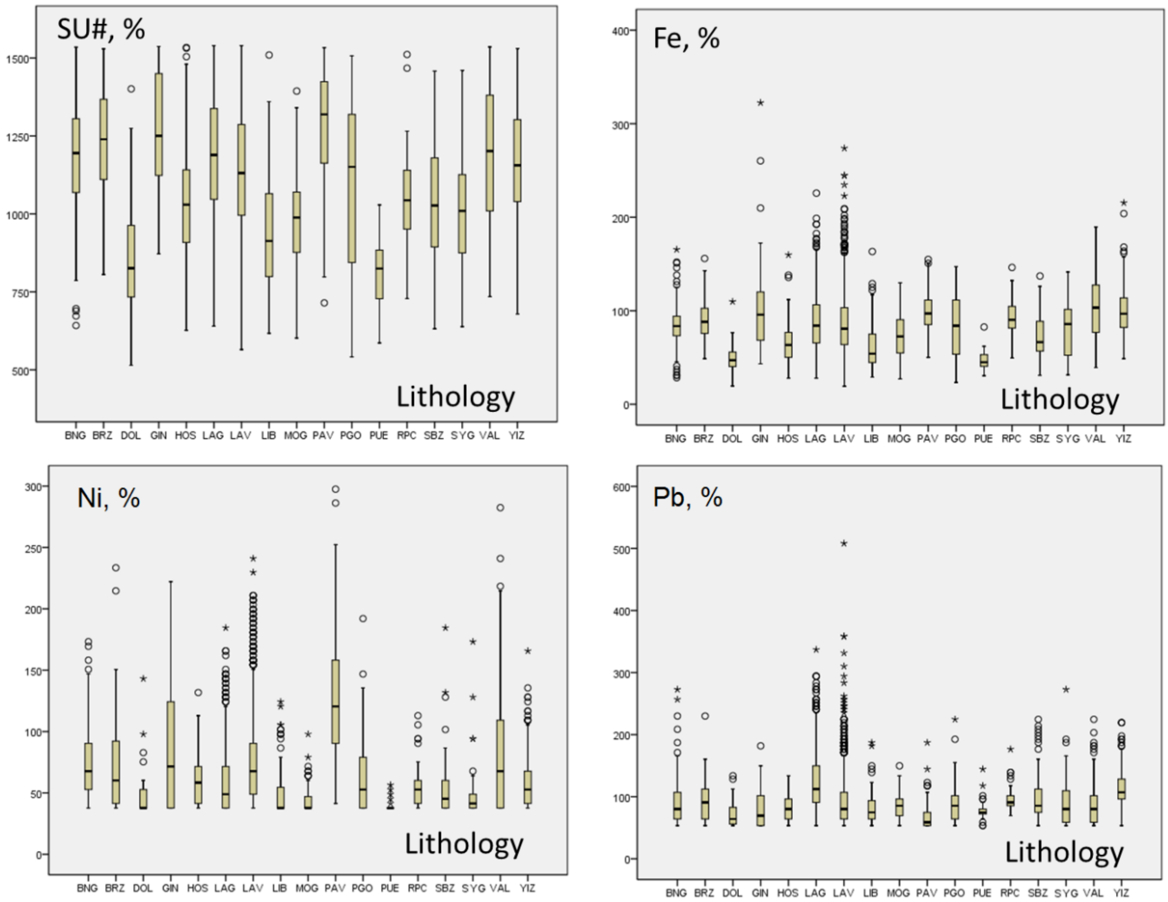


**Figure 5**
Box-plots for selected variables, samples related to geological units as % of means.

**Table 4 -** The averages of the contents of chemical elements and Rγ for the samples related to each geological domain. LC = lithological code; NNN = number of samples. High values, intermediate values and low values related to mean were identified as bold, underlined and gray respectively.

| LC/NNN | Rγ | Fe | Ba | P | Cu | Cr | Zn | Pb | Ni | V | Mn | Co | Y | SU# |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PUE/31 | 65 | 2,0 | 497 | 192 | 13 | 16 | 46 | 15 | 10 | 47 | 918 | 10 | 16 | 815 |
| DOL/35 | 73 | 2,1 | 481 | 216 | 16 | 23 | 43 | 14 | 13 | 55 | 915 | 11 | 16 | 873 |
| LIB/103 | 78 | 2,6 | 509 | 234 | 17 | 25 | 49 | 15 | 14 | 52 | 955 | 13 | 17 | 945 |
| MOG/80 | 79 | 3,1 | 649 | 237 | 14 | 22 | 53 | 16 | 12 | 60 | **1039** | 11 | 22 | 994 |
| SYG/63 | 73 | 3,4 | 676 | 243 | 14 | 27 | 52 | 17 | 13 | 58 | 941 | 10 | 26 | 1015 |
| SBZ/86 | 77 | 3,0 | 670 | 250 | 16 | 28 | 56 | 18 | 14 | 56 | **1059** | 12 | 21 | 1039 |
| RPC/45 | 70 | 3,9 | 450 | 258 | **22** | 31 | 55 | 18 | 15 | 61 | 841 | **16** | 19 | 1051 |
| HOS/46 | 83 | 2,9 | 551 | 277 | 20 | 32 | 53 | 16 | 17 | 60 | 979 | 13 | 22 | 1055 |
| PGO/54 | 85 | 3,5 | 605 | 291 | **23** | 31 | 57 | 17 | 17 | 53 | 911 | 15 | 22 | 1106 |
| GLA/2040 | 84 | 3,6 | 551 | 307 | 21 | 38 | 61 | 17 | 20 | 64 | 966 | 13 | 22 | 1138 |
| YIZ/380 | 79 | **4,1** | 646 | 330 | **22** | 33 | 62 | **21** | 15 | 58 | 836 | **16** | 23 | 1167 |
| BNG/170 | 87 | 3,5 | 659 | 312 | **24** | 36 | 64 | 17 | 20 | 62 | 884 | 15 | 24 | 1175 |
| LAG/621 | 111 | 3,7 | 617 | 342 | 17 | 30 | 63 | **23** | 16 | 52 | 726 | 13 | **34** | 1186 |
| VAL/155 | 91 | **4,3** | 639 | 306 | 18 | **55** | 62 | 16 | 23 | **65** | 821 | 12 | 25 | 1195 |
| BRZ/91 | 94 | 3,8 | **812** | **357** | 20 | 40 | **70** | 17 | 19 | **66** | 864 | 13 | 29 | 1239 |
| NPT/53 | 107 | **4,3** | **727** | **375** | 17 | 48 | **67** | 16 | 23 | **65** | 830 | 11 | **34** | 1265 |
| PAV/197 | 79 | **4,1** | 563 | 315 | 21 | **74** | **68** | 12 | **35** | **74** | 885 | 13 | **29** | 1290 |
| Mean | 83 | 3,4 | 606 | 285 | 19 | 35 | 58 | 17 | 17 | 59 | 904 | 13 | 23 | 1091 |
| Unit | c/s | % | | | | | ppm | | | | | | | %mean |

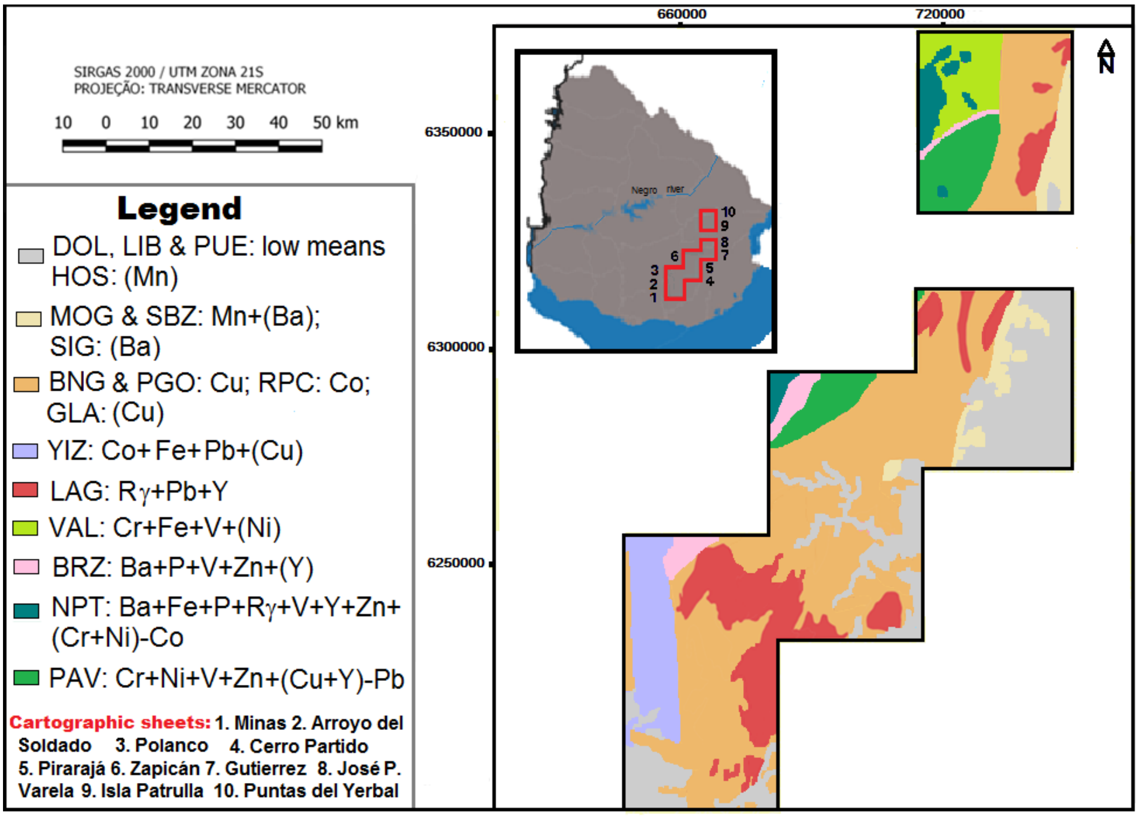


**Figure 6**

Geochemical signatures related to the geological domains. Positive signs, parentheses and negative signs indicate enrichment, potential enrichment and impoverishment respectively.

**Table 5 -** Geochemical signatures of the anomalous groups (A3, A4, A5, A8, A9 and A11) determined by cluster analysis. NNN = number of samples.

| Variable | A3 | A4 | A5 | A6 | A8 | A9 | A11 |
|---|---|---|---|---|---|---|---|
| Ba, ppm | 715 | 554 | 351 | **906** | 314 | **847** | 484 |
| Co, ppm | 22 | 21 | **38** | 22 | 22 | 31 | 29 |
| Cr, ppm | 54 | 133 | **531** | 60 | 66 | 47 | 260 |
| Cu, ppm | 32 | 31 | 47 | 24 | **109** | 28 | 37 |
| Fe,% | 6.1 | 5.9 | **8.2** | 5.7 | **9.1** | 5.9 | 6.7 |
| Mn, ppm | 1414 | 1168 | 1369 | 1293 | 1221 | **5659** | 1308 |
| Ni, ppm | 29 | 66 | **258** | 34 | 34 | 34 | 130 |
| P, ppm | 503 | 375 | 307 | **1692** | 391 | 407 | 311 |
| Pb, ppm | **28** | 16 | 12 | 16 | 13 | **29** | 14 |
| Rγ, c/s | **102** | 80 | 71 | 79 | 73 | 87 | 78 |
| V, ppm | 81 | 93 | 133 | 92 | **204** | 77 | 109 |
| Y, ppm | **41** | 32 | 23 | **38** | 34 | 28 | 27 |
| Zn, ppm | **97** | 87 | **96** | 91 | 91 | **96** | **96** |
| NNN | 473 | 321 | 22 | 54 | 46 | 60 | 100 |

Note: Maximum values in bold, intermediate values underlined.

**Table 6** - Anomalous groups features. Parentheses indicate secondary values. Fe-oxi: adsorption on Fe-oxides.

| Group | NNN | Enrichment | Spatial relation (GIS) | Probable genesis |
|---|---|---|---|---|
| A3 | 473 | Pb+Rγ+Y+Zn+(P)+(Mn) | GLA, PAV & some granites | Granites, Sulphides |
| A4 | 321 | (Cr+Ni) | PAV & mafics | Mafic |
| A5 | 22 | Co+Cr+Fe+Ni+Zn+(Cu+V) | Ultramafic (North) & lithological | Ultramaphic |
| A6 | 54 | Ba+P+Y | PAV (Zapican sheet) & specific | Phosphates |
| A8 | 46 | Cu+Fe+V+(Y) | GLA (Isla Patrulla sheet) | Fe-oxi, volcanic |
| A9 | 60 | Mn+Ba+Pb+(Co) | GLA & dispersed | Mn-nodules |
| A11 | 100 | Zn+(Co+Cr+Fe+Ni+V) | A4 & A5 related | Fe-oxi, Sulphides? |

Filippini-Alba *et al.* (2001) showed Cu enrichment of Lavalleja Group in the sheets Gutierrez, José P. Varela, Pirarajá and Zapican (Fig. 1) using Cu-residuals from a regression model using factors (principal components). Low contrast of DOL, LIB and PUE could be associated to the impoverishment in Fe deriving in low adsorption on oxides, superficial environmental phenomena (FINK *et al*., 2016; ROQUIN; ZEEGERS, 1987); fact confirmed by high Fe values in anomalous groups with means greater or equal than 5.7% (Table 5). Gasparatos (2012) described occurrence of Fe-Mn concretions and nodules in soils with Ba and Pb in some instances, what could explain the Ba+Mn+Pb+(Co) signature (A9). Mn nodules were mentioned in inedited reports of the geochemical exploration program in Uruguay related to imprecision of chemical analysis (nugget effect), introducing errors in the sieving stage.

According to Govett (1983) and Govett and Atherden (1988), massive volcanic-sedimentary sulphide deposits generally represent positive regional anomalies of Fe, Mg, and Zn, sometimes Mn, with local variations and a probable Na-Ca depleted zone associated, with dimensions ranging from a few hundred to more than 1,000 meters. Smaller positive anomalies are associated with trace elements in the ore (Cu, Pb, Zn, etc.). There is little knowledge about enrichment in Co, $H_2O$ and Rb and depletion in Ni and Sr on a local scale. Some of these propositions partially agree to A3 with Ni impoverishment and Pb-Zn-(Mn) enrichment and A11 signatures with Zn enrichment and Fe high if compared with geological units means.

Roquin and Zeegers (1987) considered stream sediment geochemistry and the influence of 30 lithological units selected in basement areas from France. Two main differentiation factors were commonly identified: (1) a dilution effect of trace elements by a barren siliceous phase related to various environmental parameters such as the nature of the substratum and overburden, or the type of material sample; (2) a coprecipitation effect of Zn, Ni, Co, Cu and P with Fe-Mn hydroxides, marked by a frequent association between these elements and, in Brittany, by their enrichment in stream sediments compared to the soils.

Filippini-Alba and Oliveira (2001) indicated two kinds of anomalies; some related to Fe-minerals and, the others to Mn-minerals in the Lavalleja Group (GLA), Isla Patrulla sheet. The occurrence of volcanic rocks, metamorphic rocks and dolomitic-calcareous is common in this area. The volcanic rocks associated to GLA showed a Cu+V signature in several geochemical inedited reports mentioned at the beginning.

## 4. CONCLUSION

A set of 5378 overbank sediment samples from Precambrian terrains of Uruguay, collected in the 80's, were mainly considered in this study. Data were classified as background (4296 samples) or anomalies (1082 samples) by the sum of 13 variables transformed as percentage of the means. The background data were associated to the geological units by GIS, therefore, nine "homogeneous" signatures were defined. Three of them included several geological units with low to moderate contrasts and specific characteristics values of Ba, Co, Cu and Mn. The other six geochemical signatures were associated to a specific lithology of igneous and metamorphic rocks. The Fe content could be related to trace enrichment as the process mentioned by Roquin and Zeegers (1987), due to depletion in low-contrast geological units, especially DOL, LIB and PUE, and enrichment in geological units related to igneous and metamorphic rocks (NPT, PAV, VAL and YIZ).

Cluster analysis of the anomaly data file allowed defining seven anomaly groups and six extreme samples (outliers). Four anomaly groups (A3, A4, A5 and A8) were associated to specific lithology, specially LAG, GLA and PAV. Anyway, A4 could be related to sulphide deposits too, along with A11. The remaining groups, A6 and A9 could be related to superficial phosphates and occurrence of Mn-nodules respectively. A mineralogical study could help to resolve this question.

This study represents a first approach that should be continued by analyzing each characterized group in a detailed way, as well as including the total number of samples currently available.

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