

1 THE USE OF A COMBINED PORTABLE X RAY FLUORESCENCE AND  
2 MULTIVARIATE STATISTICAL METHODS TO ASSESS A VALIDATED  
3 MACROSCOPIC ROCK SAMPLES CLASSIFICATION IN AN ORE  
4 EXPLORATION SURVEY.  
5

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25 Pattern Recognition Techniques, Ore Exploration, Cu-(Ag) Deposits.  
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1 **Abstract**

2

3 The combination of “ex-situ” portable X Ray Fluorescence with unsupervised and  
4 supervised pattern recognition techniques such as hierarchical cluster analysis, principal  
5 components analysis, factor analysis and linear discriminant analysis have been applied  
6 to rock samples, in order to validate a “in situ” macroscopic rock samples classification  
7 of samples collected in the Boris Angelo mining area (Central Chile), during a drill-hole  
8 survey carried out to evaluate the economic potential of this Cu deposit. The analysed  
9 elements were Ca, Cu, Fe, K, Mn, Pb, Rb, Sr, Ti and Zn. The statistical treatment of the  
10 geological data has been arisen from the application of the Box-Cox transformation  
11 used to transform the data set in normal form to minimize the non-normal distribution  
12 of the data. From the statistical results obtained it can be concluded that the  
13 macroscopic classification applied to the transformed data permits at least, to  
14 distinguish quite well in relation to two of the rock classes defined (70.5 % correctly  
15 classified ( $p < 0.05$ )) as well as for four of the five alteration types defined “in situ”  
16 (75% of the total samples).

17

1 **1. Introduction**

2  
3 The extraction of metals from the earth crust initially requires the identification  
4 of the areas in which they have anomalous concentration in relation to the host rock of  
5 the ore mineralization and, in general sense, to the background in the mining zone. In  
6 this sense, the geological characterization of the potential host rocks of ore  
7 mineralization is crucial and must be the preliminary objective in any exploration  
8 survey.

9  
10 In relation with this fact, two fundamental stages must be covered, the  
11 establishment of the geological cartography and the drill-hole survey. The former  
12 because permits the knowledge of the main geological features (lithologies, structures,  
13 mineralization evidences, etc.) and the later because gives an invaluable set of data over  
14 the geology under the surface. From the study of the information obtained in these  
15 stages it is possible to get a three dimensional idea about the existing rocks and their  
16 characteristics. Thus recognition and classification of the different rock types, as well as  
17 its alteration pattern, play an important role which could be critic in the selection of the  
18 areas that could be adequate to explore host ore bodies with economic interest.

19  
20 During the initial field campaign necessary in order to obtain the data, a lot of  
21 samples are generates. In this sense, they must be classified attending criteria closely  
22 related to the type of deposits to be exploited, e.g. type of lithologies, hydrothermal  
23 alteration patterns among others. In the most of the cases these criteria are applied “in  
24 situ” in remote areas without confirmatory analytical information from a laboratory,  
25 and, in the best of the cases, using basic equipment like a magnifying glass or some safe  
26 and easily portable chemical reagent. In this way, it could be helpfully to dispose of  
27 qualimetric tools that could validate this macroscopic rock samples classification in  
28 order to facilitate and accelerated the remained work necessary to determine the  
29 goodness of the ulterior mining exploration of the zone investigated.

30  
31 Bearing in mind these reasons, the use of analytical techniques as portable X-ray  
32 fluorescence (P-XRF) combined with statistical pattern recognition techniques can be  
33 offered as an adequate tool in order to obtain a feasible model that could permits the

1 assessment of a validated macroscopic rocks samples classification in an ore exploration  
2 survey.

3  
4 Up to the present day, the use of field portable X-ray fluorescence (P-XRF)  
5 analysers [1-5] has been demonstrated be adequate in order to solve questions related  
6 with a great variety of deals, e.g. for the assessment of the composition of painting  
7 materials in order to offer information about their conservation and/or restoration  
8 procedures [6,7], for archaeological studies [8,9], for the screening and assessment  
9 studies about metalloids and/or heavy metals in contaminated or potentially  
10 contaminated areas [3,4,10-14], FDA regulated products [15], or metal contents in  
11 waters [16], among others. On the other hand, the relatively low cost of these devices  
12 permits the possibility of their use in lab for routine analysis in quality control  
13 assessments.

14  
15 In parallel, it has been demonstrated that the use of unsupervised and supervised  
16 pattern recognition techniques permits to extract reliable information from analytical  
17 parameters for exploratory assessment of geological sets [17-19], mainly due to they  
18 allow (a) to verify associations among variables, (b) to group or to cluster samples with  
19 respect to comparable chemical or geological descriptors, and (c) to search multivariate  
20 data classification on the basis of known class membership of those objects.

21  
22 Nowadays, copper is one of the most demanded materials on the metal market  
23 showing a growing demand perspective at the present such as the future. Together with  
24 this growing demand, the exploration of this metal has been widespread for the entire  
25 world to satisfy the copper supply. In this context, Chile is the first copper-producing  
26 country holding a 36% of the world production of this metal.

27  
28 Boris Angelo Cu-(Ag) deposit is located in the “stratabound Cu-(Ag) belt” [20]  
29 in the Costal Cordillera, Central Chile. It corresponds to practically unknown deposit in  
30 this belt, thus the study carried out in the area can be considered as a typical case study  
31 of an exploration survey of a copper deposit. In this paper, a normalized data matrix  
32 obtained from P-XRF measurements of rocks samples from a “preliminary ore  
33 exploratory survey” has been subjected to different pattern recognition techniques in

1 order to confirm the rock classification parameters of samples taken during the drill-  
2 hole survey made in the Boris Angelo area.

## 3 4 **2. Material and Methods**

### 5 6 *2.1. Studied area and macroscopic classification defined*

7  
8 The Boris Angelo Cu-(Ag) deposit is located in the easternmost Coastal  
9 Cordillera, in Central Chile, between 32°30' S and 70°40' W (Fig. 1). It is part of the  
10 Cretaceous stratabound Cu-(Ag) deposits belt, which are also known as “Chilean  
11 Manto-type” Cu-(Ag) deposits. The geology of the deposit area is characterized by  
12 volcanoclastics sequences intruded by different small subvolcanic bodies. Table I shows  
13 the four different lithologies recognized in the zone and its most representative  
14 characteristics. As well as, the Table 1 included the coded values assigned to them in  
15 the macroscopic classification made “in situ”.

### 16 17 **FIGURE 1**

### 18 19 **TABLE 1**

20  
21 From the point of view of the alteration patterns, the area of the metallic deposit  
22 is affected by hydrothermal alteration, caused by the interaction between hot and  
23 slightly acidic fluids and the host rocks [21]. These fluids can leach metals (with  
24 economic interest) and re-concentrate them. As mentioned above, the recognition and  
25 cartography of alteration patters in the rocks is a useful tool used by exploration  
26 geologist as evidence to localize enriched-metals areas with economic potential. The  
27 most common classification method, and the simplest visual method too, is that which  
28 defined the type of alteration as a function of the most abundant or most obvious  
29 mineral in the altered rock. Table I shows the five different hydrothermal alterations  
30 recognized in the zone, on the basis of the occurrence of certain “key minerals” or “key  
31 mineral assemblages” product of the hydrothermal alteration, and its most  
32 representative characteristics. In order to facilitate the analysis of the data, a second  
33 numerical code has been assigned to the alteration types used in the study. These codes  
34 have also been included in Table 1.

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## 2.2. Sampling preparation and measurement

During the field campaign 44 rocks samples, corresponding to ore grade zones and barren zones, were taken from five different drill-hole cores selected (see Figure 1). The samples were coded and placed into sealed plastic bags in order to their preservation and transportation to the “Minera Las Cenizas S.A.” mining facilities where they were powdered (until  $< 100$  microns particle size) and homogenised using standard procedures before their transportation to the laboratory.

The monitored parameters were the concentration of Ca, Cu, Fe, K, Mn, Pb, Rb, Sr, Ti and Zn. The measurements were made in the laboratory to select the better measure conditions; the equipment used in this study was a field portable X-ray fluorescence analyser NITON XLt 792 (Niton, Billerica, USA), with a 40 kV X-ray tube with Ag anode target excitation source and a Silicon PIN-diode with a Peltier cooled detector. As part of the standard set-up routine, variables as type of holder (zip sealed plastic bag or polyethylene sample cups with Mylar X-Ray Fil (TF-160-255; Gauge 0.00024”-6  $\mu\text{m}$ , 2.5' diameter) obtained from the supplier, source count time (60, 90 and 120 s) and matrix effects among others were tested.

In relation to the holder to be used in the procedure, the influence of the type of material used was studied analysing a set of 15 holders for each type of containers without sample. No statistical differences ( $P = 0.95$ ) were found between the holders supplied by NITON and the plastic bags used in the exploratory survey to storage the samples. In all the cases, the content of the elements were lower than those expected in the samples, not being necessary to used the average element content to correct the measurements. For ulterior analysis the zip sealed plastic bags were chosen.

In relation with the influence of the source count time the best results were obtained using 90s. These variables were then kept fixed for the rest of measurements. On the other hand, no matrix effect was detected using the program algorithm included in the analyser software. The analyser was calibrated using the silver and tungsten shielding on the inside shutter. After data acquisition, the results were downloaded to a portable PC for further processing. The results obtained for the rocks samples analysed

1 (expressed as the arithmetic means of five replicates of each sample) are shown in Table  
2 2.

3 **TABLE 2**

4  
5 The RPD found for each measured element in the five replicated analysis of the  
6 samples has been:  $5,9 < \text{RPD}_{\text{Ca}} < 7,8$ ;  $6,9 < \text{RPD}_{\text{Cu}} < 9,9$ ;  $5,8 < \text{RPD}_{\text{Fe}} < 9,2$ ;  $7,1 <$   
7  $\text{RDP}_{\text{K}} < 9,5$ ;  $9,2 < \text{RPD}_{\text{Mn}} < 11,9$ ;  $12,6 < \text{RPD}_{\text{Pb}} < 15,2$ ;  $13,9 < \text{RPD}_{\text{Rb}} < 15,1$ ;  $7,8 <$   
8  $\text{RPD}_{\text{Sr}} < 9,9$ ;  $6,9 < \text{RPD}_{\text{Ti}} < 9,3$ ;  $13,1 < \text{RPD}_{\text{Ca}} < 15,0$ .

9  
10 The accuracy of the method for all the elements except Rb, was corroborated  
11 analysing nine replicates of two Certified Materials: CRM052-050 (RT Corporation,  
12 Salisbury, United Kingdom) and RTS-1 (Canadian Certified Reference Methods  
13 Project, CANMET, Ottawa, Canada). According to the US EPA Method 6200  
14 recommendations for soil samples [22], the accuracy was estimated by the relative  
15 percent difference (RPD) between the concentration in the reference material and the  
16 concentration measured (expressed as arithmetic mean of the nine replicates) by P-XRF,  
17 in all the cases results were in good agreement with the quality US EPA Method (RPD  
18  $< 10$  for Cu, Fe, Mn, Ti and Zn,  $10 < \text{RPD} < 25$  for the rest of the elements).

19  
20 The establishment of the accuracy in the determination of Rb was made by  
21 means of an “in house validation protocol”. Thus, three sets of spiked matrix matched  
22 samples (nine replicates) containing known Rb concentrations (one level for each set of  
23 spiked samples) were measured. The RPD estimated was 12, which is in good  
24 agreement with those obtained for the rest of the elements.

25  
26 The precision was estimated as intermediate precision by the relative percentage  
27 deviation percentage (RPD) of the nine measurements of each reference materials or  
28 spiked-matrix samples for Rb. In all the cases the obtained RPD values are lesser than  
29 15. In order to estimate the detection limits sets of nine replicate samples that contained  
30 the target elements at concentration levels close to the detection limit estimated by US  
31 EPA Method 6200 [22].

32  
33  
34 *2.3. Data treatment and statistical methods*

1  
2 Figure 2 shows the statistical procedure used to the data treatment. Initially, to  
3 check the fit of the data to a normal distribution, Kolmogorov-Smirnov, Shapiro-Wilks  
4 and skewness score normality tests were applied. In all the cases, statistical evidences at  
5 95% confidence interval showed that not all variables are normally distributed.

## 6 7 **FIGURE 2** 8

9 In order to transform the data set into normal form, Box-Cox transformation was  
10 used [17, 23-25]. To study the correlation structure between normalized variables the  
11 Spearman rank-order correlations (Spearman R coefficient) were used, due to the  
12 samples are less sensitive to outliers than the Pearson coefficients.

13  
14 In all the cases, the univariate and multivariate statistical treatment of the data  
15 was performed using: (a) Statgraphic Centurion XV (15.2.05 version) for Windows  
16 (Statpoint Technologies Inc, Warrenton, USA) and Matlab Version 7.0.4 R14 (The  
17 Mathworks, Inc.) and the PLS Toolbox Version 3.0.4 (eigenvector Research, Inc.).

### 18 19 20 *2.4. Unsupervised pattern recognition methods: Cluster Analysis (HCA), Principal* 21 *Component (PCA) and Factor Analysis (FA)* 22

23 Hierarchical agglomerative HCA was performed on the normalized data set by  
24 means of Manhattan (city-block) distance -a particular case of Minkowski distance  
25 (taxicab geometry)- as similarity measurement and Ward's method as amalgamation  
26 rule. These criterions have been selected with two objectives: (i) to find at each stage  
27 those two clusters whose merger gives the minimum increase in the total within group  
28 error sum of squares (Ward objective) and, (ii) to dampen the effect of outliers bearing  
29 in mind using city-block distance the average differences across dimensions are not  
30 squares. It was applied to the Box-Cox transformed monitoring matrix data set in order  
31 to observe the relationship between natural grouping observed and the two criteria of  
32 macroscopic classification made (lithologies and alteration patterns). On the other hand  
33 in order to verify the natural grouping obtained in HCA, a PCA was applied to the  
34 standardized normalized data set. Finally, to reduce the interdependence of the data set



1 of standardized normalized variables and to obtain knowledge of the underlying  
2 structure of the data, FA was applied. In this case the factorization type used was a  
3 principal component which supposes that all of the variability of the data corresponds  
4 exclusively to common factors. The orthogonal rotation of the axis defined by PCA, and  
5 obtained maximizing (Varimax rotation) produces new groups of variables called  
6 varifactors (VFs), which usually group the studied variables in accordance with  
7 common features which can include unobservable, hypothetical and/or latent variables  
8 [26].

### 10 2.5. Supervised pattern recognition methods: Linear Discriminant Analysis (LDA)

11  
12 This method has been applied in order to obtain a discriminant model that  
13 permits us validated the “in situ” macroscopic rock samples classification of the sample  
14 assuming the number of groups or classes, as well as, the group membership of each  
15 sample taken. Thus, by means of linear discriminant analysis, a discriminant function  
16 has been built up for each group on raw data. The classification functions associated to  
17 each group defined could be used to determine to which group each sample most likely  
18 belongs. In this study, LDA were performed on the Box-Cox transformed measured  
19 data.

## 21 3. Results and discussion

### 23 3.1. Macroscopic classification made on the basis of lithology criteria.

24  
25 The Dendogram resulting from HCA of normalized data set is represented in  
26 Figure 3. It can be seen that assuming a  $D_{\text{linkage}} = 0.8 D_{\text{maximum}}$ , the samples could be  
27 grouped in two different clusters: (i) Cluster I, constituted by 29.7% of the samples.  
28 According the rock codes, it contents samples of the four defined lithologies. From  
29 which, there are included 100% of the rocks samples defined like porphyritic dykes  
30 (rock code 11) and brecciated porphyritic sub-volcanic rocks (rock code 13). (ii) Cluster  
31 II, constituted by the 70.3% of the samples, it can be observed that it is characterized by  
32 the biggest city-block distance (high significant clustering). Belonging to this cluster it  
33 can be found 93.5% rocks samples defined as porphyritic sub-volcanic rocks (rock code  
34 12) and 40% of the samples defined as volcanoclastic rocks (rock code 14).

1  
2 **FIGURE 3**  
3

4 The PCA (made on the basis of eigenvalues  $> 1$  criterion) facilitated the  
5 explanation of the original 10 geochemical variables in a reduced space by three sets of  
6 the calculated principal components (PCs) which explaining about 73.9% of the total  
7 variance. The analysis of the data (see Table 3(a)) shows that PC1 (41.6% of the total  
8 variance) is mainly influenced positively by the normalized concentration of Ca, Sr and  
9 Ti, and negatively by the normalized concentration of K and Rb. PC2 (19.9% of the  
10 total variance) is mainly influenced positively by the normalized concentration of Fe,  
11 Mn and Zn, and PC3 (which explains the 12.4% of the total variance) influenced  
12 positively by Pb, Zn and Cu.  
13

14 **TABLE 3**  
15

16 On the other hand, from the scattered plot obtained, considering PC1 and PC2  
17 (Figure 4(a)) two group of samples (A and B) can be observed. Group A is mainly  
18 characterized by negative values of the PC1 and PC2 whereas Group B is characterized  
19 by positive values of the PC1. In relation to the samples lithological classification made,  
20 Group A is formed by one lithology class, i.e. porphyritic sub-volcanic rocks and  
21 contents 93.5% of all of the samples coded as 12. Group B, more heterogeneous than  
22 the one, collects 100% of the samples classified as porphyritic dykes (rock code 11),  
23 brecciated porphyritic sub-volcanic (rock code 13) and volcanoclastic rocks (rock code  
24 14), as well as two samples coded as rock code 12.  
25  
26

27 **FIGURE 4**  
28

29 In relation with the previous HCA it can be observed that, although the natural  
30 behaviour of the samples is quite similar, the lineal combination of the normalized  
31 values of concentrations of the elements made by PCA permit us the grouping of the  
32 samples into two groups well defined: Group A, constituted by porphyritic sub-volcanic  
33 rocks and Group B, constituted mainly for the rest of the lithologies classes.  
34

1 When the FA was applied, the Varimax rotation of the axes defined by the PCs  
2 explains again about 73.9% of the total variance of the normalized data, but modify the  
3 weight of the normalized variables in the three varifactors (VFs) obtained by means of  
4 the eigenfactor >1 criterion (see Table 3(b)). The scattered plot of the first two  
5 varifactors is shown in Figure 5(a). It can be observed again two different groups of  
6 rock samples (A and B) which can be considered as identical as those obtained by PCA.

## 8 **FIGURE 5**

9  
10 In general, the unsupervised pattern recognition methods applied to the Box-Cox  
11 transformed concentrations of the analysed elements by P-XRF permit asses that in all  
12 cases 61.4% of the samples are “naturally” grouped as belonging to the macroscopic  
13 group named porphyritic sub-volcanic rocks (rock code 12). The samples  
14 macroscopically classified as porphyritic dykes and brecciated porphyritic sub-volcanic  
15 rocks (rock codes 11 and 13 respectively) present a slightly defined patter of  
16 distribution between them (Fig. 4). The dispersion shown by rocks classified like  
17 volcanoclastics rocks (14) could be attributed to the compositional heterogeneity  
18 characteristics of them.

19  
20 In order to verify the natural grouping obtained and to validate the macroscopic  
21 classification, by means a statistical significant driscriminant model, a LDA was  
22 performed. The discriminant functions were calculated considering the Box-Cox  
23 normalized metals concentrations that mainly affect to VF1. On these bases, i.e. WCa,  
24 WFe, WK, WRb, WSr and WTi, three discriminant orthogonal functions were  
25 calculated. DF1 and DF2 contribute 99.20% to the total discriminant power being both  
26 functions statistically significant at 95% percentage. Eq. 1 and 2 represent the  
27 expression of these functions.

$$28 \quad DF1_{\text{lithol.}} = -0.9 WK + -0.4 WCa + 0.2 WFe + 0.5 WRb + 0.6 WSr + 0.8 WTi \quad [\text{Eq. 1}]$$

$$DF2_{\text{lithol.}} = -0.9 WK -0.1 WFe + 1.6 WRb + 0.6 WSr -0.2 WTi \quad [\text{Eq. 2}]$$

29  
30  
31 In order to evaluate the adequation of the classification model obtained, the samples  
32 were split into six groups and two levels for a 6-fold cross validation inner group by

1 means of Venetian blinds. The percentages of variance captured by the model were  
2 72.80 %. Figure 6(a) shows the scatter plots of observations in the space of discriminant  
3 functions.

#### 4 5 **FIGURE 6**

6  
7 Table 4(a) shows the classification percentages obtained from each class  
8 macroscopically defined. It can be observed that the predicted model with DF1 and  
9 DF2, considering the normalized geochemical information obtained with P-XRF  
10 measurements, classify satisfactory the 70.45 % of the data. These facts could be closely  
11 related to (i) the heterogeneous composition of the “volcanoclastics rocks” (rock code  
12 14), (ii) The similarity of the original composition between the “brecciated porphyritic  
13 sub-volcanic rocks (rock code 13)” and “porphyritic sub-volcanic rocks (rock code 12)”,  
14 as well as the matrix composition of the first rock type, (iii) the state of aggregation  
15 (powdered particles with < 2mm) in which the samples are measured that does not  
16 permit to appreciate the brecciated structure.

#### 17 18 **TABLE 4**

### 19 20 21 *3.2. Macroscopic classification made on the basis of hydrothermal alteration criteria*

22  
23 In relation with the macroscopic classification made on basis of hydrothermal  
24 alteration criteria, from the analysis of the Dendogram (see Figure 3) can be observed  
25 that, in this occasion Cluster I is also the most heterogeneous. It is constituted by  
26 56.25% of samples coded as propylitic alteration (alteration code 21), 100% of samples  
27 classified as “chloritic alteration” and “carbonatization” (alteration codes 25 and 22)  
28 and 50% of samples coded as “argillic assemblages” (alteration code 24). Whereas  
29 Cluster II is constituted by 100% of samples macroscopically defined as “albitic  
30 alteration” (alteration code 23), 50% of samples defined as “argillic assemblages”  
31 (alteration code 24) and by 43.75% of samples defined like propylitic assemblages  
32 (alteration code 21).

1           The results arisen from PCA (see Figure 4(b)) permit us consider again two  
2 groups: Group A constituted by 100% of samples as “albitic alteration” (alteration code  
3 23), 45.45% of rock samples assigned as “propylitic alteration (alteration code 21) and  
4 50% of rock samples assigned as “argillic assemblages” (alteration code 24). Whereas,  
5 Group B includes 68.75% of samples assigned to “propylitic alteration” (alteration code  
6 21), as well as samples defined as carbonatization (100%), argillic assemblages (50%)  
7 and chloritic (100%) alterations respectively.

8  
9           In relation with the information obtain from FA, the scattered plot of the first  
10 two varifactors is shown in Figure 5(b). It can be observed again two different groups of  
11 rock samples (A and B) which can be defined as those obtained by PCA. Thus, Group A  
12 is mainly constituted by 100% of “albitic alteration” (alteration code 23), meanwhile  
13 Group B is mainly constituted by samples belonging to “propylitic alteration”  
14 (alteration code 21) most of them characterized by high values of VF1 and VF2 and  
15 widespread distributed.

16  
17           On the other hand, VF1 could be considered in close relation with alteration  
18 process, because most of the elements with highest weight, i.e. Ca, K, Rb and Sr could  
19 be involved in hydrothermal process [21]. These facts are in good agreement with  
20 positive influence of WCa, WSr and WTi, and negative influence of WK and WRb in  
21 VF1 found in Group B, constituted by samples with propylitic assemblages and chloritic  
22 and carbonatization alterations. Additionally, this is too concordant with the mineralogy  
23 (possibly unaltered plagioclase like main mineral phase) of porphyritic (andesitic)  
24 dykes. The effect of Ti could be attributed to the presence of ilmenite in the ground  
25 mass of dykes. The samples classified as “albitic alteration” has a higher negative  
26 influence of WK and WRb, this fact could be due to Na widespread replacement  
27 involved in the plagioclase albitization process. This last mineral could be constituted  
28 (as initial composition) by significant amounts of K an Rb in its structure.

29  
30           VF2 is influenced by the normalized concentrations of base metals as Mn and  
31 Zn, while VF3 are influenced by Cu and Pb. These elements could be related with ore  
32 mineralization process, nevertheless all the samples show a similar scattered distribution  
33 pattern in the diagrams without significance statistical differences inter samples.

1 Finally, in order to obtain a feasible classification model a PLS-LDA was made.  
2 In this case, considering geochemical features i.e. (a) elements closely related to  
3 hydrothermal alterations, i.e. WCa, WK, WRb, WSr and (b) the element with  
4 economical interest, WCu. On these bases, four discriminant orthogonal functions were  
5 calculated. DF1 and DF2 contribute 89.13% to the total discriminant power being both  
6 functions the most statistically significant at 95% percentage. Eq. 3 and 4 show the  
7 expressions of these functions,

$$8 \quad DF1_{alt} = 0,6 WCa - 1,1 WK + WRb + 0.3 WSr - 0.5 WCu \quad [Eq. 3]$$

$$9 \quad DF2_{alt} = WCa + 0.8WK - 0.2 WRb - 0.6 WSr - 0.1 WCu \quad [Eq. 4]$$

10 On the other hand, in order to evaluate the adequation of the classification model  
11 obtained, the samples were split into six groups and two levels for a 6-fold cross  
12 validation inner group by means of Venetian blinds. For this stage the analyses were  
13 performed the percentages of variance captured by the model were 72.80 % for  
14 lithology and 73.32% for alteration. Figure 5(b) shows the scatter plots of observations  
15 in the space of discriminant functions.

16  
17 Table 4(b) shows the classification percentages obtained from each type of alteration  
18 macroscopically considered. It can be observed that the predicted model considering (i)  
19 geological features and (ii) chemical information obtained with P-XRF measurement  
20 classify satisfactory the 75 % of the data. The heterogeneity in the predicted types  
21 obtained for the samples assigned to “propylitic alteration” could be attributed to the  
22 fact that this kind of alteration could content, at micro-scale level, small bodies  
23 corresponding to a different alteration process (e.g. carbonatization, chloritic, etc.) not  
24 detectable with the equipment used in field campaign sampling.

#### 25 26 27 **4. Conclusions**

28  
29 The statistical treatment of the Box-Cox transformed geological data obtained  
30 from “ex-situ” portable X Ray Fluorescence measurements of ore exploratory samples  
31 with unsupervised and supervised pattern recognition techniques such as HCA, PCA,  
32 FA and LDA has been shown as a helpfully tool for validate the “in-situ” macroscopic

1 rock samples classification applied to an exploratory survey in a potential mining area.  
2 From the DLA it can be concluded that in relation with the macroscopic rock samples  
3 classification based on lithology classes assuming a probability level of 80% the  
4 discriminant model obtained confirms correctly 81.8% of the analyzed samples. When  
5 the alteration types are considered, the discriminant model obtained permits to confirm  
6 four of the five alteration types defined “in situ” (75% of the total samples). Thus, it can  
7 be pointed out that the classification assessed could be applied to facilitate and  
8 accelerated the remained work necessary to determine the goodness of the ulterior  
9 mining exploration.

10  
11 On the other hand, the proposed approach could be apply directly “in situ” without pre-  
12 treatment of the rocks samples during exploratory in those cases in which the  
13 characteristic of the samples could be well assessed.

#### 14 15 16 **Acknowledgments**

17  
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## 1 **References**

- 2
- 3 [1] S. Piorek, Trends in Analytical Chemistry 13 (1994), 281-285.
- 4 [2] A. Argyraki, M. H. Ramsey, P. J. Potts, Analyst (1997), 122, 743-749.
- 5 [3] P. J. Potts, M. H. Ramsey, J. Carlisle, Journal of Environmental Monitoring 4  
6 (2002), 1017-1024.
- 7 [4] J. Chou, G. Clement, B. Bursavich, D. Elbers, B. Cao, W. Zhou, Environmental  
8 Pollution 158 (2010), 2230-2234.
- 9 [5] P.J. Potts, in J. Potts and M. West (Eds.), Portable X-ray Fluorescence  
10 Spectrometry: Capabilities for in-situ analysis, RSC Publishing, London (2008), pp 1-  
11 12.
- 12 [6] F. Rosi, A. Burnstock, K. J. Van den Berg, C. Miliani, B. G. Brunetti A. Sgamellotti,  
13 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 71 (2009),  
14 1655-1662.
- 15 [7] G. Van der Snickt, K. Janssens, O. Schalm, C. Aib'eo, H. Kloust, M. Alfelda, X-Ray  
16 Spectrom. 39 (2010), 103-111.
- 17 [8] S. C. Phillips, R. J. Speakman, Journal of Archaeological Science 36 (2009), 1256-  
18 1263.
- 19 [9] A. J. Nazaroff, K. M. Prufer, B.L. Drake, Journal of Archaeological Science 37  
20 (2010) 885-895.
- 21 [10] P. L. Drake, N. J. Lawryk, K. Ashley, A. L. Sussell, K. J. Hazelwood, R. Song,  
22 Journal of Hazardous Materials 102 (2003) 29-38.
- 23 [11] C. Kilbride, J. Poole, T.R. Hutchings, Environmental Pollution 143 (2006) 16-23.
- 24 [12] T. Radu, D. Diamond, Journal of Hazardous Materials 171 (2009) 1168-1171.
- 25 [13] K. Hürkamp, T. Raab, J. Völkel, Geomorphology 110 (2009) 28-36.
- 26 [14] M. Ramsey, in J. Potts and M. West (Eds.), Portable X-ray Fluorescence  
27 Spectrometry: Capabilities for in-situ analysis, RSC Publishing, London (2008), pp 39-  
28 55.
- 29 [15] P. T. Palmer, R. Jacobs, P. E. Baker, K. Ferguson, S. Webber, Journal of  
30 Agricultural and Food Chemistry 57 (2009), 2605-2613.
- 31 [16] F.L. Melquiades, P.S. Parreira, M.J. Yabe, M.Z. Corazza, R. Funfas, C.R.  
32 Appoloni, Talanta 73 (2007) 121-126.
- 33 [17] M. G. Bagur, S. Morales, M. López-Chicano Talanta, 80 (2009), 377-384.



- 1 [18] F. Martín-Peinado, S. Morales-Ruano, M. G. Bagur-González, C. Estepa-Molina,  
2 Geoderma 159 (2010), 76-82.
- 3 [19] M.G. Bagur-González, C. Estepa-Molina, F. Martín-Peinado, S. Morales-Ruano,  
4 Journal of Soils and Sediments. DOI: 10.1007/s11368-010-0285-4 (On line from  
5 09/2010).
- 6 [20] V. MaksaeV, M. Zentilli, Chilean Strata-bound Cu-(Ag) Deposits: An Overview, in  
7 Porter, T.M. (Ed.), Hydrothermal Iron Oxide Copper-Gold & Related Deposits: A  
8 Global Perspective, PGC Publishing, Adelaide 2(2002), pp 185-205.
- 9 [21] H. L. Barnes, Geochemistry of Hydrothermal Ore Deposits, third ed., Wiley, John  
10 & Sons, 1997.
- 11 [22] U.S. EPA, 2006. XRF technologies for measuring trace elements in soil and  
12 sediment. Niton XLt 700 Series XRF Analyzer. Innovative technology verification  
13 report EPA/540/R-06/004.
- 14 [23] G.E.P. Box, D.R. Cox, Royal Statistical Association, B26 (1964) 211-250
- 15 [24] M. Meloun, J. Militký, M. Forina, in PC-Aided Statistical Data Analysis vol. 1  
16 (1992) Ellis Horwood, Chichester, United Kingdom.
- 17 [25] M. Meloun, M. Sňanka, P. Němec, S. Krřitkova, K. Kupta, Environmental Pollution  
18 137 (2005) 273-280
- 19 [26] C. Pérez-López in Estadística Práctica con STATGRAPHICS, Pearson Education  
20 S.A. (2002), Madrid, Spain.
- 21

1 **FIGURE CAPTIONS**

2

3 **Figure 1.** Geological map of the Boris Angelo area. 1. Porphyritic dykes 2 & 3.  
4 Brecciated porphyritic sub-volcanic rocks 4. Porphyritic sub-volcanic rocks 5.  
5 Volcanoclastics rocks 6. Fault 7. Mineralized vein-fault 8. Contact 9. Drill-hole A, B, C  
6 and D. Cross section showing the drill holes position and samples location.

7

8 **Figure 2.** Scheme of the statistical procedure used for data treatment.

9

10 **Figure 3.** Dendrogram resulting from HCA of the Box-Cox normalized data set (R: rock  
11 code; A: alteration code; S: sample).

12

13 **Figure 4.** Scatterplots obtained from PCA of the Box-Cox normalized data set using:  
14 (a) rock codes and (b) alteration codes.

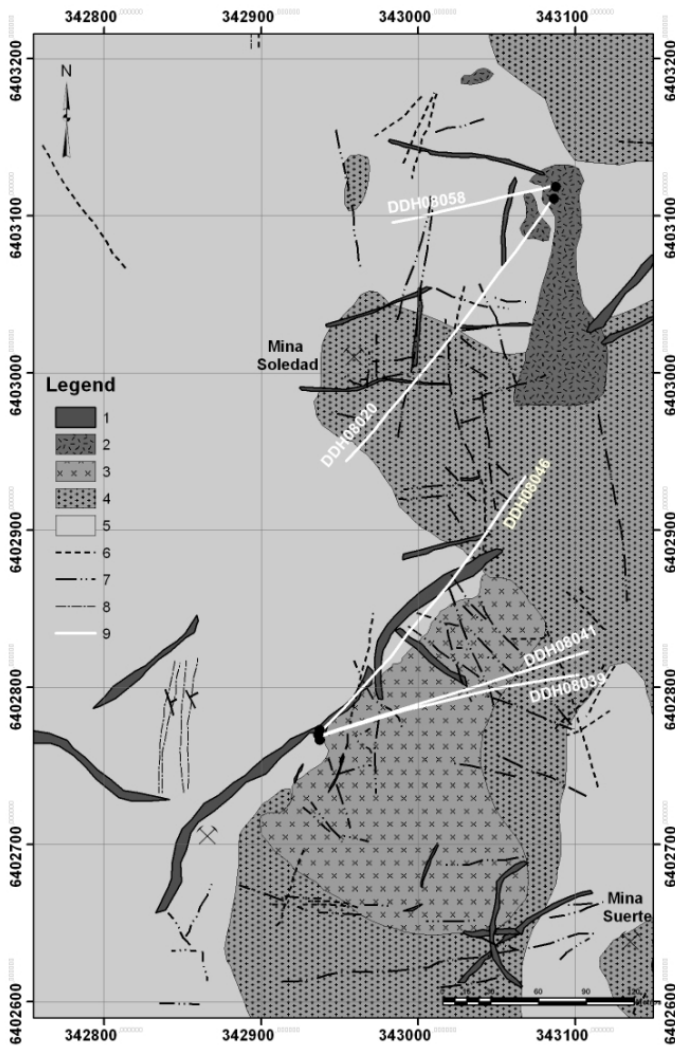
15

16 **Figure 5.** Scatterplots obtained from FA of the Box-Cox normalized data set using (a)  
17 rock codes and (b) alteration codes.

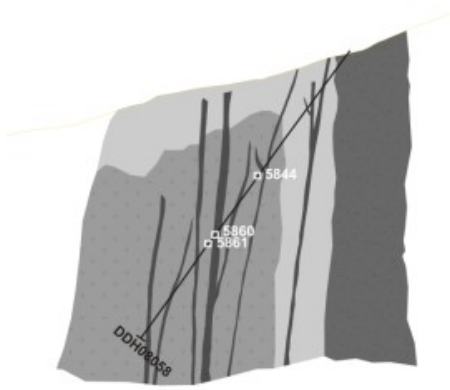
18

19 **Figure 6.** Scatterplots obtained from Discriminant Functions of the Box-Cox  
20 normalized data set using (a) rock codes and (b) alteration codes.

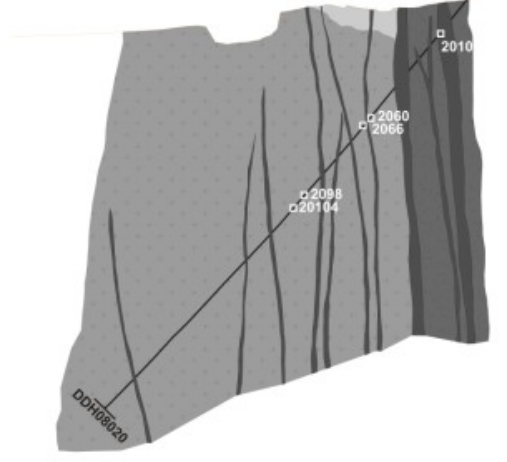
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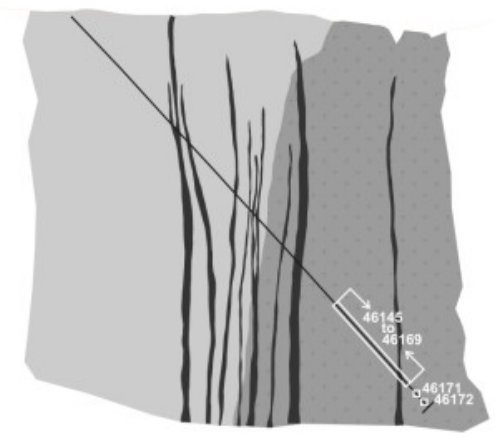
A. DDH08058 cross section



B. DDH08020 cross section



C. DDH08046 cross section



D. DDH08039-41 cross section

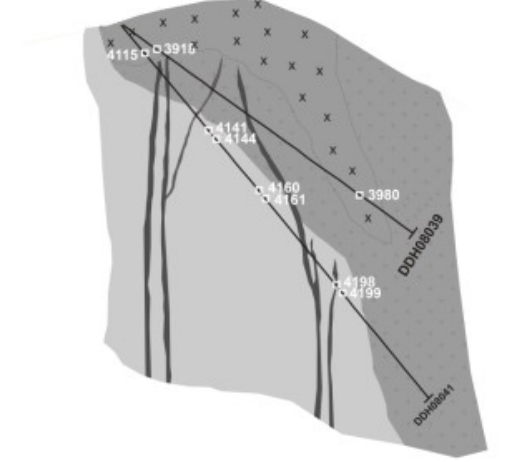
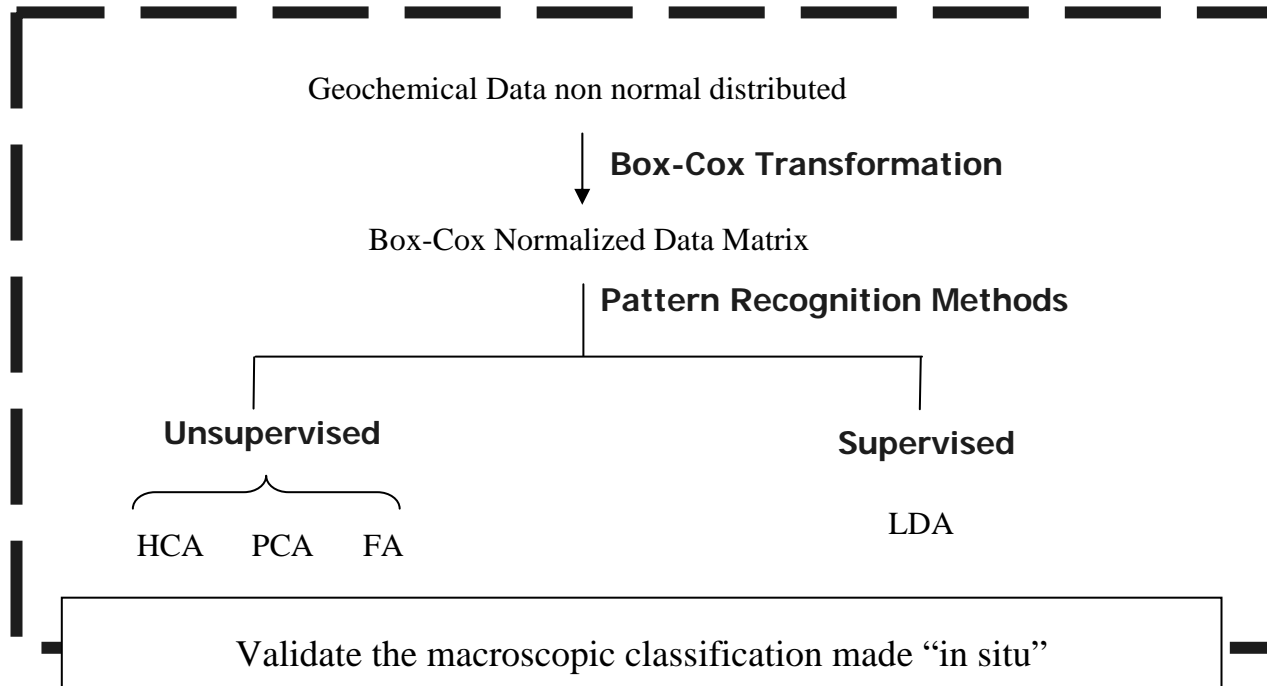


Figure 1



**Figure 2**

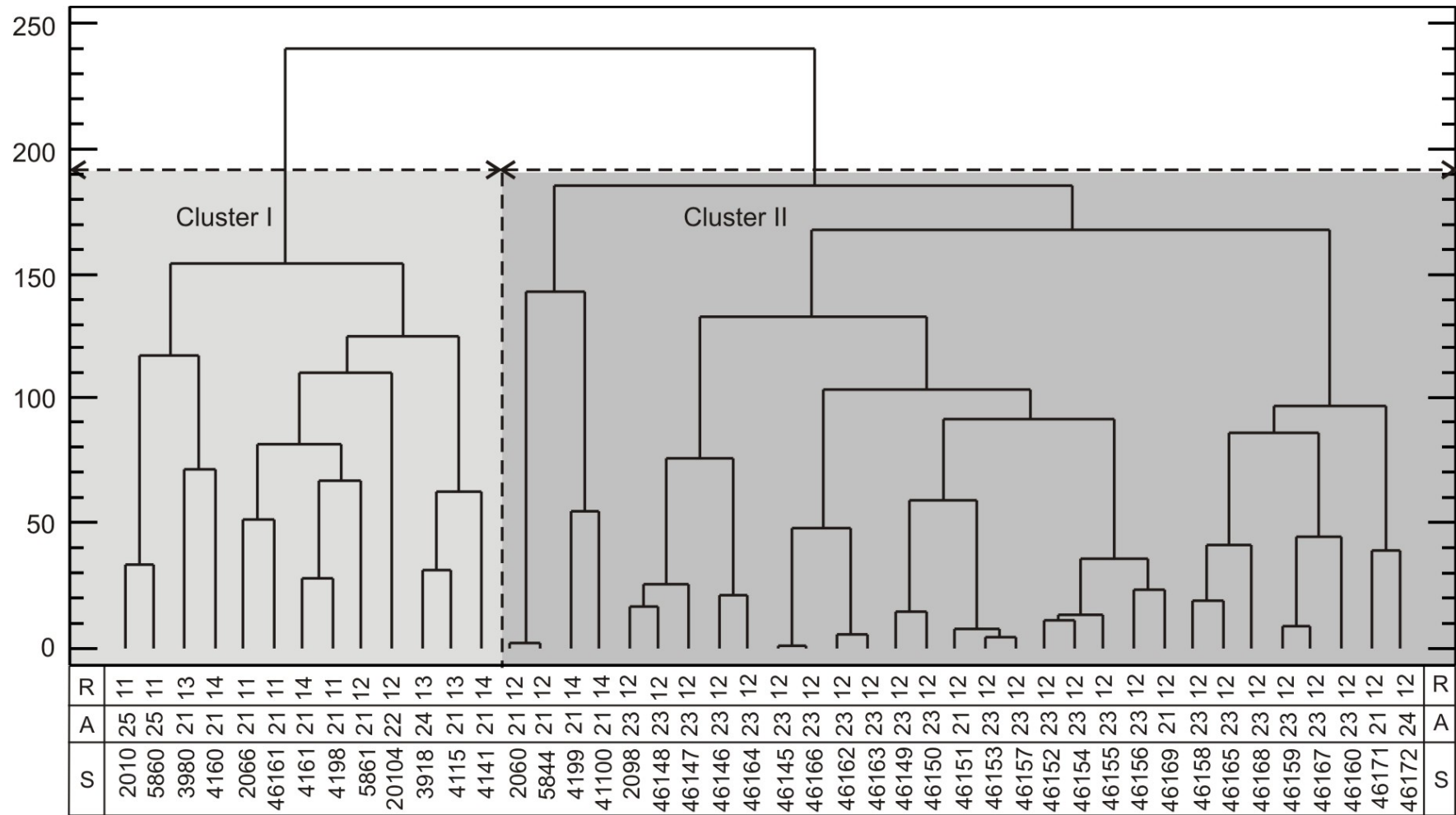
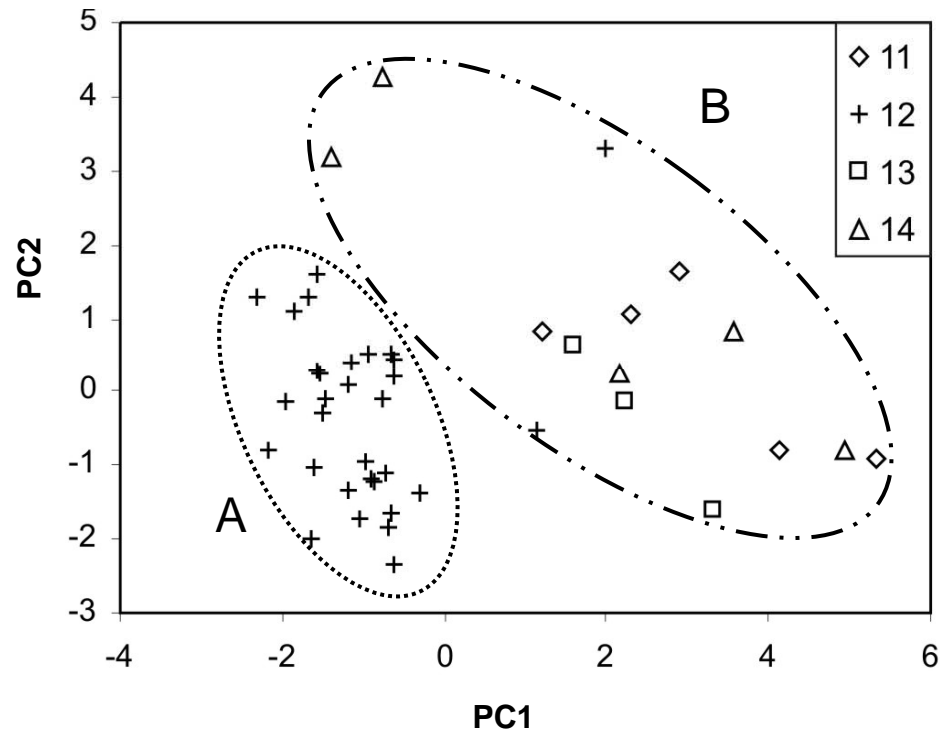
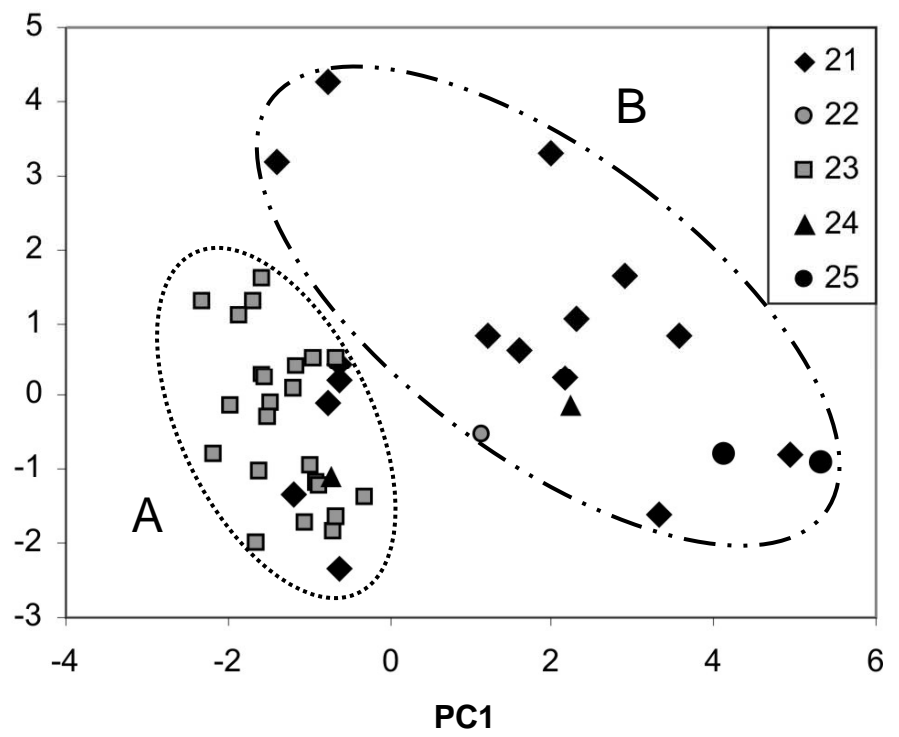


Figure 3



(A)



(B)

Figure 4

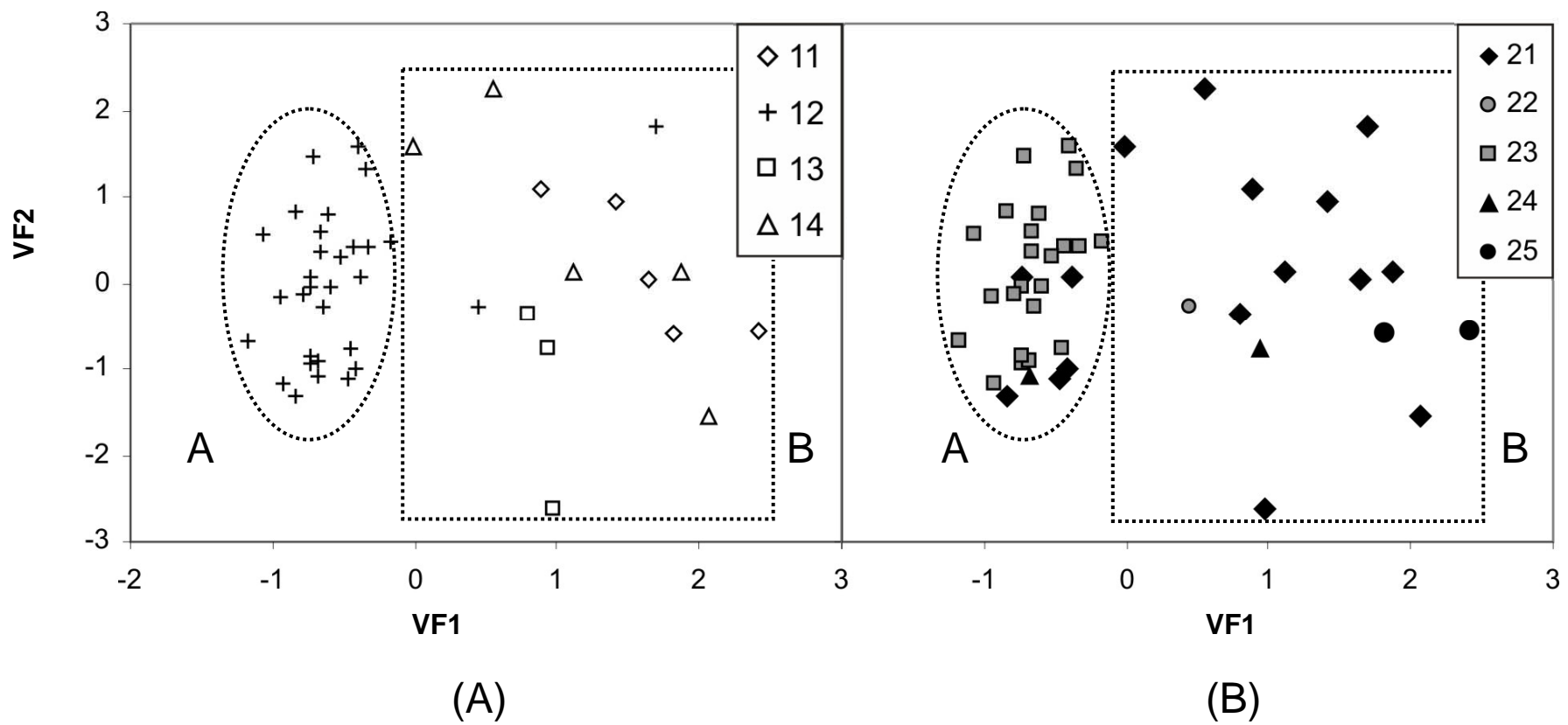
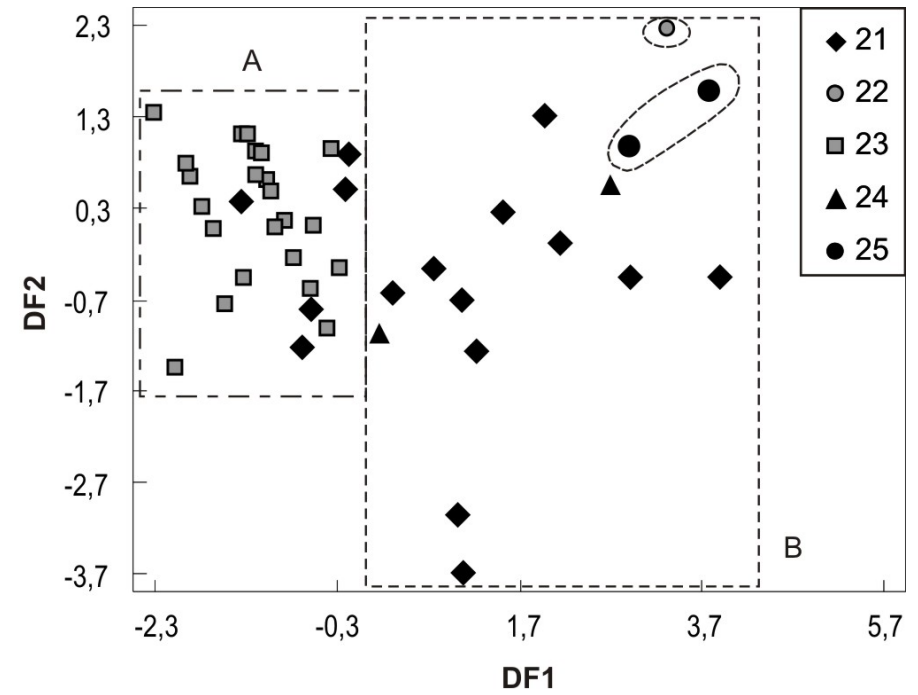
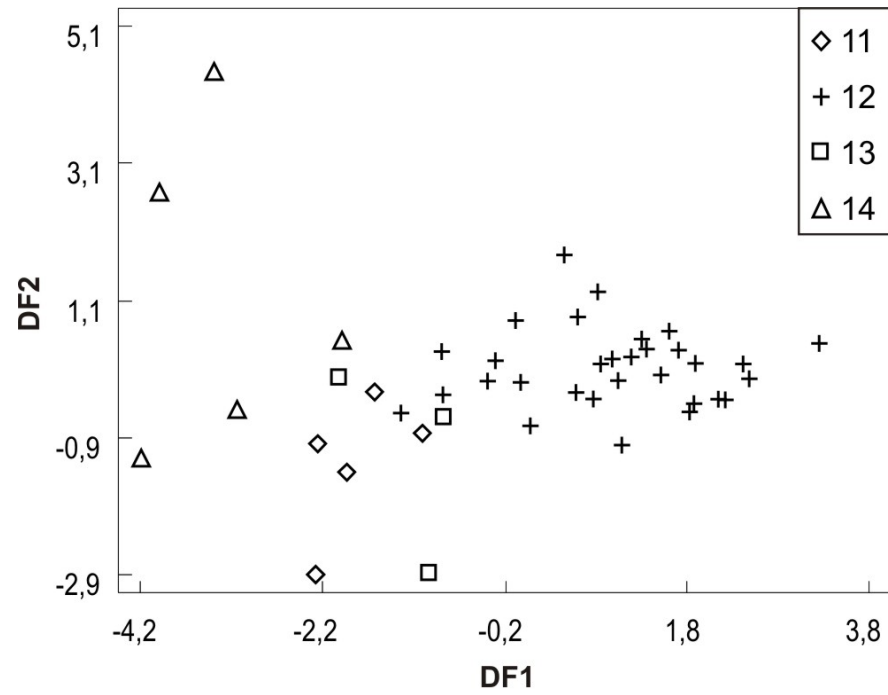


Figure 5



**Figure 6**



**TABLE 1. Lithological types (A) and hydrothermal alteration types (B) identified in the studied zone.**

**(A)**

<b>Classes</b>	<b>Characteristics</b>	<b>Coded values</b>
Porphyritic dykes	Small and tabular bodies with andesitic composition. Porphyritic to aphanitic texture with plagioclase and occasionally amphibole phenocrysts.	11
Porphyritic sub-volcanic rocks	Sub-volcanic intrusive body (stock). Porphyritic texture with plagioclase and amphibole phenocrysts.	12
Brecciated porphyritic sub-volcanic rocks	Brecciated texture sub-volcanic intrusive body (stock). Brecciated and porphyritic texture with plagioclase and amphibole phenocrysts.	13
Volcanoclastic rocks	Tuff, breccias and agglomerated sequences. Homoclinal structure.	14

**(B)**

<b>Alteration</b>	<b>Characteristics</b>	<b>Coded values</b>
Propylitic	Chlorite (Chl), epidote (Ep), calcite (Cac) and hematite (Hem) assemblages.	21
Carbonatization	Calcite veins.	22
Albitic	Strong replacement of plagioclase by albite or albite veins presence.	23
Argillic assemblages	Assemblages of undetermined clay minerals, Fe oxy-hydroxide. This alteration is mainly related with fault zones.	24
Chloritic	Veins and replacement of rock components by chlorite.	25

**TABLE 2. Analytes concentrations in the rock samples analysed**

Sample	Code		Content of elements analyzed (expressed as mg/kg)									
	Rock	Alteration	Ca	Cu	Fe	K	Mn	Pb	Rb	Sr	Ti	Zn
2010	11	25	65394	90	59518	8918	1255	< l.o.d	20	554	4698	77
20104	12	22	62591	356	35454	11934	1508	31	38	396	1908	118
2060	12	21	33347	20899	44028	17251	1509	146	48	372	1978	< l.o.d
2066	11	21	34559	376	63901	15345	1747	14	39	595	5742	79
2098	12	23	30490	782	39927	19037	1789	26	52	327	2233	179
3918	13	24	39603	130	45353	15216	1183	177	46	487	3015	94
3980	13	21	36430	455	46006	8933	1149	57	23	362	2939	34
41100	14	21	23879	10143	64067	17028	1800	60	85	410	3955	103
4115	13	21	33144	798	46765	14652	1225	86	38	449	3251	109
4141	14	21	33634	95	57738	17780	1253	40	52	608	4681	96
4160	14	21	54627	271	42096	7456	1126	49	24	908	4727	78
4161	14	21	43300	244	54505	12096	1389	34	34	704	5196	98
4198	11	21	35326	649	60672	11675	1523	79	31	519	5320	84
4199	14	21	24932	21193	74146	12254	2118	81	62	391	3011	182
46145	12	23	30026	1109	39501	18823	1405	36	57	388	2249	125
46146	12	23	28999	1372	36744	19900	1641	152	54	341	2239	132
46147	12	23	31156	1342	42245	19365	2003	44	54	402	1970	147
46148	12	23	29162	1457	43010	21714	1868	27	60	345	2124	135
46149	12	23	27233	985	38604	20166	1475	14	59	321	2403	114
46150	12	23	28988	741	33599	19807	1429	15	58	350	2071	135
46151	12	21	29941	165	33961	19946	1395	20	56	384	2130	110
46152	12	23	29218	478	37989	19713	1378	19	53	421	2083	92
46153	12	23	28530	446	34185	18404	1381	21	49	405	2154	95
46154	12	23	27669	1250	38656	18521	1600	24	51	388	2190	93
46155	12	23	27794	1075	43310	20612	1598	18	58	406	2082	104
46156	12	23	30885	1658	40289	19044	1568	29	45	420	2254	112
46157	12	23	29943	876	33427	18759	1359	22	53	346	2121	106
46158	12	23	27928	379	35874	17373	1203	21	46	331	2159	82
46159	12	23	27100	348	33360	17850	1331	29	49	441	2100	75
46160	12	23	26597	813	32892	21555	1292	19	59	577	1979	76
46161	11	21	34623	203	42404	14304	1613	19	42	376	4617	131
46162	12	23	30826	1960	37317	17308	1336	32	52	286	2299	110
46163	12	23	31330	1244	37513	17092	1452	27	57	295	2151	86
46164	12	23	28131	350	39190	20512	1606	50	60	342	2254	94
46165	12	23	32414	2239	34170	17103	1216	22	47	320	2071	74
46166	12	23	30772	2109	36361	17134	1464	36	53	394	2389	128
46167	12	23	24912	978	37848	18888	1329	27	46	448	2017	68
46168	12	23	29855	743	36164	16095	1251	24	41	402	1979	97
46169	12	21	26345	525	40945	18021	1435	33	51	435	2064	102
46171	12	21	25233	164	37103	19325	1103	30	54	422	2010	79
46172	12	24	25949	274	36263	17169	1122	139	56	369	2155	105
5844	12	21	36269	216919	43426	17828	1385	152	58	411	1963	< l.o.d
5860	11	25	49599	108	51867	13772	1266	19	31	678	4819	67
5861	12	21	47808	514	58262	14273	2177	92	40	444	5686	161

**TABLE 3. Standardized coefficients of Weights of Box-Cox transformed variables in Principal Component and Factorial analysis functions.**

<u>Variables</u>	<u>Principal Components</u>			<u>Varimax rotated Varifactors</u>		
	<u>PC1</u>	<u>PC2</u>	<u>PC3</u>	<u>VF1</u>	<u>VF2</u>	<u>VF3</u>
<b>WCa</b>	<b>0.4</b>	0.0 <sub>2</sub>	- 0.1	<b>0.4</b>	0.0 <sub>2</sub>	-0.1
<b>WCu</b>	- 0.3	0.3	<b>0.4</b>	-0.3	0.3	<b>0.4</b>
<b>WFe</b>	0.3	<b>0.5</b>	0.0 <sub>5</sub>	0.3	<b>0.5</b>	0.0 <sub>5</sub>
<b>WK</b>	<b>- 0.4</b>	- 0.1	- 0.2	<b>-0.4</b>	-0.1	-0.2
<b>WMn</b>	- 0.2	<b>0.6</b>	- 0.2	-0.2	<b>0.6</b>	-0.2
<b>WPb</b>	0.0 <sub>4</sub>	0.3	<b>0.7</b>	0.0 <sub>4</sub>	0.3	<b>0.7</b>
<b>WRb</b>	<b>- 0.4</b>	0.2	- 0.0 <sub>1</sub>	<b>-0.4</b>	0.2	-0.0 <sub>1</sub>
<b>WSr</b>	0.3	0.0 <sub>2</sub>	- 0.1	0.3	0.0 <sub>2</sub>	-0.1
<b>WTi</b>	<b>0.4</b>	0.3	- 0.1	<b>0.4</b>	0.3	-0.1
<b>WZn</b>	- 0.2	<b>0.4</b>	<b>- 0.4</b>	-0.2	<b>0.4</b>	<b>-0.4</b>

**TABLE 4. DLA classifications obtained for the rock samples analysed.**

**(a) Criteria: Lithology of the samples**

<u>Classes</u>	<u>Code</u>	<u>Samples</u>	<u>Predicted</u>			
			<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>
<b>Porphyritic dykes</b>	<b>11</b>	5	0 (0.00%)	5 (100%)	0 (0.00%)	0 (0.00%)
<b>Porphyritic sub-volcanic rocks</b>	<b>12</b>	31	0 (0.00%)	31 (100%)	0 (0.00%)	0 (0.00%)
<b>Brecciated porphyritic sub-volcanic rocks</b>	<b>13</b>	3	0 (0.00%)	3 (100%)	0 (0.00%)	0 (0.00%)
<b>Volcanoclastic rocks</b>	<b>14</b>	5	0 (0.00%)	5 (100%)	0 (0.00%)	0 (0.00%)

**(b) Criteria: Alteration types**

<u>Alteration</u>	<u>Code</u>	<u>Samples</u>	<u>Predicted</u>				
			<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>	<u>25</u>
<b>Propylitic</b>	<b>21</b>	16	6 (37.50%)	1 (6.25%)	3 (18.75%)	4 (25%)	2 (12.50%)
<b>Carbonatization</b>	<b>22</b>	1	0 (0.00%)	1 (100%)	0 (0.00%)	0 (0.00%)	0 (0.00%)
<b>Albitic</b>	<b>23</b>	23	1 (4.35%)	0 (0.00%)	22 (95.65%)	0 (0.00%)	0 (0.00%)
<b>Argillic assemblages</b>	<b>24</b>	2	0 (0.00%)	0 (0.00%)	0 (0.00%)	2 (100%)	0 (0.00%)
<b>Chloritic</b>	<b>25</b>	2	0 (0.00%)	0 (0.00%)	0 (0.00%)	0 (0.00%)	2 (100%)