Combining portable X-ray fluorescence and clustering methods for mineral exploration. A case study in Batigelas (Ossa-Morena Zone, Portugal)

Combinando fluorescência de raios-X portátil e métodos de clustering em prospeção mineral. Um caso de estudo em Batigelas (Zona de Ossa-Morena, Portugal)

Nogueira, P.[1,2*], Afonso, P. [1,3], Roseiro, J.[2], Maia, M.[2], São Pedro, D.[2], Matos, J.[4] & Batista, M.[4]

[1] Departamento de Geociências da Escola de Ciências e Tecnologia da Universidade de Évora. Apartado 94, 7000 Évora, Portugal.
[2] Instituto de Ciências da Terra. Apartado 94, 7000 Évora, Portugal.
[3] Departamento de Física da Escola de Ciências e Tecnologia da Universidade de Évora. Apartado 94, 7000 Évora, Portugal.
[4] Laboratório Nacional de Energia e Geologia (LNEG), Campus de Aljustrel; Bairro da Vale d´oca 14, 7601-909 Aljustrel
* pmn@uevora.pt

Resumo: Batigelas é uma ocorrência mineral no setor de Alter do Chão-Elvas, Zona de Ossa-Morena, que foi estudada pelo Serviço de Fomento Mineiro através da avaliação geoquímica de solos e geofísica terrestre. Os resultados obtidos justificaram a realização de uma sondagem carotada. Trabalhos recentes de geoquímica de solos com recurso a uma fluorescência de raios-X portátil permitiram obter novos resultados para a caracterização da região.
A aplicação de métodos de *clustering* (aglomeração hierárquica e k-média) para a análise dos dados permitiram, não só pormenorizar a anomalia inicial identificada como também identificar as unidades geológicas aflorantes na região.
Os resultados obtidos salientam a importância da aplicação desta técnica em situações de prospeção mineral.

Palavras-chave: Batigelas, Fluorescência de raios-X portátil, k-média, aglomeração hierarquica

Abstract: Batigelas is a mineral occurrence in the Alter do Chão-Elvas sector of the Ossa-Morena Zone that was investigated by the Serviço de Fomento Mineiro including soil geochemistry and terrestrial geophysics. The results obtained justified the execution of a drill hole. Recent soil geochemistry work using portable X-ray fluorescence has yielded new results for the region.
The application of clustering methods (hierarchical and k-means clustering) to the analyses allowed to detail not only the initial anomaly identified, but also to identify the outcropping of geological units in the region.
The results obtained highlight the importance of applying this technique in mineral exploration campaigns.

Keywords: Batigelas, Portable X-ray fluorescence, k-means, hierarquical clustering

Introduction

Throughout the 50s until the 70s decades of the 20th century, the Serviço de Fomento Mineiro (SFM), conducted a systematic sampling campaign and further soils geochemical analysis in the national territory. These campaigns included a set of samples that were summarily analysed and stored for future studies. One of the expeditious techniques used was a colorimetric test that identifies the existence of heavy metals (HM) in soils, namely copper, lead and zinc. The results provided a bulk value for heavy metals, in ppm, not quantifying each element. Occasionally, when in the presence of an anomaly, combined with other geophysical target it was justified the realization of logged drill holes, to evaluate the potential existence of a mineral deposit.

Batigelas, located in the Alter do Chão-Elvas Sector (ACES), is an example of an anomalous occurrence of heavy metals in soils in contrast with the soil geochemical background. This anomaly occurs along with a favourable geophysical magnetic anomaly.

The drill hole revealed the presence of sulphides including pyrrhotite, chalcopyrite and pentlandite. Notwithstanding the results, no further studies were conducted, after the first promising results.

The ZOM3D is a project funded by national and European funds aiming the valorisation of the geological resources in this region. Batigelas was one of the selected mineral occurrences to conduct additional studies.

Geological background

The ACES of the Ossa-Morena Zone include geological metasedimentary units that range from Neoproterozoic to Cambrian in age, Ordovician mafic-ultramafic and peralkaline rocks, as well as a carboniferous granitoid complex (Araújo *et al.*, 2013 and references therein). The Batigelas mineral occurrence is in the northern part of the ACES where a sequence of carbonated and Neoproterozoic metasedimentary rocks contact with peralkaline rocks in a NW-SE regional trend. Southwest from the Batigelas area outcrops the mafic-ultramafic complex at Northeast is found the contact between the ACES and the Blastomilonitic zone, see Figure 1.

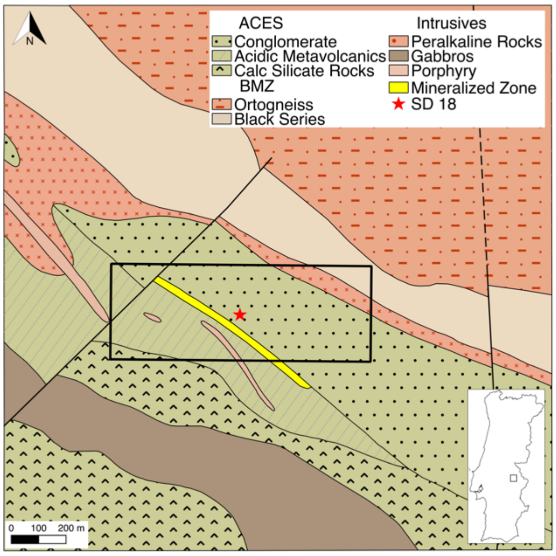

Figure 1. Geological units in the Batigelas area. The rectangle outlines the study area. Adapted from 1:500.000 Portuguese geological map.

Methods

Herein the results of a high-resolution geochemical soil campaign are presented and discussed. The analyses were performed "*in situ*", using a portable X-Ray Fluorescence (P-XRF) from Skyray Instruments, in a regular mesh (20×8=160 points) around the historic drill hole site. The 'Mineral Mode' of the equipment was used and nine major constituents and fifteen trace elements were detected in the selected samples.

The data analysis, used a multivariate statistical approach, including the computation of hierarchical and k-means clustering. The obtained maps were generated using the Inverse Distance Weighted interpolation method.

Geochemical results

The area studied during the SFM campaign covers a 4km×2km area, with a sampling mesh of 100m×100m. Figure 2 shows the interpolated results for the heavy metals, obtained from the data.

This figure clearly identifies a anomalous zone where the high resolution P-XRF campaign was conducted.

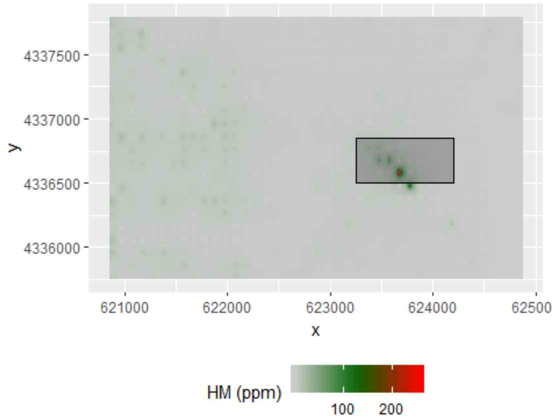

Figure 2. Interpolation of the results for SFM soil heavy metals geochemistry. The rectangle represents the P-XRF campaign (this study).

The map in Figure 2 displays the SFM heavy metals values, the anomaly aligns with the regional trend overlapping perfectly with the mineralized zone defined in Figure 1.

The P-XRF campaign detected major elements including SiO_2, Al_2O_3, MgO, Fe_2O_3, CaO, K_2O, MnO, TiO_2 and P_2O_5; and the trace elements Sr, Rb, Zr, V, Cr, Ni, Sn, Cu, Zn, Pb, As, Mo, Ga, Nb and Y.

The MgO, Al_2O_3, Ga and Mo were rejected as they were detected in a reduced number of samples and, therefore, without statistical significance. The P-XRF analyses constraints found in literature (see Hou *et al.* 2004 or Bourke & Ross, 2014) apply to our study, namely the limits of detection of the elements and the possible interferences between elements.

The correlation between the major elements is not very strong in any case, nevertheless, K_2O, Fe_2O_3, MnO, TiO_2 show good positive correlations. For the trace elements, Pb-Zn-As and the pairs Sr-Y and Cu-Nb display strong positive correlations.

Two clustering methods were used to identify the main geochemical features of the soils in the studied area: i) hclust: hierarchical clustering and ii) k-mean clustering.

For the major elements, hclust and k-mean grouped the data in the same assemblages (Table 1).

For the trace elements the groups defined by both clustering methods are different in some extent (Table 2). Cr and Sn change from group (bold); with four clusters Rb, V and Ni also present different affinities (underlined).

Table 1. Groups (G1-G4) of major elements as divided in 2, 3 and 4 clusters.

	HCLUST and KMEANS		
	N=2	N=3	N=4
G1	SiO_2, CaO, P_2O_5	SiO_2, CaO	SiO_2
G2	Fe_2O_3, K_2O, MnO, TiO_2	Fe_2O_3, K_2O, MnO, TiO_2	Fe_2O_3, K_2O, MnO, TiO_2
G3		P_2O_5	CaO
G4			P_2O_5

The transpose of the data matrix is used to identify the cluster of each observation, therefore allowing to create maps of the different assemblages.

These maps were created for two, three and four clusters, using both methods, to evaluate the geographical distribution of the clusters and its geological implication.

Table 2. Trace elements divided in 2, 3 and 4 groups according to both clustering methods.

	HCLUST		
	N=2	N=3	N=4
G1	Zn, Pb, As, Cu, Nb	Zn, Pb, As	Zn, Pb, As
G2	Sr, Y, Zr, Rb, V, Ni, **Cr, Sn**	Sr, Y, Zr, Rb, V, Ni, **Cr, Sn**	Sr, Y
G3		Cu, Nb	Zr, Rb, V, Ni, **Cr, Sn**
G4			Cu, Nb

	KMEANS		
G1	Zn, Pb, As, Cu, Nb, **Cr, Sn**	Zn, Pb, As	Zn, Pb, As
G2	Sr, Rb, V, Ni, Y, Zr	Sr, Rb, V, Ni, Y, Zr	Sr, Rb, V, Ni, Y
G3		Cu, Nb, **Cr, Sn**	Zr
G4			Cu, Nb, **Cr, Sn**

Figure 3 presents the map of hclust method for two clusters for major elements (A) and trace elements (B). This approach can be done using any number of clusters allowing to evaluate the spatial role of each cluster.

Figure 4 displays the k-means results for 3 clusters for major elements (A) and trace elements (B).

Discussion

Hclust and k-mean applied to major elements provide the same groups (*cf.* Table 1). This might be due to i) the limited number of variables available to create the clusters and ii) the major elements reflect mainly the chemical differences in the geological units.

For the trace elements both methods separate the calcophile group (susceptible to be incorporated in the crystal structure of sulphides, as Pb, Zn and As) from elements that are present in other forms and with different origins (e.g. Rb, Zr or Y).

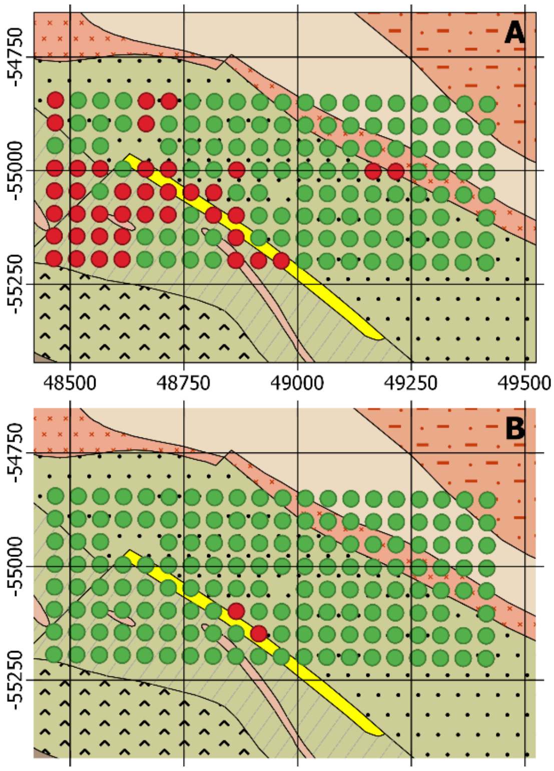

Figure 3. Hclust for two clusters. (A) Major elements, red dots G1, green dots G2 (table 1); (B) Clusters of trace elements, red dots G1, green dots G2 (table 2). Geological legend see figure 1.

Using the data from major elements, the maps created provided a plausible indicator of the underlying geology, identifying the geochemical contacts of the two hidden main geological units (Figure 3A and 4A). The data from trace elements besides from separating the mineralized zone (possible a reflection of the presence of sulphides, represented by the green stars) from non-mineralized (Figures 3B and 4B) can also separate the same two geological units (Figure 4B).

Conclusions

The main geological units can be identified using both methods of cluster analysis and, consequently, P-XRF combined with cluster analysis is an good tool for high resolution geochemical mapping, providing fast plausible "*in situ*" results.

The presence of a mineralized zone could be identified with success demonstrating that this combination of techniques might be used in mineral exploration campaigns, providing fast and detailed results with cost-effectiveness.

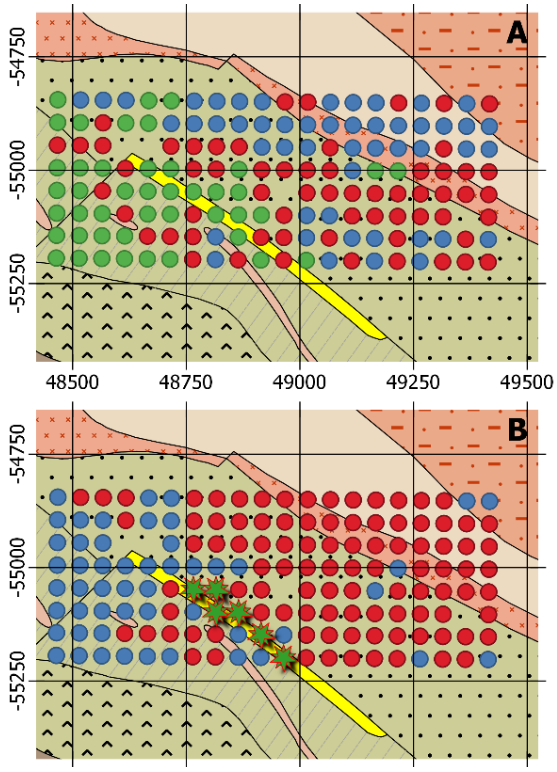

Figure 4. K-means for three clusters. (A) Major elements, red dots G1, green dots G2, blue dots G3 (table 1); (B) Trace elements, red dots G2, green dots G3, blue dots G1 (table 2); Geological legend see figure 1.

Acknowledgments

This work is a contribution to the project ZOM3D: ALT20-03-0145-FEDER-000028, funded by Alentejo 2020 through the FED-ER/FSE/FEEI. The authors also acknowledge the funding provided to Institute of Earth Sci-ences through the contracts UID/GEO/04683/2013 with FCT and COMPETE POCI-01-0145-FEDER-007690.

References

Araújo, A., Piçarra de Almeida, J., Borrego, J., et al., 2013. As regiões central e sul da Zona de Ossa-Morena. In: R. Dias et al. (Eds), Geologia de Portugal, Volume 1, Escolar Editora, 509-549.

Bourke, A., & Ross, P. S. (2016). Portable X-ray fluorescence measurements on exploration drill-cores: comparing performance on unprepared cores and powders for 'whole-rock'analysis. Geochemistry: Exploration, Environment, Analysis, 16(2), 147-157.

Hou, X., He, Y., & Jones, B. T. (2004). Recent advances in portable X-ray fluorescence spectrometry. Applied Spectroscopy Reviews, 39(1), 1-25.