ABANDONED MINE SLAGS ANALYSIS BY EPMA WDS X-RAY MAPPING

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Abstract

The mining activity on the Iberian Pyritic Belt (Portugal and Spain) started before Phoenician times, became particularly intense during the Roman occupation of the Iberian Peninsula (for gold) and after the industrial revolution (for gold, copper, zinc, lead and sulphur).

The commonest ore of this region is a massive polymetalic sulphide accumulation, where pyrite (FeS_2) is the main mineral, with variable concentrations of chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS), arsenopyrite ($FeAsS_2$), other sulphides and sulfosalts which include minor elements like Mn, Co, Ni, Se, Cd, Sb, Te, Hg and Bi. Some of the main and minor elements of these ores are hazardous and the drainage basins of pollutant source areas often induce health concerns in the resident population. Electron microprobe study followed previous optical and XRD analysis of the slags. The study focused on the identification of phases how sulphide and metallic phases are distributed within the material and infer about leachable elements during weathering. Electron microprobe X-Ray maps show evidences of different behavior between the elements: Ca and Zn are completely leached; iron is retained in oxyhydroxides, lead and arsenic precipitate as sulphates.

Electron microprobe studies are essential to understand complex materials as earth materials. Nevertheless, care is required to a correct interpretation of data and most quantitative compositional data are not trustworthy.

Introduction

Abandoned mine slags are non-stable waste products of various compositions and the source of important environment contaminations [1], [2]. The problem is particularly serious at the abandoned mine of S. Domingos (southern Portugal) where the acid mine drainage is very intense. Moreover, since the main exploration purpose was the extraction of sulphur, large piles of metals-enriched slag were left “in-situ” for at least forty years. The soil contamination is so strong that several square kilometres exhibit a complete depletion of vegetation resembling a desert-area or display small clusters of metal hyper-accumulator plant species (Figure 1). It is indeed a serious problem, which may be the first cause also of water stream contaminations.

Fig1: Foto taken near S.Domingos abandoned mine

The contamination overcame to human population and a comparison study of scalp hair analysis [3] related higher levels of As, Cu and Zn in downstream (Santana de Cambas) local population than those living a upstream the contamination source (Corte do Pinto).

The neoformation materials control the metals that are or are not transported by surface waters because some heavy metals can be scavenged by them [2]. The capability of these phases to retain pollutant metals in acidic environments of abandoned mines is being studied, but transferability is not direct to other climatic conditions and availability of components. However, to establish a link between pollutant metal and retainer mineral, microanalytical techniques such as the electron microprobe analyzer, with adequate capability to detect phases and minor elements are required, although the complex phases encountered.

Electron microprobe is a powerful technique that is used to study this type of materials. An approach consists of analyzing the several primary and secondary phases through quantitative analysis. However the phases are complex (Fig. 2a and 2b) and good uniform polishing is hard to achieve. In this work we focus in electron backscattered images and X-Ray map imaging in order to understand what happens during weathering and where elements are distributed.

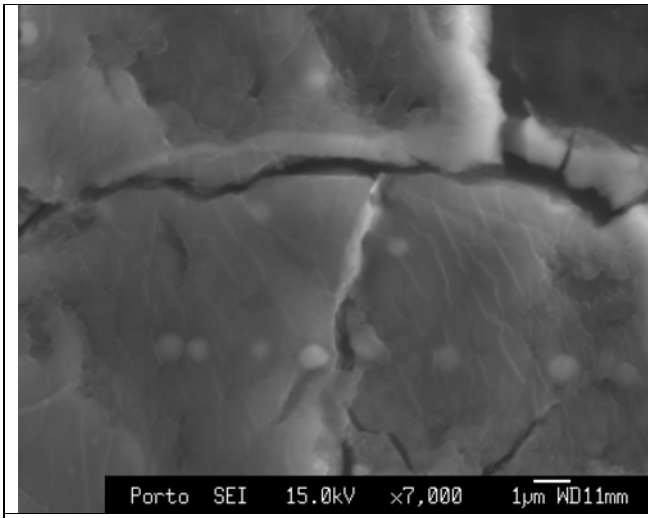


Figure 2a- Secondary electron image of a detail of the weathered product

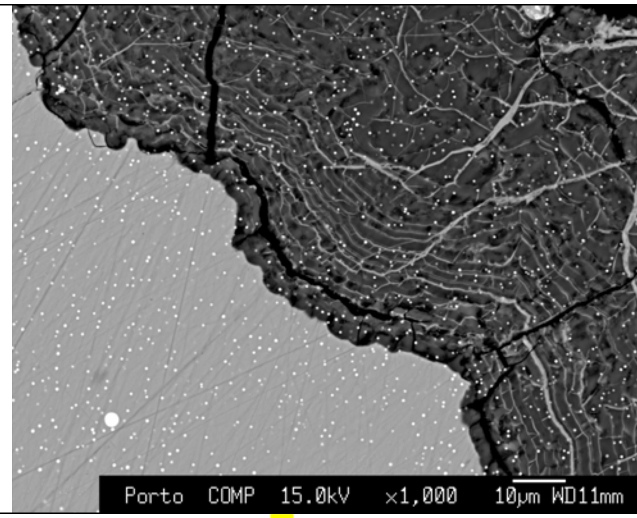


Figure 2b: Backscattered electron image of the glass showing its interface with weathered product. Sub micrometric spherules are of Iron, Copper, Zinc and Lead sulphides.

Method

Samples are weathered slags resulting from ustulation metallurgic process. In a previous work [4], non weathered slags were observed by microscopy. It was shown the existence of silicate glass, olivine, hematite and sulphides in unweathered slags. X-ray diffraction revealed that most of the material in under amorphous state. Olivine is fayalitic and the weathering products are mainly goethite, semi-amorphous illite, quartz and jarosite group minerals.

For observation with the electron microprobe, we selected samples where weathered zones were visible. Figure 3 show electron backscattered images of some examples.

After direct observation at higher magnification just as in Figures–2a and 2b, we conclude that at normal operation, the volume involved in the analysis does not contain all the excitation volume because sub micrometric particles and thin deposit layers are spread in the samples. The beam will excite these sub micrometric particles of sulphides and the resulting fluorescence effects influence the results of analysis. Quantitative analysis of these slags must be taken only as information to evaluate the possible contents of present phases.

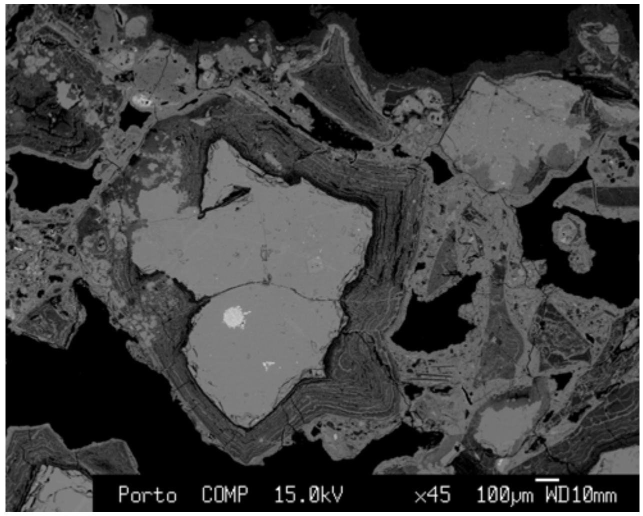


Fig3a- Electron backscattered image of S. Domingos weathered products

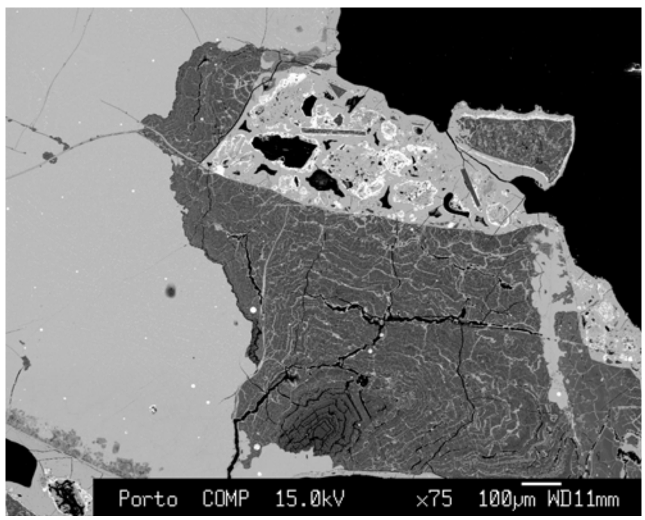


Figure 3b: Electron backscattered image of S. Domingos weathered product showing the area of Figure 5- X-Ray map

WDS intensity maps are possible and can be effective in understanding spatial distribution of elements in slags, but care must be taken in order to check possible peak and/or background overlaps However the high peak to background ratio of WD spectrometers allow in general to obtain the type of information needed. In this work quantitative analysis was performed using 15KV, 10nA for most phases with 20s counting times. Wavelength – dispersive maps we used 15kV and 70nA and 20ms dwell time. These operating conditions proved to be sufficient for observing all selected elements. The mapping of lead was done using PETH crystal and TAPH was decided to map As to avoid peak overlap between PbLα and AsKα lines..

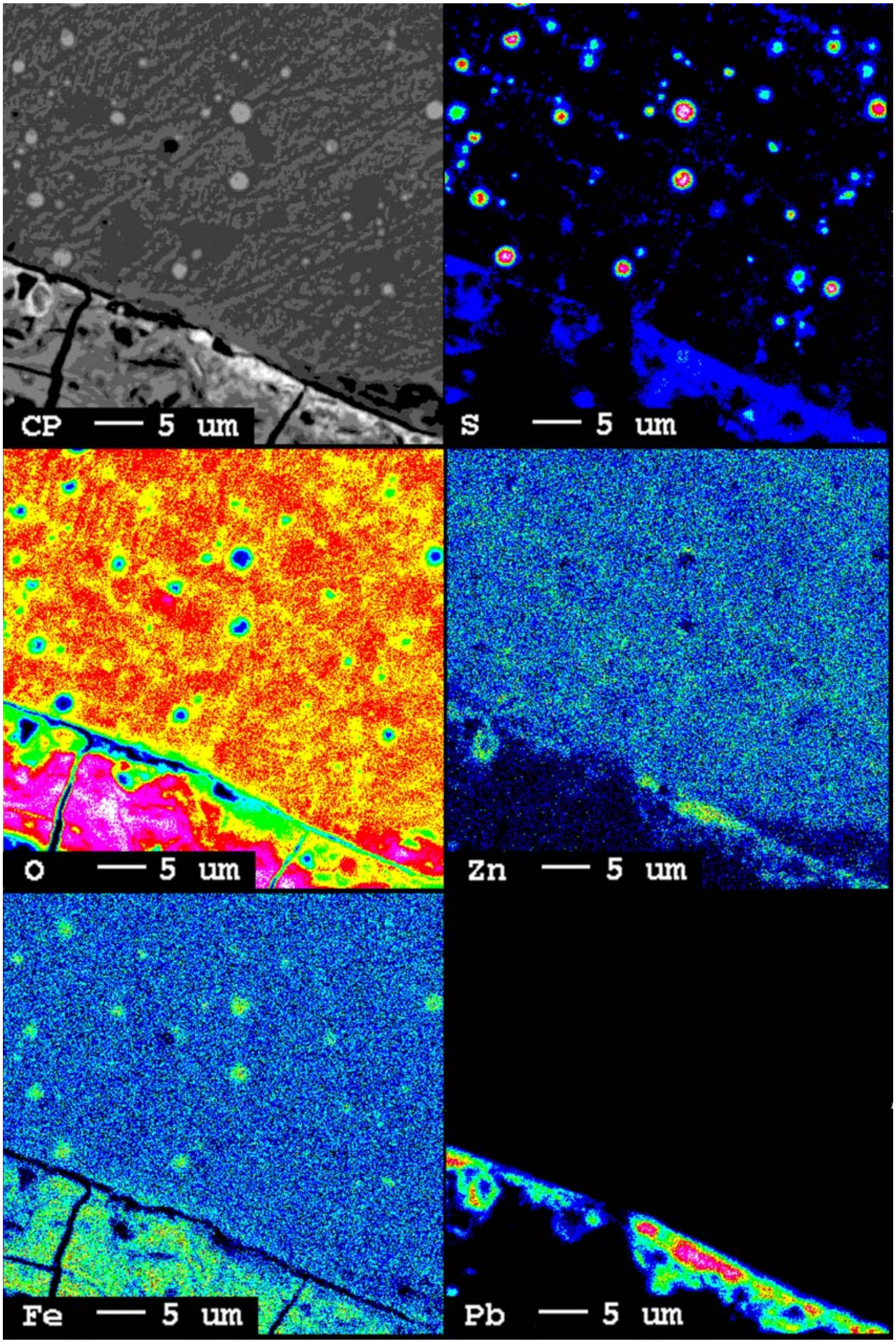
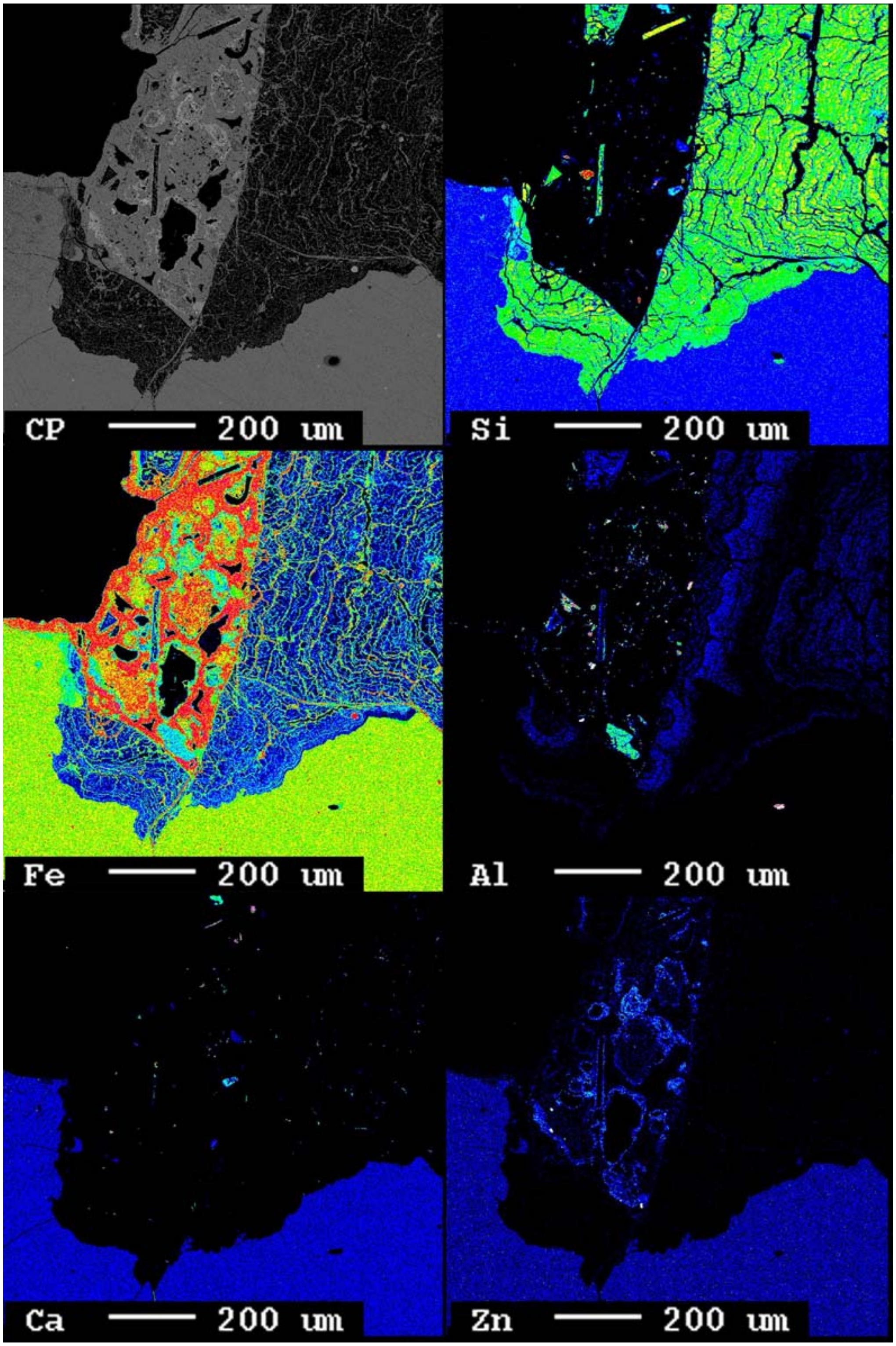

CP — 5 um
S — 5 um
O — 5 um
Zn — 5 um
Fe — 5 um
Pb — 5 um

Figure 4: X-Ray map of the outer area of a slag, showing a iron, lead and arsenic rich deposit (1700∗magnification)



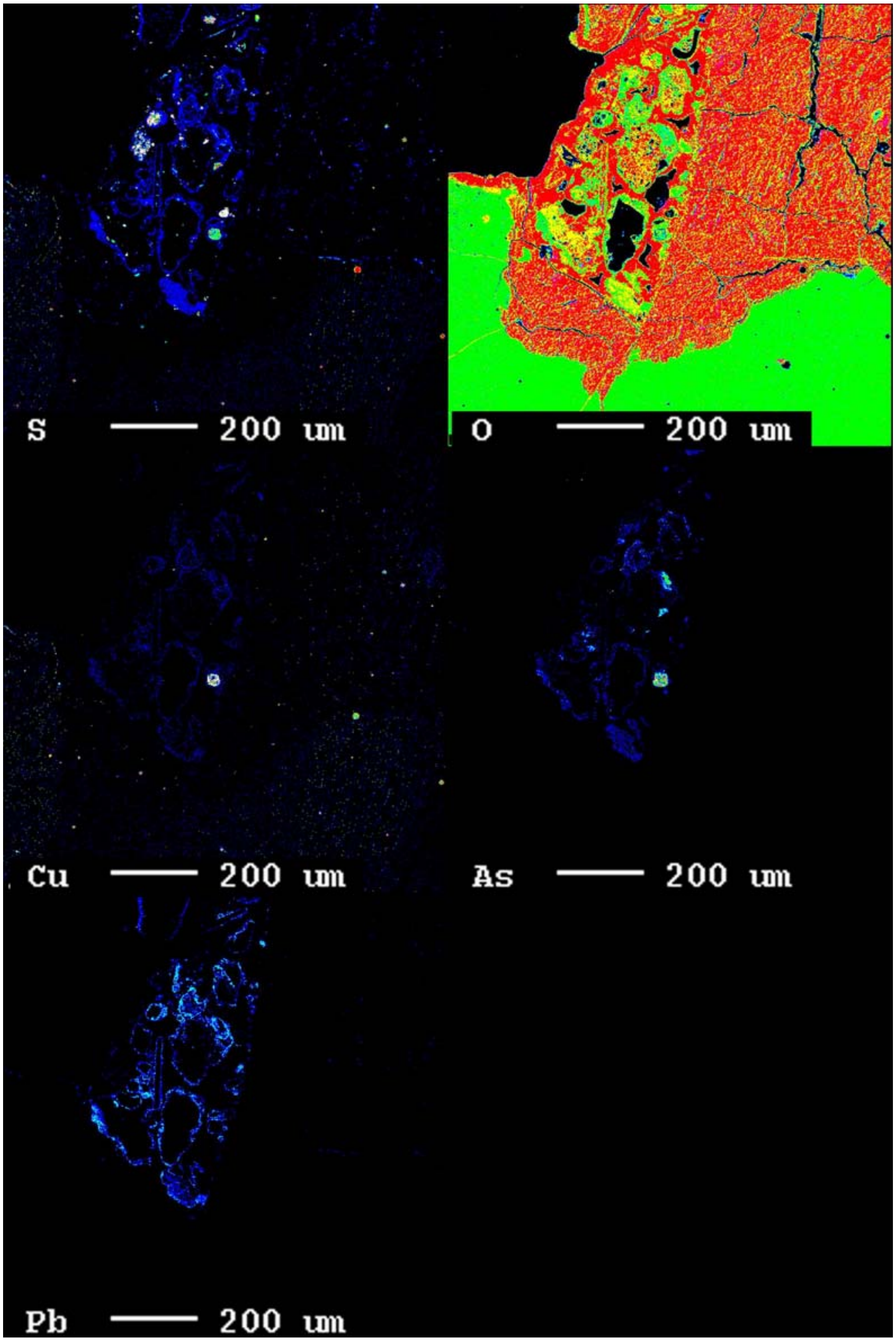

S
200 um
O
200 um
Cu
200 um
As
200 um
Pb
200 um

Figure 5- X-Ray map of weathering products and unweathered slag (lower zone) showing the relative distribution of Si, Fe, Al, Ca, Zn, S, O, Cu , As, Pb. It is visible alternating iron and silicon zones and sulphates areas. The last ones coincide with Pb and As enrichments.

Results

The weathering products involve the unweathered slags. These exterior zones are characterized by alternate silica and iron rich zones. The composition of different phases of slags varies considerably. Major elements vary composition within the following ranges:

Wt%	Unweathered slags	Weathering silica rich products	External iron rich products
SiO2	35,25 - 45,24	65,38 - 70,20	1,18- 2,95
CaO	1,05 - 12,6	0,06 - 0,27	0,02 - 0,04
FeO*	37,94 - 54,87	4,81-12,2	33,74 - 71, 48
S	1,13 - 2,57	0,5 - 3,1	1,42 - 7,31

* Part of the calculated FeO is not combined with oxygen but with sulphur

The micrometric spherules of sulphides were also analysed and major elements have compositions that fall within the following ranges S (23,52 – 34,75 %), Fe (41,97 – 63,87%), Zn (0,1 – 8, 67%), Cu (0,98- 16,11%), Pb (0,04- 0,45/%).

One aspect that is revealed immediately after the 2 maps observation (fig. 4 and 5) is that Zn and Ca are not retained by secondary phases. Arsenic, lead and sulphur are occurs together probably in a sulphate phase. In the unweathered slags the sulphides concentrate S, Cu and Fe (Fig 4).

These results complement those previously reported [4], and are based on the same type of samples.

Concluding remarks

In secondary phases iron is retained in oxyhydroxides and lead and As (fig. 4) precipitate as sulphates (enriched in S and O). The mutual exclusory character of Si and Fe is visible Aluminium is associated to the Si and Zn and Cu seems to be retained by iron oxide compounds.

The geochemical behaviour of the highly pollutant metals Pb and As demonstrates the potential role of the neoformed phases in control their dispersion. The seasonal stability of sulphates (precipitated in the summer and dissolved in winter) is an additional factor that must be considered in future studies about the dynamic of metal contamination by abandoned mines.

The sulphide abundance inside slags, observed at the images and maps and confirmed through analysis, is visibly high. In particular, there are innumerous micrometric spherules, which, once at the surface are easily leachable. During rainy seasons, the weathered products are transported along watercourses contaminating soils and water streams. It is a continuous process along the years and constitutes a serious environment aggression with direct consequences to the health, moreover that recent studies alerted already to higher contaminant levels at the old mine area and of human scalp hair[3].

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[2] Álvarez-Valero A.M, Pérex-Lopez, Matos, J. Capitán, M. A., Nieto J.M., Sáez R. J., Delgado M.m, Carabalho M., Potential environmental impact at São Domingos mining district (Iberian Pyrite Belt, SW Iberian Peninsula): evidence from a chemical and mineralogical characterization (2008), Environ Geol, Vol 55 (8), pp 1797

[3]Pereira R, Ribeiro R, Gonçalves F (2004) Scalp hair analysis as a tool in assessing human exposure to heavy metals (S., Domingos mine , Portugal) Sci. Tot Environ., 327, 81-92

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