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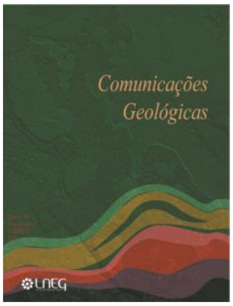
Geochemical exploration and assessment of environmental impacts in the Portuguese sector of the Iberian Pyrite Belt



Prospeção geoquímica e avaliação do impacto ambiental no setor português da Faixa Piritosa Ibérica

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Abstract: This work intends to briefly report the history and application of geochemical exploration techniques in the Iberian Pyrite Belt (IPB). The use of geochemistry in IPB for exploration purposes started in 1950's. Together with geophysics, the soil geochemical exploration surveys performed over several decades were responsible for important discoveries such as Carrasco and Feitais ore-bodies. However, the continuous development of analytical methods and the progress in data processing/modelling led to significant changes in the planning of sampling surveys, and their specific objectives, as well as in the accuracy of geochemical anomalies definition and corresponding interpretation. As a consequence, the number of samples involved in each survey was significantly reduced, but the chemical elements analysed with improved detection limits were considerably extended; additionally, geochemical anomalies were better resolved. Notwithstanding this evolution, data obtained in early soil geochemical surveys (notably by the Serviço de Fomento Mineiro) are still useful in the development of preliminary approaches at a regional scale. Over the years, many studies were made for exploration and environmental assessments, the most relevant of them reported in this chapter. Natural distributions of chemical elements were also identified in these studies as background (if pristine conditions are present) or baseline (depending how disturbed is the area covered by the sampling survey) values. Large part of IPB was, and still is, subjected to poly-metallic mineral exploration or mining, being also the focus of environmental evaluation and/or remediation projects on particular areas that, being the target of long-lasting human intervention, represent paradigmatic case-study examples. The exploration and exploitation works carried out by national and foreign private companies were, and still are, very important for innovative achievements in IPB along with copious contributions from the Portuguese R&D public institutions. Presently, LNEG possesses a vast quantity of geochemical data that can be provided for companies that wish to start their activity in the IPB; some of these datasets are compiled to a unique integrative map also presented in this work. Stream-sediments geochemistry, hydrogeochemistry and lithogeochemistry (of outcropping rock and drill-core samples) represent also important sources of geochemical data in regional or detailed studies over specific target areas in the IPB. However, these techniques are beyond the scope of the present paper which aimed at providing a general overview of the importance of soil geochemistry studies in the current knowledge of the IPB.

Keywords: Geochemical exploration, environmental impact, Iberian Pyrite Belt, mining taillings resources.

Resumo: A geoquímica é aqui abordada através da história da sua utilização na Faixa Piritosa Ibérica (FPI) e correspondente influência na evolução do conhecimento sobre os recursos minerais, distribuição natural dos elementos químicos e avaliação ambiental desta importante província metalogenética. Ao longo do tempo usaram-se na FPI técnicas analíticas cada vez mais precisas para determinar a concentração de um número crescente de elementos químicos. As campanhas de prospecção geoquímica tornaram-se assim progressivamente mais dispendiosas, levando à redução do número de amostras colhidas e analisadas em cada expedição. Consequentemente, no início da década de 1990, foi abandonado o uso de redes densas de amostragem de solos, muitas vezes elaboradas segundo uma esquadria retangular, como prática de rotina em campanhas de prospeção estratégica e tática, desenvolvidas pelos serviços do Estado vocacionados para este tipo de estudos, nomeadamente o Serviço de Fomento Mineiro (SFM). Reconhece-se, no entanto, que mesmo com um número reduzido de elementos químicos e baixa resolução analítica, a elevada densidade de amostragem combinada com diversas técnicas de geofísica desempenhou papel crucial na descoberta de jazigos de sulfuretos maciços na FPI, como são exemplo as massas Carrasco e Feitais em Aljustrel. Presentemente, as atividades de prospeção são maioritariamente desenvolvidas por empresas mineiras com contratos de pesquisa outorgados pelo Estado Português. O Laboratório Nacional de Energia e Geologia (LNEG) é o atual depositário de uma vasta informação de estudos geoquímicos, com destaque para um grande volume de dados produzido pelo SFM e por empresas. As bases de dados do LNEG são frequentemente requisitadas para efeitos de reavaliação de setores estratégicos da província e, em alguns casos, para reprocessamento de dados e reanálise de amostras físicas existentes em arquivo. Estudos geoquímicos desenvolvidos em áreas específicas da FPI são apresentados sumariamente neste artigo, abordando a importância do mapeamento geostatístico multivariado e multifractal de dados de geoquímica, para além de contribuir para a definição dos fundos (concentrações) naturais dos elementos metálicos com interesse económico; isto é, procurando identificar critérios objetivos úteis à separação entre o fundo geoquímico, o nível de referência e a anomalia. Todos estes estudos revelam que as formações constituintes do Complexo Vulcano Sedimentar (CVS - Devónico Superior – Carbónico Inferior) são fontes de metais como o Cu, Zn e Pb, podendo haver ainda alguma contribuição das sequências de metassedimentos pertencentes ao Grupo Filito-Quartzítico (Devónico Médio - Devónico Superior) e ao Grupo do Chança (Devónico Superior). Após um período de intensa prospeção e pesquisa mineral até finais dos anos 90 seguiu-se cerca de uma década e meia de abrandamento desta atividade na Europa, a qual foi, na FPI, gradualmente substituída por estudos de diagnóstico ambiental, procurando responder a novas inquietações sociais e políticas. Alguns desses estudos são também abordados de forma sumária neste capítulo, salientando os que contribuíram para a identificação e caracterização dos principais centros mineiros da FPI, geradores de grande volume de resíduos mineiros e importante drenagem ácida. Salientam-se ainda os sítios da província onde a atividade mineira decorreu por longo período de tempo (ex. S. Domingos, Aljustrel, Lousal e Caveira), em épocas em que o impacto ambiental não fazia parte das preocupações sociais, políticas e económicas das empresas mineiras e das entidades reguladoras. Nestes mesmos locais, e muito recentemente, como resposta à necessidade conjunta de tratamento/valorização de resíduos e salvaguarda da segurança de abastecimento de matérias-primas minerais na Europa (reduzindo a sua dependência externa e fomentando o seu crescimento económico), outros estudos geoquímicos têm vindo a ser realizados. Estes visam a identificação de novas oportunidades e mercados para os resíduos mineiros históricos, considerando-os como recursos secundários de matéria-prima que, por vezes, contêm quantidades acessórias de metais escassos e valiosos, alguns especialmente importantes na manufactura de componentes da "alta tecnologia". A prospecção geoquímica não se restringe à geoquímica de solos, muito embora o presente artigo lhe seja inteiramente dedicado por a mesma representar uma abordagem geral dos trabalhos desenvolvidos na FPI, ao longo de mais de meio século.

Palavras-chave: Prospeção geoquímica, impacto ambiental, recursos em escombreiras mineiras, Faixa Piritosa Ibérica.

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1. Introduction

Geochemical exploration methods were applied for the first time in the Iberian Pyrite Belt (IPB) in 1954, shortly after the consolidation of their modern foundations (*e.g.* Hawkes, 1957; Hawkes and Webb, 1962). These regional-scale exploration surveys were carried out together with geophysical (gravimetric, magnetic and electric) inspections by the 1st "South Brigade" of the Serviço de Fomento Mineiro (SFM) and represented a significant progress in mineral exploration activities all over the country. At the same time, a dedicated laboratory was installed at the SFM facilities in Beja to enable an optimised processing of samples (soils and stream-sediments) and their analysis for base metals (mainly Cu, Zn and Pb) by colorimetric methods and complementary wet chemical analytical procedures (*e.g.* Borralho, 1970).

The so-called strategic geochemistry surveys designed and performed by SFM in the nineteen fifties, as well as their extensions, were completed in the following two decades. They relied on regional, high-density stream-sediment (or soil) sampling grids to delimit anomalous sources potentially tracing the *locus* of ore-forming systems. Various regional geochemical maps were produced and interpreted at that time, providing ever improving images of the base metals distribution over large areas of the Portuguese mainland, in what concerns background values and confirmed geochemical anomalies (within the uncertainty limits imposed by the errors inherent to the analytical methods used).

In a second detailing stage, positive geochemical anomalies overlaping with specific geophysical signatures were examined by means of thorough (tactic) exploration surveys, consisting of detailed geological reconnaissance coupled with systematic soil-geochemistry and additional geophysical studies. For these refining surveys, soil samples were collected at the 100 m ×100 m (sometimes, 50 m ×50 m) grid points used for gravimetric surveys. Outstanding results of this methodology in the IPB are the identification of Aljustrel-Carrasco and Feitais mineralised areas (Direcção Geral de Geologia e Minas, 1990). Later, as in many other regions around the World, other geochemical approaches (such as multi-element analysis and isotope geochemistry for soil, stream-sediments and rock samples) were gradually introduced, projected the mineral exploration in the IPB under a new light (*e.g.* Asarco, Billinton, Sociedade Mineira Rio Artezia geochemistry exploration surveys). During this period, the accuracy of the analytical methods was greatly improved and numerical procedures to handle ever increasing geochemical databases were introduced. As a result, mineral exploration became much more expensive, and there was a considerable reduction of the areas covered by new sampling grids. In fact, in the last two decades, systematic exploration surveys in the IPB were confined to commissioned areas and, with few exceptions, have been carried out by the industry in order to comply with State demands and legal obligations included in the exploration permits. All the exploration data produced since the fifties were deposited in the Portuguese Geological Survey. Presently, this role is fulfilled by the Laboratório de Geologia e Minas included in LNEG, which, upon request, will make available for perusal the vast database meanwhile accumulated.

Old mining works were pursued under a superseded perspective (the supply paradigm) and left an important legacy of environmental problems largely responsible for the negative image commonly projected onto the mineral industry. A significant negative impact was observed in 1998 linked to the Aznalcollar mine dam rupture (Andalusia) and related extreme chemical impact in the downstream area, including the Doñana Natural Park. In the IPB, this is particularly conspicuous in places where long-term, although discontinuous, exploitation of sulphide ores took place leaving behind large accumulations of oxidizing sulphide-bearing mine wastes. Well known examples in Portugal are the S. Domingos, Aljustrel, Lousal and Caveira mines (*e.g.* Oliveira, 1977; Batista *et al.*, 2000; Ferreira da Silva *et al.*, 2005; Alvarez, *et al.*, 2008; Mateus *et al.*, 2008; Abreu *et al.*, 2010; Candeias *et al.*, 2011; Maia *et al.*, 2012). Acid mine drainage, particulate dispersion from waste dumps and misuse of the mine waste materials by local authorities, are the main problems identified so far in these sites; they contribute to the physical-chemical dispersion of metals/metalloids and generate superficial anomalous haloes of variable magnitude unrelated to any mineralization of the country rocks (*e.g.* Matos and Martins, 2006). In the last twenty years, the environmental impact of old mining works was extensively studied and created a powerful argument for the enforcement of a long set of high-demanding rules to be fulfilled by the mining industry all over the European Union (*e.g.* Mine Waste Directive, 2006/21/EC). This legal framework (designed to cope with the environmental problems posed by abandoned mines and to stall the need to spend large amounts of money to recover extant and future sites), together with a long period of low prices for many commodities, contributed to a significant investment decrease of the mining industry in the IPB. Signs of an inversion of this negative cycle started in 2005, and by 2009 the recovery was fully consolidated; by the end of 2012, the legal permits for mineral exploration in the IPB covered an area of about 2,500 km^2. Chemical elements dispersion around abandoned mines may also create difficulties in soil and stream-sediments geochemical data interpretation due to the possible generation of false anomalies (*i.e.* spatial clusters of relatively high contents of a certain element, or a set of elements, tracing some kind of Human-disturbed source). Rehabilitated mining areas like Aljustrel and Lousal (EDM rehabilitation project) are characterized by waste movement and new exotic materials used in tailing covering (*e.g.* transported soils used in impermeable layers in the top of the Algares, Aljustrel mine sector). Indeed, false geochemical anomalies of target elements in soils and stream-sediments can be expected due to heterogeneous spreading of materials from waste piles and tailings to areas outside the old mining sites. Such heterogeneous dispersion stems from differences in the geochemical behaviour of the elements involved, for instance formation of specific organo-metallic complexes. Furthermore, adsorption rates may vary as a function of changes in pH-Eh conditions and differential behaviour in presence of different soil clay minerals and Fe and Al oxide-hydroxides, organic carbon from microbial activity. These differences may also be the result of mineralogical and textural differences of the regolith. Therefore, to avoid this problem, geochemical collectors had to sample deeper soils and avoid high organic content alluvial sediments, as well as oxidised cups. The present paper intends to briefly report the history and application of geochemical exploration techniques in the Iberian Pyrite Belt.

2. Natural geochemical distributions and their relationship to ore-forming systems

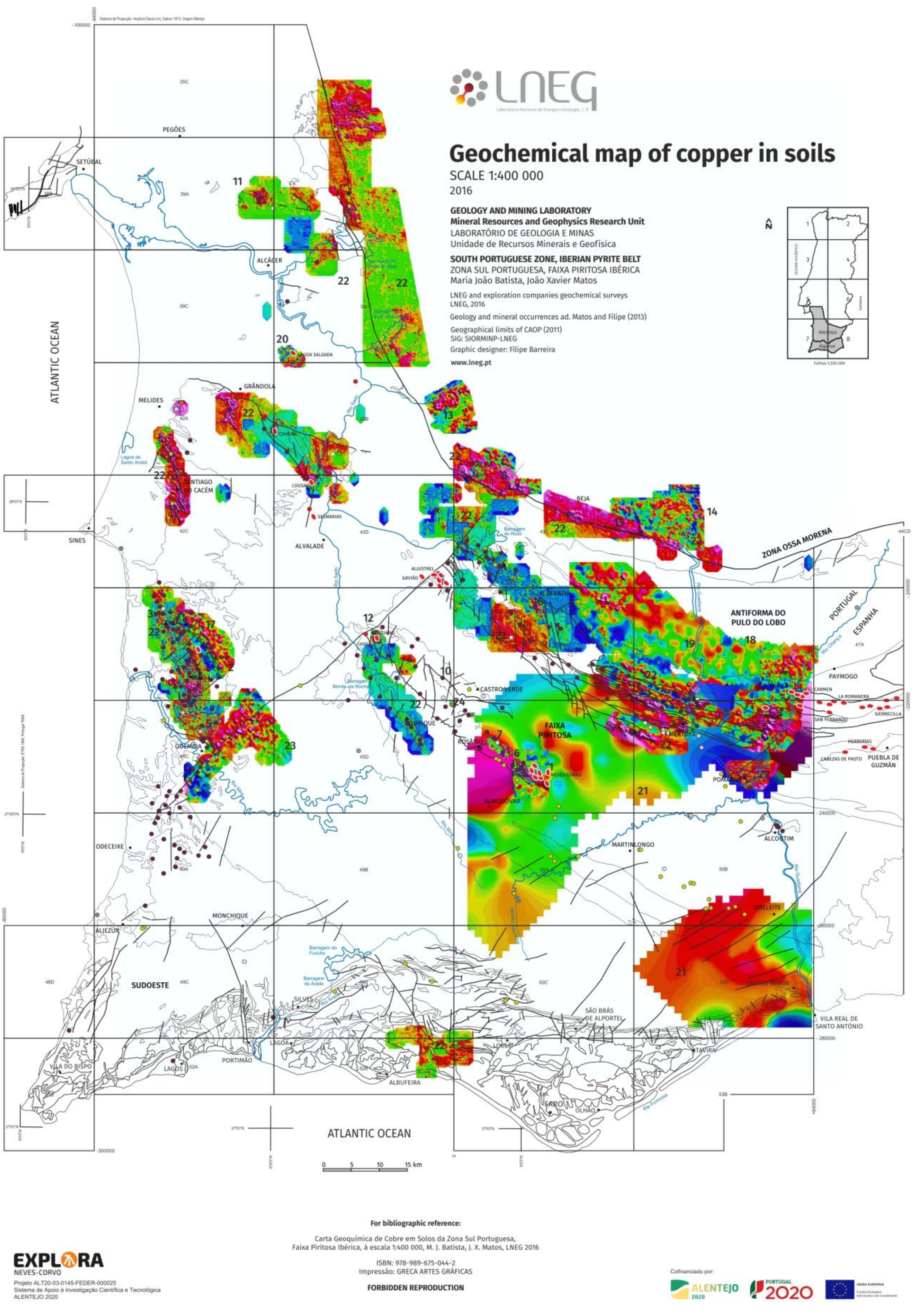
The main purpose of any geochemical exploration survey is the detection of positive (multi-)element anomalies that trace the existence of natural sources enriched in mineral phases bearing those very same elements. Anomaly distribution is a simple portrait of the spatial compositional variation induced by the local or regional architecture of the geological substratum (which may host ore bodies of variable size, constitution and morphology) strongly deformed by the physical-chemical dispersion mechanisms occurring at each site. The compositional variability of the substratum may be of primary or secondary origin, but, whatever the case may be, the observed anomalies may either stand over their sources or appear somewhat displaced by surface mechanisms; anomaly location *per se* is thus an unreliable indication of the location of a mineralized rock volume, although worth being investigated. Despite of this, geochemical anomalies always indicate that in a location, which can be determined by careful geochemical observation and reasoning, there is a source of chemical elements that differs significantly from the surrounding country rocks. However, that source does not need to be an orebody and may be simply an accumulation of metal-bearing detritus acted upon by weathering and supergene physical and/or chemical dispersion of variable intensity. Mutual interaction of all these processes may thus lead to the formation of (sub-)superficial anomalies which represent derivative haloes that may be located far away from their original sources, due to the heterogeneous solubility of many (primary or secondary) mineral phases and subsequent selective mobility of many elements (Batista *et al.*, 2012d). Special care must be taken whenever very old mining activities have brought large amounts of materials to conditions very far away from equilibrium and the mining works themselves are already largely obliterated and so difficult to recognise. For all these reasons, attention should be paid not only to the concentrations of the elements of interest (and associated pathfinders), but also to the conditions that may determine its chemical behaviour during dispersion processes (primarily, pH, Eh, solubility of salts, co-precipitation, sorption, formation of complexes and colloidal solutions). In addition, the influence of the geomorphic and meteorological features of the surveyed region should not be ignored, as they have a significant impact in critical attributes displayed by regolith/soil profiles and hydrological flows. In the Portuguese IPB sector, soils are mostly incipient and supported by an ill-developed regolith; the topography is dominated by soft rolling hills and plains locally disrupted by sharper peaks mainly due to differential erosion controlled by lithological and structural factors. Under a Mediterranean climate with an increasing influence of the Atlantic Ocean towards the West, the soils (mostly Leptosols) are potentially vulnerable to erosion and desiccation, hindering practices of intense arable farming. Nevertheless, the strong seasonal character of run-off, the landscape characteristics and the native vegetation cover impede, in general, considerable soil-erosion. Near the western and southern Atlantic coast large areas are covered by forest (quercus, eucalyptus and pinus) that permits moderate soil preservation (*e.g.* Grândola, Cercal, Monchique and North Algarve mountains) (Pena *et al.*, 2020).

Anomaly separation requires an unambiguous identification of threshold values, which mark the upper and lower limits of “natural” variation (geochemical background) showed by a particular population of data (elements concentration). However, threshold determination is not a trivial task and in many common applications threshold values are set arbitrarily, although various procedures to quantify them objectively do exist (*e.g.* Hawkes and Webb, 1962; Granier, 1973; Tukey, 1977; Barbier *et al.*, 1979; Reimann *et al.*, 2005). Conventional univariate and/or multivariate statistics, complemented by interpolation methods, are commonly used tools (*e.g.* Huber, 1981; Hampel *et al.*, 1986; Rousseeuw and Leroy, 1987; Barnett and Lewis, 1994; Reimann and Filzmoser, 2000; Dutter *et al.*, 2003). Alternative approaches involve multi-fractal models (*e.g.* Cheng *et al.*, 1994, 1996; Gonçalves, 2001; Gonçalves *et al.*, 2001; Jesus *et al.*, 2013), which allow the prediction of local continuity of concentration values, particularly when variogram or correlogram analysis is not usable (Agterberg, 2012). The use of more than one media of superficial compartments analysed at regional scale to separate anomalies was tested using a generalised multivariate regression called Partial Least Square Regression modeling the Y (bedrock chemical concentrations-independent variables) in X matrix (soil chemical concentrations-dependent variables) (Selinus and Esbenson, 1995). Another example of use of different media was successfully applied in the Neves Corvo mine region of the IPB. In this case, a multiple regression analysis in stepwise mode was applied to two sets of soil samples from the same sites, which were collected in different time periods and jointly analysed. In this case, multi-collinearity was overcome with mean comparison of populations to assure the independency of the X-matrix variables (Batista *et al.*, 2012a). Multi-element anomaly separation and threshold computation using area-concentration multi-fractal models were recently used to investigate: (1) a wide Cu, Zn, Pb and Co dataset of 4,230 stream-sediment samples covering the whole South Portuguese Zone, where the IPB is included (Feliciano *et al.*, 2008; Gonçalves and Mateus, 2019); (2) the Cu, Zn, Pb, Co, Cr and Ni concentrations in stream-sediments collected in 1,034 sites by the Sociedade Mineira Rio Artezia Lda (SMRA), along an irregular grid covering the NE domain of IPB (Luz *et al*., 2012); (3) the Cu, Zn and Pb spatial distribution of contents in soils picked by SMRA in 4415 sites of regular grids extending across the NE domain of IPB (Luz *et al.*, 2013a); and (4) the Cu and Zn soil-geochemistry making use of the SFM database reporting concentration values for 13,000 sites (Luz *et al.*, 2013b; Luz *et al.*, 2015) located in the same IPB domains. Batista *et al.* (2001) and Batista (2003) used as threshold, in the soils of the Neves Corvo mine area, the first order anomalous values obtained from box-and-whisker plot, which is

$$L1 = Q_3 + 1.5H$$

where $H = Q_3 - Q_1$ and Q_3 and Q_1 correspond to the third and the first quartiles, respectively.

Figure 1 contains a collection of soil Cu geochemical maps available for the IPB superimposed to a simplified geological map of Southern Portugal (Batista and Matos, 2016 and geology ad. Matos and Filipe Eds., 2013).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Geochemical map of copper in soils
SCALE 1:400 000
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SOUTH PORTUGUESE ZONE, IBERIAN PYRITE BELT
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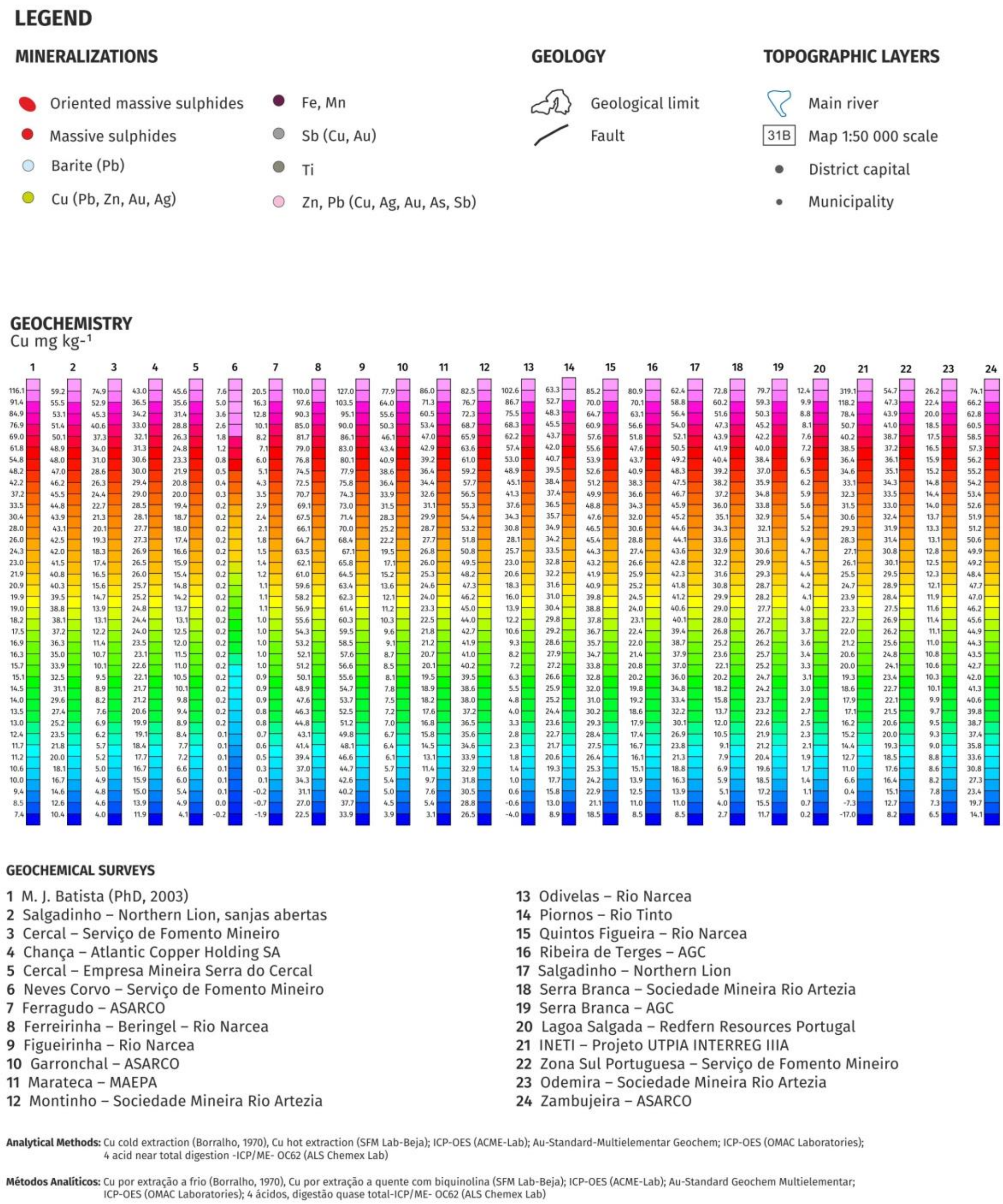

Figure 1. Collection of soil copper geochemical maps available for the IPB superimposed to a simplified geological map of Southern Portugal (Batista *et al.*, 2016 and geology ad. Matos and Filipe Eds., 2013). Numbered colour scales correspond to the different surveys and the corresponding range of values represent a different campaign.

Figura 1. Conjunto de cartas de Geoquímica de solos da FPI sobrepostas a uma carta geológica simplificada (Batista *et al*., 2016 e geologia ad. Matos and Filipe Eds., 2013). As escalas de cores numeradas correspondem a diferentes amplitudes de valores e a diferentes campanhas de prospeção.

The copper geochemical maps result from data obtained by SFM [total base metals and Cu by cold extraction with dithizone, (C13H12N4S) and hot extractions where Cu and Zn were obtained with biquinoline (C18 H12N2)]. In the same maps, data obtained from recent surveys performed by industry are also plotted, representing Cu contents measured with modern analytical procedures (that include ICP methods), as demonstrated in the diagram of figure 2. Despite of differences found in concentration values, which reflect distinct analytical sensitivities and contrasting responses of the analytical methods used, it is always evident that geological formations belonging to the Volcano-Sedimentary Complex (VSC, Upper Devonian – Lower Carboniferous) display higher Cu contents than those of the Baixo Alentejo Flysch Group geological formations. These are represented by turbidite sediments. In detail, at Pomarão antiform structure (see Fig. 3), the SFM copper soil geochemistry shows a clear anomaly associated with the VSC hematitic rich purple shales of the Borra de Vinho Formation. Similar correlation is observed at Cidrão and Serrinha IPB sectors (Matos et al., 2009); these are represented by turbidite sediments.

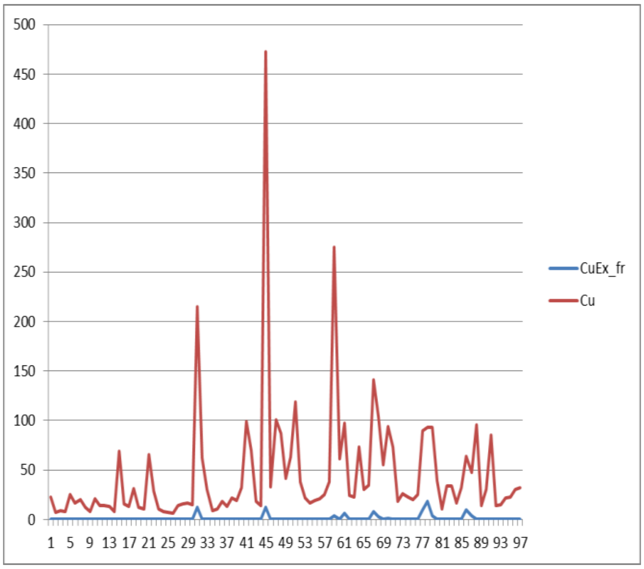

Figure 2. Comparative diagram of Cu (mg kg^{-1}) contents measured by colorimetry of cold extraction solutions (blue line; data compiled from LNEG archives) and by ICP-OES following *aqua regia* extraction (red line) in the very same specimens (the latter using archived samples, about 20 years after the sampling survey).

Figura 2. Diagrama comparativo de concentrações de Cu (mg kg^{-1}) medido por colorimetria por extração a frio (linha azul; dados compilados do arquivo do LNEG) e por ICP-OES após extração com *aqua regia* (linha vermelha) nas mesmas amostras (as últimas utilizando as amostras de arquivo, cerca de 20 anos depois da campanha de amostragem).

A systematic comparison of results from soil geochemical surveys with different aims shows that anomalies overlap, although they become better resolved when tighter sampling grids and more accurate analytical methods are used (Fig 4). Therefore, the main reasons for the success of strategic and tactic surveys conducted by SFM was definitively their dual geochemical/geophysical character and the very high sampling densities used for the geochemical sampling.

Numerous prospects were identified with this internally consistent methodology, some of them including orebodies of variable geometry, dimension and grade, later confirmed by drilling (see the IPB exploration drill-holes location in Matos and Filipe Eds., LNEG 2013). Several exploration success examples can be referred in the Portuguese IPB sector, like the Serrinha Marateca region case study (LNEG surveys developed to Maepa Company; Matos *et al.*, 2009; Ramalho and Matos, 2009) where sulphide veins were intersected by the SE11-01 Maepa drill-hole, in an exploration target zone defined by favourable geology (felsic VSC volcanics with silica + sericite alteration) + electromagnetic conductors + Cu, Zn, Pb, As and Mn soil geochemistry anomalies. Other positive example is the Valcôvo sector (Serra Branca region in the northern IPB; Castelo Branco and Sá, 1997; Luz *et al*., 2013a, b), where thrust fault-controlled sulphide mineralizations were intersected by the VC2 SMRA drill hole, following gravimetry + Cu, Zn, soil geochemistry anomalies. Other examples can be referred like drill-holes performed by SFM (Carvalho, 1979; Queiroz *et al*., 1989) and EMSC at Cercal area, which were planned to identify the sources of geochemical anomalies in favourable geological and geophysical scenarios. At Caveira mine area, the Cu/Zn soil geochemistry mapping shows the enrichment of Cu in the upper

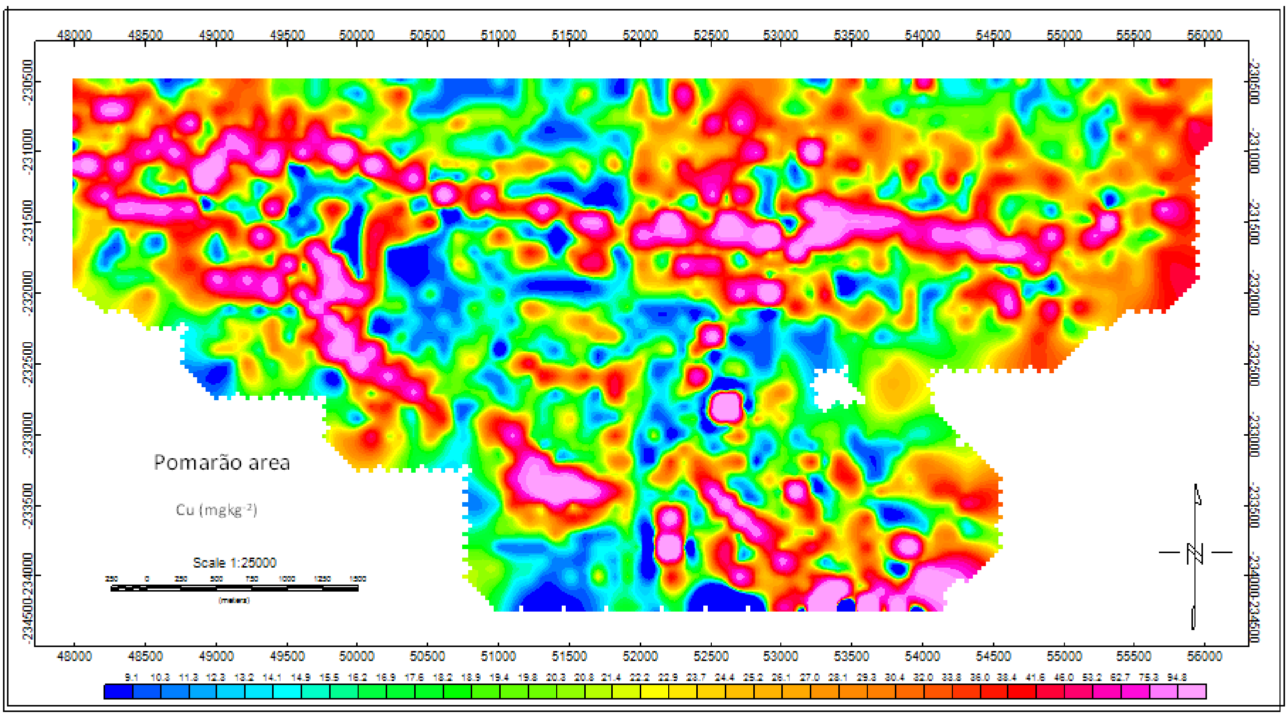

Figure 3. Copper distribution in the Pomarão Anticlinal formations.

Figura 3. Distribuição do cobre no anticlinal do Pomarão.

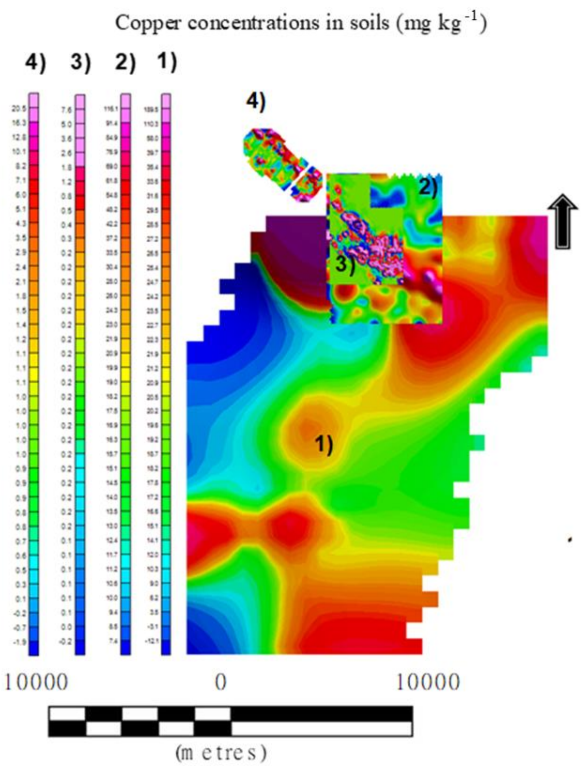

Figure 4. 1) low-density and high-resolution Cu-soil geochemical map (UTPIA project, Batista *et al*., 2010); 2) high-resolution Cu-soil geochemical map based on a 500x500 m sampling grid (SFM) established over the Rosário-Neves Corvo Volcano-Sedimentary structure prior to the discovery of the Neves-Corvo ore-system and analysed recently (Batista, 2003); 3) high-density (100 x 100 m) sampling grid (SFM) and low-resolution Cu-soil geochemical map over the same Rosário-Neves Corvo structure; 4) Cu-soil geochemical map ASARCO data from 1996 to the northwest of the same structure (ASARCO, Pacheco *et al*., 1996).

Figura 4. 1) mapa de Cu em solos com baixa e elevada densidade (UTPIA project, Batista *et al*., 2010); 2) mapa de Cu de elevada resolução analítica em solos numa malha de 500x500 m (SFM) sobre a estrutura do Complexo Vulcano-Sedimentar Rosário-Neves Corvo anteriormente à descoberta do sistema mineralizante de Neves-Corvo e analisados recentemente (Batista, 2003); 3) mapa de Cu de baixa resolução analítica e elevada densidade (100 x 100 m; SFM) sobre a mesma estrutura Rosário-Neves Corvo; 4) Mapa de Cu em solos de área a noroeste da estrutura do Complexo Vulcano Sedimentar Rosário-Neves Corvo (ASARCO, Pacheco *et al*., 1996).

Volcano-Sedimentary Complex units, represented by volcanic sediments, shales with nodules, purple shales, cherts and jaspers, black shales and important mafic intrusive and extrusive volcanics (Matos *et al*., 2015). The Zn data reflect the development of supergene enrichment with high concentration in areas close to *gossan*. According to these authors, at Caveira, the geology-gravity-geochemistry data combination used could correspond to a successful tool in predictive studies.

Similar conclusions were reached through the re-assessment of the SFM and/or the SMRA Cu, Zn and Pb-soil geochemical data available for the NE domain of the IPB (Luz *et al.*, 2013a, b). In these works, threshold computation and anomaly separation were carried out using the area-concentration multi-fractal model. The resulting anomaly maps show that volcanic rocks represent the prevailing sources of Cu and, to a lesser extent, Pb. The main sources of Zn are associated with sediments of the Phyllite-Quartzite Group (IPB) and of the Gafo and Atalaia formations (Chança Group included in the Pulo do Lobo Terrane, PLT). It was also concluded that, in this region, the upper limit of background Cu, Zn and Pb values in soils derived from PLT metasedimentary sequences are of the order of 20, 55 and 20-30 mg kg^{-1}, respectively. Significant contributions from volcanic rocks, common in soils developed over the IPB Volcano-Sedimentary Complex, modify the Cu-, Zn- and Pb-soil contents and thus the corresponding threshold values, which become scattered in the intervals 25-45, 40-60 and 20-90 mg kg^{-1}, respectively. The lower limit of more significant Cu-, Zn- and Pb-soil anomalies are within the 30-50 mg kg^{-1}, 90-115 mg kg^{-1} and 45-60 mg kg^{-1} intervals, respectively, when metasedimentary provenance dominates, and within the 30-70 mg kg^{-1}, 70-90 mg kg^{-1}, and 33-100 mg kg^{-1} intervals when abundant volcanic-derived components exist. Proximity to mineralized sediments and volcanics is indicated by Cu, Pb and Zn soil contents above ca. 100 mg kg^{-1}, 120-150 and 250 mg kg^{-1}, respectively. Most of the anomalies display strong anisotropy and structural control because their ultimate origin result from chemical changes due to syn- to late-orogenic metal re-distribution within rock-domains subjected to strong deformation and hydrothermal activity.

In another study of elements concentration distribution in stream-sediments collected all over the NE domain of the IPB (Luz *et al*., 2012), anomalous Cu, Zn, Pb (as well as Cr) and Ni contents are usually confined to the 45-55 mg kg^{-1}, 100-120 mg kg^{-1}, 45-60 mg kg^{-1} and 55-70 mg kg^{-1} intervals, respectively, being around 30 mg kg^{-1} for Co. In these sediments, the regional threshold values are 20, 45, 30 and 15 mg kg^{-1} for Cu, Zn, Pb and Co, respectively. Anomalies in Cu, Zn, Pb, Co, Cr and Ni are delimited by first order local threshold values of 40, 94, 70, 21, 37, and 42 mg kg^{-1}, respectively. The most important anomalies are clustered to the ESE of the Trindade – Chança region, being also strongly confined. These anomalies reflect mixed contributions from country rocks, namely: i) volcanic units included in the Gafo Formation (Chança Group) and in the Volcano-Sedimentary Complex of the IPB, possibly complemented by metasediments belonging to the IPB Phyllite-Quartzite Group; ii) diverse weathering products resulting from mining exploitation activities in the old S. Domingos and Chança mines (massive sulphides exploitations); iii) hydrothermal infillings of different fault zones; and iv) mafic volcanic rocks included in the Pulo do Lobo Formation. Finally, it should be noted that there is a strong compatibility between the threshold values referred to above and those reported by Feliciano *et al.* (2008) for a stream-sediments database covering the whole South Portuguese Zone; for a general re-assessment of this dataset see also Gonçalves and Mateus (2019).

In the southern sector of the IPB different statistical methodologies combined with Pb isotopic studies were successfully applied in identifying the Pb sources in soils and *Cistus ladanifer* L. plants of the lower sector of the Guadiana River basin in both Portuguese and Spanish margins (Batista *et al*., 2013). Two geogenic and two anthropogenic sources of Pb were identified using Pb isotopes. Elevated Pb concentrations are mostly related to the occurrence of sulphide-rich ores, Volcano-Sedimentary Complex formations and mining. These are often put in evidence by multiple regression analysis (MRA). Nevertheless, caution was needed in interpreting statistical and isotopic results; therefore, the combination of both techniques was important. Elements such as Ca, Na, Cu and As, show higher concentrations in soils developed over different siliclastic metasediments belonging to the IPB Phyllite-Quartzite Group. Lead is enriched in soils above felsic volcanic rocks from the IPB Volcano-Sedimentary Complex, which has been identified by the relationship between topsoil median values of different lithologies and grand subsoil median values. In the same soil samples, Fe, As, Co, Ni and Cr contents are depleted. Translocation of Pb to the aerial parts of plants is insignificant in all the three plant species analyzed (*Cistus ladanifer* L., *Thymus vulgaris* L., *Lavandula stoechas* L. ssp. *luisieri*), except near

Table 1. Factorial analysis of PC extraction and identification of the Cu possible pathfinders in each area after re-processing data obtained in surveys conducted by ASARCO (Pacheco *et al*., 1996) and SMRA (Mora, 2001)

Tabela 1. Análise factorial de extração em CP e identificação de possíveis indicadores do Cu em cada área após reprocessamento de dados obtidos em campanhas conduzidas por ASARCO (Pacheco *et al*., 1996) e SMRA (Mora, 2001).

Area (% variance explained in the 1st and 2nd axis)	Total elements used in PCA	Correlated with the occurrence of Cu (> 0.7) and PC extraction using Kaiser criteria
Moitinhos (62%)	As, Ba, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Rb, S, Sc, V, Zn	(axis 2) As, **Cu**, Pb, Zn
Garronchal (54%)	Cu, Pb, Zn, Ni, Co, As, Fe, Mn, Ba, Cr, V, Al, Sr, Nb, Sc	(axis 1) **Cu**, Ni, Co, Fe, Mn, V, Al
Zambujeira (64%)	Cu, Pb, Zn, Ni, Co, As, Fe, Mn, Ba, Cr, V, Al, Nb	(axis 1) **Cu**, Zn, Ni, As, Fe, Cr, Al

mine sites, where lower pH of soil increases the Pb bioavailability (Batista, 2010).

The use of multi-element analytical data obtained in a single survey can be quite helpful in recognizing pathfinders for a given metal target. Recent studies carried out in the Moitinhos, Garronchal and Zambujeira areas (Tab. 1) and reveal that Cu-soil anomalies can be roughly traced by several pathfinders.

These were put in evidence by the analysis of Principal Components (PC) extracted through classical factorial analysis with *Varimax rotation* in order to maximize the variance and the application of the Kaiser criteria used to retain only eigenvalues above unity during PC extraction (Kaiser, 1960). The results, summarised in table 1, suggest that several elements may serve as proxies to anomalous bedrock Cu concentrations; however, the set of associated pathfinders will differ according to the composition of the bedrock and the local details of the processes that rule the selective chemical mobility of metals/metalloids in soil solutions and/or run-off and creek waters.

3. Geochemical imprints of historical mining: environmental impact and the use of mining wastes as secondary resources

The concept of "*geochemical baseline*" was officially introduced in 1993 (International Geological Correlation Program, IGCP Project 360) and refers to the variation of an element concentration in the superficial environment at a given time, therefore measuring the natural background and (diffuse) anthropic contributions (Salminen and Tarvainen, 1997; Salminen and Gregorauskiene, 2000). Geochemical multi-element baselines are therefore needed to evaluate the present state of the surface environment, providing also guidelines and quality standards for environmental legislation and political decision-making, especially in the assessment of contaminated soils (Darnley *et al*., 1995; Salminen and Tarvainen, 1997; Baize and Sterckeman, 2001). In Portugal, the geochemical database is incomplete and varies significantly for different regions and geological backgrounds, since most of the data were collected for mineral exploration purposes and do not meet the requirements set up internationally for establishing national environmental baselines (Ferreira *et al*., 2001; Inácio *et al*., 2008). Nevertheless, in many cases, the available geochemical data sets can be used to build various local/regional reference baselines, even if only in a tentative or rough way. That seems to be the case of the SFM geochemical surveys carried out in areas with (very) low agriculture activity and characterized by ill-developed regoliths, as happens in the IPB main areas; in these conditions, there is not much difference between topsoils and subsoils (usually at about 20-40 cm depth) provided that the fraction analysed is below 100 mesh. In fact, the (regional) threshold values computed for the NE domain of the IPB (Luz *et al*., 2013a, b) are in good agreement with the topsoil Cu and Zn median contents reported in Galán *et al*. (2008) for the IPB/South Portuguese Zone (SPZ) in Spain (32 mg kg^{-1} and 78.5 mg kg^{-1}, respectively). In the Spanish side of the SPZ, the highest median values of Cu (57.4 mg kg^{-1}) were found in topsoils derived from the IPB felsic igneous rocks; again, this is compatible with conclusions drawn above concerning threshold variations in function of rock type prevalence.

Mobility of chemical elements from soils to sediments resulting from upstream mines into the lower N-S sector of the Guadiana River Basin, located in southern Portugal and Spain, to the Atlantic Ocean was also studied. The geometric mean of Cu and Zn concentrations of soils and sediments was obtained in the same range of the previously presented concentrations (28 mg kg^{-1} and 37 mg kg^{-1} Cu in soils and sediments, respectively; 65 and 79 mg Zn kg^{-1} in soils and sediments, respectively). When relationships between upstream soils and downstream sediments are established, higher median values in upstream soils were observed for Co, Ni, K, Pb, Mn and Ti; on the contrary, Cu, Zn, Al, As, Ba, Br, Ca, Cr, Fe, Mg and Na contents are higher in downstream sediments. Lead was considered the less mobile element and Zn the highly mobile of the base metals in the lower Guadiana River (Batista *et al*., 2012d).

Some recent studies were also performed in the Neves-Corvo area to evaluate element cumulative enrichment in soils due to mining activities (Batista *et al*., 2012a). Soil samples collected by SFM in the early seventies (henceforth referred to as the first survey), preserved in the LNEG archive, were re-analysed, along with a new set of samples collected in the same locations (from now on referred to as the second survey) about 10 years after the beginning of Neves-Corvo exploitation (1988). Multi-element content distributions were characterised, including independent variables such as those revealing similar central tendency values (median, mean and mode) that may trace specific lithological sources: Al, Ca, Fe and Mn labelled as zero or one in samples derived from the Baixo Alentejo Flysch Group and/or the IPB Volcano-Sedimentary Complex, respectively. Further data analysis (stepwise regression modelling) of Cu contents displayed by soil samples from an undisturbed area of the first survey performed allowed a clear detection of the fingerprints of various parental rocks, within and around the area where the Neves-Corvo mine was built some years later. However, the separation between natural and mining-induced Cu concentrations was not clear-cut when samples belonging to the second survey were used in the previously calibrated model; indeed, background maps of the second survey maps still show signs of Cu contents due to mining activity instead of the background record only. Therefore, residual maps show a smaller area of mining-induced concentrations (Batista *et al.*, 2012a).

Despite of the difficulty in discriminating unambiguously the contribution of old mining works to geochemical anomalies in soils and stream-sediments that may also originate in the bedrock natural enrichment in the same elements as those liberated artificially, many studies have been developed in the IPB with the objective to search for innovative criteria and/or alternative methods to respond to such problem (*e.g.* van Geen *et al.*, 1997; Freitas *et al.*, 2004; Batista *et al.*, 2007; Abreu *et al.*, 2008; Álvarez-Valero *et al.*, 2008; Durães *et al.*, 2008; Abreu *et al.*, 2010; Pérez-López *et al.*, 2010; Luís *et al.*, 2011; Santos *et al.*, 2012, 2014). All these studies are fundamental for the analysis of risk assessment related to abandoned mining sites, contributing also to the appraisal of the net balance between active intervention (in order to mitigate/remediate the environmental impact) and natural attenuation processes.

According to the conclusions of a recently completed project regarding "Abandoned Mines" (Santos Oliveira, 1997; Santos Oliveira *et al.*, 2002; Matos and Martins, 2006; EDM and DGEG Report, 2011), the way how large mines operating in the IPB in the past were decommissioned led to environmental impacts of different nature and magnitude (mostly dependent on the methods used in ore exploitation and processing, as well as on the dimension, composition and stability of mining residues). Aljustrel, São Domingos, Lousal and Caveira were identified as the leading problematic places, with evidence for intense long-term acid mine drainage (AMD), along with other impacts on the surface environment which create numerous difficulties in the design of remediation strategies. At São Domingos and Aljustrel, different materials deposited along the main streams and in the dump areas trace the historical evolution of ore processing in those sites, while seepage waters indicate variable pH-Eh conditions (Tab. 2).

These acid waters promote the precipitation of a suite of minerals in response to the cyclic nature of wet/dry weather, such as copiapite, jarosite, melanterite, iron (hydr)oxides (*e.g.* Gonçalves *et al.*, 2007; Abreu *et al.*, 2010; Maia *et al.*, 2012). High concentrations of Cu, Pb, Zn, As, Sb in accumulated mining residues and As, Cd, Cu, Hg, Pb, Sb and Zn in seepage waters of, for instance, São Domingos, are the result of differential chemical mobility in the course of a very long time of oxidation and hydrolysis experienced by sulphide ores, slag and other metal-bearing residues deposited since mine closure in various piles distributed over a significant area (Matos and Martins, 2006; Batista, 2000; Alvarez-Valero *et al.*, 2008; Abreu *et al.*, 2010; Mateus *et al.*, 2011; Batista *et al.*, 2012b).

Table 2. Areas (m^2) of mining wastes and affected by AMD in IPB mines and downstream AMD length (after Abreu *et al.*, 2010).

Tabela 2. Áreas (m^2) afetadas por DAM em minas da FPI e comprimentos de DAM a jusante da exploração (após Abreu *et al.*, 2010).

Wastes	Caveira	Lousal	Aljustrel	S. Domingos
Mining wastes	217103	66294	675046	1696384
AMD	1239	21383	284085	273250
Downstream AMD	3.3 km	5 km	17 km	10 km

Given their particular compositional attributes or incipient exploitation, the environmental impacts related to Chança and Montinho (South from massive pyrite), as well as to Ferragudo, Balança and Cercal (Fe-Mn oxides), are considerably smaller (Alvarenga *et al.*, 2002; Abreu *et al.*, 2012; Matos and Martins, 2006). Moreover, the longevity of the abandoned state which is for instance the case of Brancanes, where mining closed in the beginning of the 20th century, may also stabilize the environmental signature of the pollutants in what soil-plant uptake is concerned (Batista *et al.*, 2007).

Decommissioning of the mining area of Aljustrel took place during the past decade and considerably reduced the production of AMD towards the surrounding areas. The works done included dam construction and diverted water channels to minimize the interaction of acid waters with rain waters and consequent overflow to nearby creeks, as it occurs in the area of the old mining dumps, or in the area of the current ore processing plant. However, the natural flow of the acid pools from the old mining dumps still occurs to the Água Forte stream, a 10 km long stream that runs northwards to the Roxo stream. Two kilometres downstream its source in the acid pools, this stream receives organic-rich, high pH-low Eh, municipal wastewater that causes a substantial perturbation in an otherwise environmental dangerous but stable acid drainage system (Candeias *et al.*, 2010; Maia *et al.*, 2012). Once again, the wet/dry weather cycles are fundamental to understand the dynamics of this system. The main effects of the municipal wastewater in the flow of the acid water are pH neutralization, dilution and induced Fe precipitation with a noticeable dissolved As reduction (Maia *et al.*, 2012). However, the mixture of mine acid water and municipal wastewater only occurs in the rainy season, and most of the year the latter organic-rich water input is the single most important contributor to the flow in the Água Forte stream. Therefore, the point where waste water enters the stream channel becomes a site where the active reductive dissolution of Fe oxy-hydroxides and hydroxysulfates occurs, with the consequent release of several transition metals, and a lowering of the pH to values similar to those contributed by the acid waters at the same spot (Maia *et al.*, 2012). Such example is an excellent reminder of the importance of understanding the complexity and dynamic nature of AMD systems associated with environmental impact studies. In the last couple of years the risk experienced by "advanced" economies in raw-materials supply increased significantly, thus compelling the reinforcement of several political initiatives (some of them already started in 2006/07) endorsing the access to new mineral deposits and/or alternative sources for a long list of critical metals. In this framework, the European Union official strategy highlights the importance of recycling and reusing not only the manufactured residues by also wastes resulting from the (present-day and old) exploitation works. This new concept of by-product (often known as "secondary resources") is increasing in Europe, and important mines located here are now introducing efficient practices of recycling in their smelters, reprocessing mining wastes with lower grades or searching for products distinct from the ones obtained previously. In the IPB this kind of evaluation is still incipient, but the potential is vast, considering the existing volumes of residues of variable composition distributed in several old mine centres. Some studies were already performed to evaluate the potential use of slags piled up in São Domingos (Pinto *et al.*, 2007; Mateus *et al*., 2011; Batista *et al.*, 2011). Milled pyrite samples collected in São Domingos and Aljustrel were also examined and compared (Batista *et al.*, 2011, 2012c), after the detection of interesting Re concentrations in these kind of waste at Achada do Gamo (São Domingos mine; Figueiredo *et al.*, 2012). A preliminary geochemical evaluation of the potential demonstrated by mining residues piled up in the Caveira mine was reported in Mateus *et al*. (2008). Considering the available volume of wastes, the São Domingos mine presents the best re-mining scenario in the Portuguese IPB sector, being evaluated by Conasa Company in the 1990's. Based on the Conasa data inferred mineral resources of 2.38 Mt of non-conditioned volumes, with an average grade of 0.77 g/t Au and 8.26 g/t Ag in the considered 11 waste piles and six landfill bodies with an average gold grade above 0.5 g/t, totaling a metal content of 59,489 oz t Au and 633,488 oz t Ag (Vieira, 2015; Vieira *et al*., 2015; Vieira *et al*., 2016). According to these authors if the global waste piles are considered (including the mine wastes located in the urban area of the São Domingos village) the inferred mineral resource could achieve to 4.0 Mt with an average grade of 0.64 g/t Au and 7.30 g/t Ag, corresponding to a metal content of 82,878 oz t Au and 955,753 oz t Ag.

4. Concluding statement

Geochemistry was, and still is, an expensive technique, although essential in mineral exploration and in assessments of environmental impacts. Indirect approaches, such as those involving geophysics, together with geochemical methods, led to fruitful results in mineral exploration all through the IPB since the beginning of systematic exploration practices. As a result of successive, although intermittent, exploration works carried out all over the years, the geochemical data archived in LNEG are quite significant and always played an important role in evaluation studies regarding the mineral exploration potential of many regions. Moreover, previous exploration geochemistry works combined with petrography and mineralogical reports from geologists, employed by public institutions and companies, represent a remarkable heritage of the Portuguese State, contributing to significant improvements in the geological knowledge of the national territory and its economical/social relevance. Supported on this knowledge, the continuous exploration for new deposits in IPB and/or complementary ways to perform their characterisation and economic evaluation can be made: by enhancing resolution with modern geochemical techniques (such as increasing the quality control and the number of analysed elements, isotope analysis, and high resolution analytical geochemistry at the micro and nano scale) and/or application of advanced numerical data processing. This knowledge also represents a starting point for other studies searching mitigation or remediation solutions especially if metal recovery technologies are an option to be developed in the future. Geochemical studies are not confined to soil geochemistry surveys. Stream sediments geochemistry, hydrogeochemistry, and lithogeochemistry of outcropping rock and drill-core samples represent also important sources of data in regional or detailed studies over specific target areas. These techniques are beyond the scope of the present chapter which aimed at providing a general overview of the importance of soil geochemistry studies in the current knowledge of the IPB.

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References

Abreu, M. M., Tavares, M. T., Batista, M. J., 2008. Potencial use of *Erica evalensis* and *Erica australis* in phytoremediation of sulphide mine environments: São Domingos, Portugal. *Journal of Geochemical Exploration*, **96**(2-3): 210-222.

Abreu, M. M., Batista, M. J.**,** Magalhães, M. C. F., Matos, J. X., 2010. Acid Mine Drainage in the Portuguese Iberian Pyrite Belt. *In:* Brock C. Robinson (Ed.), *Mine Drainage and Related Problems*. NY: Nova Science Publishers. ISBN:978-1-61668-643-7.

Abreu, M. M., Santos, E. S., Magalhães, M. C. F., Fernandes, E., 2012. Trace elements tolerance, accumulation and translocation in *Cistus populifolius*, *Cistus salviifolius* and their hybrid growing in polymetallic contaminated mine areas. *Journal of Geochemical Exploration*, **123**: 52-60. DOI:10.1016/j.gexplo.2012.05.001.

Alvarenga, P. M., Matos, J. X., Fernandes, R. M., 2002. Avaliação do impacto das Minas de Chança e Vuelta Falsa (Faixa Piritosa Ibérica) nas Águas Superficiais da Bacia Hidrográfica do Rio Chança. *Livro de Actas do Congresso Internacional sobre Património Geológico e Mineiro*, Beja, Portugal, 611-620.

Álvarez-Valero, A. M., Pérez-López, R., Matos, J. X., Capitán, M. A., Nieto, J. M., Saez, R., Delgado, J., Caraballo, M., 2008. Potential environmental impact at São Domingos mining district (Iberian Pyrite Belt, SW Iberian Peninsula): evidence from a chemical and mineralogical characterization. *Environ. Geology*, **55**: 1797-1809. DOI: 10.1007/s00254-007-1131-x.

Agterberg, F. P., 2012. Multifractals and geostatistics. *Journal of Geochemical Exploration*, **122**: 113-122.

Barbier, J., Wilhelm, E., Sakowitsch, W., 1979. Prospection géochimique en France: evolution et tendances de la dernière décennie. *Physics and Chemistry of the Earth*, **11**: 697-702.

Baize, D., Sterckman, T., 2001. Of the necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. *Science of the Total Environment*, **264**: 127-139.

Barnett, V., Lewis, T., 1994. *Outliers in statistical data*. 3rd edition, New York, John Wiley & Sons, 608.

Batista, M. J., 2000. Environmental state in the Portuguese test site S. Domingos Mine: past and present. *Report to the European Commission*, 41.

Batista, M. J., Sousa, A. J., Serrano Pinto, M., 2001. Comparação de teores em cobre de amostras de solos em arquivo desde 1971 e em amostras colhidas nos mesmos locais em 1998 na região mineira de Neves Corvo. *VI Congresso de Geoquímica dos Países de Língua Portuguesa, XII Semana de Geoquímica na Universidade do Algarve*, Faro, 9 a 12 de Abril, 589-592.

Batista, M. J., 2003. *Comportamento de elementos químicos no sistema rocha-solo-sedimento-planta na área mineira de Neves Corvo. Implicações Ambientais* (in Portuguese). PhD Thesis, Aveiro University, 393.

Batista, M. J., Brito, M. G., Abreu, M. M., Sousa, A. J., Quental, L., Vairinho, M., 2003. Avaliação por modelação em SIG da contaminação mineira por drenagem ácida em S. Domingos (Faixa Piritosa, Alentejo). *Ciências da Terra (UNL)*, Lisboa, V. CD-ROM, M6-M10.

Batista, M. J., Abreu, M. M., Serrano Pinto, M., 2007. Biogeochemistry in Neves Corvo mining region, Iberian Pyrite Belt, Portugal. *Journal of Geochemical Exploration*, **92(2-3)**: 159-176.

Batista, M. J., 2010. *Relatório Final do Projecto UTPIA – UTilização do Pb como Indicador de vulnerabilidade Ambiental na Faixa Piritosa Ibérica (SP5.P2/02)*. INTERREG IIIA Alentejo-Algarve-Andaluzia, 96.

Batista, M. J., Matos, J. X., Figueiredo, M. O., De Oliveira, D., Silva, T. P, Santana, H., Quental, L., 2011. Assinatura geoquímica dos resíduos e produtos mineiros de S. Domingos, Aljustrel e Neves Corvo numa perspectiva de sustentabilidade. *VIII Congresso Ibérico de Geoquímica. XVII Semana de Geoquímica.* Book of Abstracts, September 24th to 28th 2011, Castelo Branco, Portugal.

Batista, M. J., Sousa, A. J., Abreu, M. M., Pinto, M. Serrano 2012a. A two-way approach for the definition of anthropogenic and natural copper anomalies at a massive sulfide mine. The case of the NevesCorvo mine in Iberian Pyrite Belt, Portugal, *Journal of*

Geochemical Exploration, **13**: 13-22.

Batista, M. J., Matos, J. X., Abreu, M. M., 2012b. Acid Drainage Potential at S. Domingos Mine. *In*: Silva, E. F., Reis, A. P., Patinha, C., Pereira, E., Rodrigues S. (Eds.), *Multidisciplinary contribution for environmental characterization and improvement at the S. Domingos mining site*. Field Trip Guidebook of the 9*th* International Symposium on Environmental Geochemistry, (Batista *et al.*), PLM-Plural S. A., 26-36. ISBN: 978-972-789-367-6.

Batista, M. J., Matos, J. X., Figueiredo, M. O., Oliveira, D, Silva, T. P., Santana, H, Quental, L., 2012c. Base and precious metals waste material of the S. Domingos & Aljustrel Mines, Portugal: potential economic benefit and improvement environmental quality. *9º International Symposium of Environmental Geochemistry*, Book of Abstracks, 22.

Batista, M. J., Abreu, M. M., Locutura, J., De Oliveira, D., Matos, J. X., Silva, C., Bel-La, A., Martins, L., 2012d. Evaluation of trace elements mobility from soils to sediments between the Iberian Pyrite Belt and the Atlantic Ocean. *Journal of Geochemical Exploration*, **123**: 61-68.

Batista, M. J., De Oliveira, D. P. S., Abreu, M. M., Locutura, J., Shepherd, T., Matos, J., Bel-Lan, A., Martins, L., 2013. Sources, background and enrichment of lead and other elements: Lower Guadiana River. *Geoderma*, **193-194**: 265-274.

Borralho, V., 1970. *Determinação de metais pesados extraíveis a frio em amostras de solos e sedimentos*. Protocolo de análise dos Serviços de Fomento Mineiro, Direcção Geral de Geologia e Minas.

Candeias, C., Ferreira da Silva, E., Salgueiro, A. R., Pereira, H. G., Reis, A. P., Patinha, C., Matos, J. X., Ávila, P. H. 2011. Assessment of soil contamination by potentially toxic elements in the aljustrel mining area in order to implement soil reclamation strategies. *Land Degradation and Development*, **22**: 565-585.

Carvalho, D., 1979. Geologia, metalogenia e metodologia da investigação de sulfuretos polimetálicos do Sul de Potugal, *Comunicações Serviços Geológicos Portuga*l, Lisboa, **65**: 169- 191.

Castelo Branco, J., Sá, L., 1997. *Área de Serra Branca, Rel. 1º Sem. 1997*. Soc. Mineira Rio Artezia, Arquivo LNEG, ID 12794, 64.

Cheng, Q., Agterberg, F. P., Ballantyne, S. B., 1994. The separation of geochemical anomalies from background by fractal methods. *Journal of Geochemical Exploration*, **51**: 109-130.

Cheng, Q., Agterberg, F. P., Bonham-Carter G. F., 1996. A spatial analysis method for geochemical anomaly separation. *J Geochem Explor*, **56**:183-95.

Darnley, A. G., Björklund, A. J., Bolviken, B., Gustavsson, N., Koval, P.V., Plant, J. A., Steenfelt, A., Tauchid, M., Xie, X. with contributions by Garret, R. G., Hall, G. E. M., 1995. *A global geochemical database for environmental and resource management: recommendations for international geochemical mapping*. Science report 19, UNESCO, Paris, 122.

Direcção Geral de Geologia e Minas, 1990. Estudos Notas e Trabalhos do Serviço de Fomento Mineiro: *Tomo Comemorativo do 50.º Aniversário do Serviço de Fomento Mineiro*, 1939-1989. Porto. Direcção Geral de Minas e Serviços Geológicos, 73.

Durães, N., Bobos, I., Ferreira da Silva, E., 2008. Chemistry and F-TIR spectroscopic studies of plants from contaminated mining sites in the Iberian Pyrite Belt, Portugal. *Mineralogical Magazine*, **72**(1): 107-111.

Dutter, R., Filzmoser, P., Gather, U., Rousseeuw, P. (Eds.), 2003. Developments in robust statistics. *International Conference on Robust Statistics 2001*. Heidelberg.

EDM and DGEG Report, 2011. The legacy of abandon mines. The context and action in Portugal. http://www.edm.pt/html/livro.html#/Separador/ (Accessed in 14 February 2014).

Feliciano, R., Mateus, A, Matos, J. X., 2008. Spatial distributions of Cu, Zn, Pb and Co contents in stream sediments of the South Portuguese Zone; implications for mineral exploration. *V Seminário Recursos Geológicos e Ambiente*, UTAD, Vila Real, Portugal, 10.

Ferreira da Silva, E., Cardoso Fonseca, E., Matos, J. X., Patinha, C., Reis, P., Santos Oliveira, J. M., 2005. The effect of unconfined Mine Tailings on the Geochemistry of soils, sediments and surface waters of the Lousal area (Iberian Pyrite Belt, Southern Portugal). *Land Degradation Development*, **16**: 213-228.

Ferreira, A., Inacio, M. M., Morgado, P., Batista, M. J., Ferreira, L., Pereira, V., Pinto, M. S., 2001. Low-density geochemical mapping in Portugal. *Applied Geochemistry*, **16**(11): 1323-1331(9).

Figueiredo, M. O., B, Silva, T. P., Veiga, J. P., De Oliveira, D., Batista, M. J., 2012. Rhenium in waste material of the sulphur factory from the S. Domingos abandoned mine (Iberian Pyrite Belt, southern Portugal): an X-ray absorption spectroscopy approach. *9th International Symposium of Environmental Geochemistry*, Book of Abstracks, 209.

Freitas, H., Prasard, M. N. V., Prates, J., 2004. Plant community tolerant to trace elements growing on the degraded soils of São Domingos mine in the south east of Portugal: environmental implications. *Environment International*, **30**: 65-72.

Galán, E., Fernández-Caliani, J. C., Gonzaléz, I., Aparício, P., Romero, A., 2008. Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South-West Spain. *Journal of Geochemical Exploration*, **98**: 89-106.

Gonçalves, M. A., 2001. Characterization of Geochemical distribution using multifractal models. *Mathematical Geology*, **33**(1): 41-62.

Gonçalves, M. A., Figueiras, J., Pinto, C., Neng, N., Sá-Pereira, P., Batista, M. J., 2007. Biogeochemical and mineralogical characteristics of the acid mine drainage system in Aljustrel and S. Domingos mines, Iberian Pyrite Belt. *Geochim. Cosmochim. Acta*, **71**: A341.

Gonçalves, M. A., Mateus, A., 2019. Delimiting geochemical anomalies in the exploration of covered deposits with multifractal methods and using stream sediment data from the Iberian Pyrite Belt, Southwest Iberia. *Ore geology Reviews*, **112**: 103018.

Gonçalves, M. A., Mateus, A., Oliveira, V., 2001. Geochemical anomaly separation by multifractal modelling. *Journal of Geochemical Exploration*, **72**: 91-114.

Granier, C. L., 1973. *Introduction à la prospection Géochimiques des gîtes métallifère*. Masson et Cie, Éditeurs, Paris,143.

Hampel, F. R., Ronchetti, E. M., Rousseeuw, P. J., Stahel, W., 1986. *Robust statistics. The approach based on influence functions*. John Wiley & Sons, New York, 502. ISBN: 978-1-118-15068-9.

Hawkes, H. E., Webb, J. S., 1962. *Geochemistry in Mineral Exploration*. Harper and Row, New York, 657.

Hawkes, H. E., 1957. Principles of Geochemical Prospecting, Contributions to Geochemical Prospecting for Minerals.Geological Survey Bulletin 1000-F. *U. S. Government Printing Office*: 1957-413438, 225-355.

Huber, P. J., 1981. *Robust statistics*. New York, John Wiley & Sons.

Inácio, M., Pereira, V., Pinto, M., 2008. The soil geochemical atlas of Portugal: overview and applications. *Journal of Geochemical Exploration*, **98**: 22-33.

Jesus, A., Mateus, A., Gonçalves, M. A., Munhá, J., 2013. Multi-fractal modelling and spatial Cu-soil anomaly analysis along the southern border of the Iberian Terrane in Portugal. *Journal of Geochemical Exploration*, **127**: 23-44.

Kaiser, H. F., 1960. The application of electronic computers to factor analysis. *Educational and Psychological Measurement*, **20**: 141-151.

Luís, A. T., Teixeira, P., Almeida, S. F., Matos, J. X., da Silva, E. F., 2011. Environmental impact of mining activities in the Lousal área (Portugal): chemical and diatom characterization of metal-contaminated stream sediments and surface water of Corona stream. *Science of Total Environment*, **409**(20): 4312-4325.

Luz, F., Mateus, A., Matos, J. X., Gonçalves, M. A., 2012. Geochemistry of stream-sediments southwards of the SW Variscan suture in Portugal; insights into element anomalies of variable origin and intensity. *Transactions of Institutions of Mining and Metallurgy*; *Section B: Applied Earth Sciences*, **121**(3): 137-150.

Luz, F., Mateus, A., Matos, J. X., Gonçalves, M. A., 2013a. Cu, Zn and Pb soil geochemistry data from the NE domain of the Iberian Pyrite Belt in Portugal; implications to mineral exploration. *Geochemistry: Exploration, Environment, Analysis*, **14**(4): 341-358.

Luz, F., Mateus, A., Matos, J. X., Gonçalves, M. A., 2013b. Cu and Zn soil abundances in the NE border of the South Portuguese Terrane (Iberian Variscides, Portugal); guidelines to mineral exploration and environmental studies. *Natural Resources Research*, 1-21. Published online 30 July 2013.

Luz, F., Mateus, A., Matos, J. X., Gonçalves, M. A., 2015. Geochemistry of soils and stream sediments in the NE border of the Iberian Pyrite Belt: implications to mineral exploration. *Workshop-Solos em Prospeção Mineira: Casos de Estudo sobre Prospeção Geoquímica de Solos. 11 December 2015, Iniciativa Comemorativa do Ano Internacional dos Solos*, 13-15.

Maia, F., Pinto, C., Waerenborgh, J. C., Gonçalves, M. A., Prazeres, C., Carreira, O., Sério, S., 2012. Metal partitioning in sediments and mineralogical controls on the acid mine drainage in Água Forte stream (Aljustrel, Iberian Pyrite Belt, Southern Portugal). *Applied Geochemistry*, **27**: 1063-1080.

Mateus A., Figueiras J., Matos J. X., Goncalves M. A., Lopes R., Labaredas, J., Beleque, A., 2008. *Condicionantes impostas a dispersao de metais acumulados em escombreiras mineiras; o exemplo de Caveira (Faixa Piritosa Ibérica). A Terra - Conflitos e Ordem*, Livro de Homenagem ao Professor Antonio Ferreira Soares, Univ. Coimbra, 373-382.

Mateus, A., Pinto, A., Alves L. C., Matos, J. X. Figueiras, J., Neng, N., 2011. Roman and modern slag at S. Domingos mine (IPB, Portugal): compositional features and implications for their long-term stability and potential reuse. *Int. J. Environment and Waste Management* **8**(1/2): 133-159.

Matos, J. X., Batista, M. J., Represas, P., Pereira, Z., 2015. Soil geochemistry and gravity inversion modelling of the Caveira massive sulphide deposit, Iberian Pyrite Belt. *Livro de Resumos do X Congresso Ibérico de Geoquímica, XVIII Semana de Geoquímica,* Laboratório Nacional de Energia e Geologia, 18-23 outubro de 2015, 108-111.

Matos, J. X., Filipe, A., Coordenadores, 2013. *Carta de Ocorrências Mineiras do Alentejo e Algarve à escala 1:400 000, versão digital*. Edição LNEG/ATLANTERRA, Lisboa. ISBN: 978-989-675-029-9.

Matos, J. X., Martins, L., 2006. Reabilitação ambiental de áreas mineiras do sector português da Faixa Piritosa Ibérica: estado da arte e perspectivas futuras. IGME, *Bol. Geológico y Minero España*, **117**(2): 289-304. ISSN 0366-0176.

Matos, J. X., Sousa, P., Ricardo, J., 2009. *MAEPA-Área de Marateca, Faixa Piritosa Ibérica. Caracterização geológica, geofísica e geoquímica da Região de Palma-Serrinha-Cordoeira, Definição de Alvos de Sondagem*. LNEG DPMM, Relatório Técnico, 66.

Mora, J., 2001. Área de Prospeção de Ourique, Rel. 1º Sem. 2001. Arquivo LNEG, ID 2748, 26.

Pacheco, V., Amaral, P., Hovart, A., Windels, W., 1996. *Castro Verde Concession Final Work Report*. Asarco, Arquivo LNEG, ID 14407, 37.

Pena, S., Abreu, M. M., Magalhães, M. R., Cortez, N. 2020. Water erosion aspects of land degradation neutrality to landscape planning tools at national scale. *Geoderma*, **363**(114093): 15.

Pérez-López, R.; Delgado, J.; Nieto, J. M., Márquez-García, B., 2010. Rare earth elemento geochemistry of sulphide weathering in the São Domingos mine área (Iberian Pyrite Belt): a proxy for fluid-rock interaction and ancient mining pollution. *Chemical Geology*, **276**: 29-40.

Pinto, A., Mateus, A., Cerqueira Alves, L., Matos, J. X., Neng, N., Figueiras, J., 2007. Detailed slag characterization relevance in environmental and economic assessments; the example of São Domingos (Iberian Pyrite Belt, Portugal). *XV Semana de Geoquimica – VI Congresso Iberico*, Vila Real (Portugal), 345-348.

Queiroz, N., Pereira, F., Bengala, J., Moreira, J., Freire, J., Viegas, L., Viana, M., Gaspar, O., Pereira, V. e Borralho, V., 1989. *Est. Not. Trabalhos SFM*, T. 50º Aniversário, Porto.

Ramalho, E. C., Matos, J. X., 2009. Prospecção eléctrica (resistividade e polarização induzida) na zona da Serrinha (Marateca) para apesquisa de sulfuretos e marcação de uma sondagem de prospecção e pesquisa., *Rel. Técnico p/ MAEPA*, URMG, LNEG, 28.

Reimann, C., Fizmoser, P., 2000. Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data. *Environmental Geology*, **39**: 1001-1014.

Reimann, C., Filzmoser, P., Garrett, R. G., 2005. Background and threshold: critical comparison of methods of determination. *Science of the Total Environment*, **346**: 1-16.

Rousseeuw, P. J., Leroy, A. M., 1987. *Robust regression and outlier detection*, John Wiley & Sons, New York, 329.

Salminen, R., Tarvainen, T., 1997. The problem of defining geochemical baselines. A case study of selected elements and geological materials in Finland. *Journal of Geochemical Exploration*, **60**: 91-98.

Salminen, R., Gregorauskiene, G., 2000. Considerations regarding the definition of a geochemical baseline of elements in the surficial materials in areas differing in basic geology. *Applied Geochemistry*, **15**: 647-653.

Santos, E. S., Abreu, M. M., Nabais, C., Magalhães, M. C. F., 2012. Trace element distribution in soils developed on gossan mine wastes and Cistus ladanifer L. tolerance and bioaccumulation. *Journal of Geochemical Exploration*, **123**: 45-51.

Santos, E. S., Abreu, M. M., Batista, M. J., Magalhães, M. C. F., Fernandes, E., 2014. Inter-population variation on the accumulation and translocation of potentially harmful chemical elements in Cistus ladanifer L. from Brancanes, Caveira, Chança, Lousal, Neves Corvo and São Domingos mines in the Portuguese Iberian Pyrite Belt. *Journal of Soils and Sediments*, **14**: 758-772. DOI: 10.1007/s11368-014-0852-1.

Santos Oliveira, J. M., 1997. Algumas reflexões com enfoque na problemática dos riscos ambientais associados à atividade mineira. *Estudos Notas e Trabalhos do Serviço de Fomento Mineiro*, **39**: 3-26.

Santos Oliveira, J. M., Farinha, J., Matos, J. X., Ávila, P., Rosa, C., Canto Machado, M. J., Daniel, F. S., Martins, L., Machado Leite, M. R., 2002. Diagnóstico Ambiental das Principais Áreas Mineiras Degradadas do País. *Boletim de Minas*, Instituto Geológico e Mineiro, **39**(2): 67-85.

Selinus, O. S., Esbensen, K., 1995. Separating anthropogenic from natural anomalies in environmental geochemistry. *Journal of Geochemical Exploration*, **55**: 55-66.

Tukey, J. W., 1977. Exploratory Data Analysis. *Addison-Wesley, Reading*, 688.

Van Geen, A., Adkins, J. F., Boyle, E. A., Nelson, C. H., Palanques, A., 1997. A 120 yr record of widespread contamination from mining of the Iberian Pyrite Belt. *Geology*, **25**(4): 291-294.

Vieira, A., 2015. *Avaliação do Potencial Mineiro das Escombreiras da Mina de S. Domingos*. MSc Thesis, Geosciences Dep., Évora University, Portugal, 155.

Vieira, A., Matos, J., Lopes, L., Martins, R., 2016. Tridimensional modelling and resource estimation of the mining waste piles of São Domingos mine, Iberian Pyrite Belt, Portugal. *Geophysical Research Abstract*s, EGU 2016, abs, 18.

Vieira, A., Matos, J. X., Lopes, L., Martins, R., 2015. Evaluation of the mining potential of the São Domingos mine wastes, Iberian Pyrite Belt. *Cong. Ibérico Geoquímica/XVIII Semana Geoquímica*, LNEG, 208-211. ISBN 978-989-675-039-8.