



Coal related fires in Portugal: New occurrences and new insights on the characterization of thermally affected and non-affected coal waste piles

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ABSTRACT

This study presents a comprehensive investigation on the petrographic and geochemical characterization of new occurrences of self-burning coal waste piles in Douro Coalfield (Portugal). It also includes a reappraisal of data about coal waste piles resulting from past mining, aiming to assess their environmental and economic potential. Burned and unburned material from two coal waste piles that ignited in 2017 were studied for petrographic, mineralogical and geochemical characterization, and for identification of thermally induced changes caused by combustion. Geochemical data relative to more than 20 coal waste piles from Douro Coalfield were integrated and enrichment of elements was investigated by comparison with reference values. The results show that the organic fraction in the thermally affected samples presents dark reaction rims, cracks, devolatilization vacuoles, plasticized edges, pyrolytic carbon and lower vitrinite reflectance, despite the presence of unaltered particles. The formation of iron oxides is also attributed to burning process. The petrographic observations allow the identification and characterization of more and less intense thermally affected materials which indicates the heterogeneity of the burning process within the coal waste piles, and gives information about newly formed minerals and attained combustion temperatures. The geochemical composition of the studied samples is generally within the range expected for Douro Coalfield coaly materials. More noticeable differences are reported to the most thermally affected sample. When considering the geochemical data about all coal waste piles from Douro Coalfield it is noticed that the majority of elements concentration increase in the burned material due to C consumption and loss of other elements by volatilization. The decrease in the concentration of As, Cd, Co, Mn, Pb, Sb, Sn, and Zn in burned material is attributed to partial volatilization of these elements at high combustion temperatures. Considering the elements slightly to significantly enriched in Douro Coalfield materials, Ba, Ga, Hf, Li, Nb, Sb, Sc, Ta, V, W, and REE are considered critical raw materials by the European Commission, while As, Co, Cr, Cu, Mo, Ni, Pb, and U represent environmental concerns. Therefore the reutilization of Douro Coalfield materials as a secondary source of critical raw materials could be economically relevant and will allow the mitigation of environmental impacts caused by their deposition.

1. Introduction

The occurrence of coal related fires has been observed and investigated worldwide, including in Portugal (Ribeiro et al., 2010a, 2016b; Stracher et al., 2011, 2013, 2015, 2019). Self-heating, spontaneous combustion and self-burning related with coal and coaly materials may occur during mining operations, transport, storage, and waste disposal. Beyond the consumption of valuable natural resources, coal related fires are of significant concern because of the risks to environment and

human health, particularly due to the uncontrolled release of harmful gases and particulate matter to the atmosphere. Adding further to these environmental concerns, leaching and mobility of contaminants such as organic compounds and hazardous elements may cause the degradation of soils, waters and ecosystems in the surrounding areas and adversely affect human health and biodiversity (Suárez-Ruiz and Crelling, 2008; Younger, 2004).

Integrative studies based on petrology, mineralogy and geochemistry of self-burning coal waste piles and the associated environmental

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impacts and human health hazards have been the subject of numerous studies (Chuncaí et al., 2014; Ciesielczuk et al., 2014; Espinha Marques et al., 2021; Finkelman, 2004; Finkelman and Stracher, 2011; Mansilha et al., 2021; Misz-Kennan and Fabiańska, 2010, 2011; Pone et al., 2007; Querol et al., 2008; Ribeiro et al., 2010a, 2011, 2012, 2013, 2015, 2016a, 2016b, 2017, 2019; Zhao et al., 2008). This comprehensive characterization of coal waste piles gives information and useful insights about the burning process, the propensity to ignition and burning and the thermal induced changes in waste materials. All together provide valuable knowledge about the environmental impacts, which is useful and necessary for definition of mitigation plans. In this context, the determination of mode of occurrence of organic and inorganic constituents is very significant due to their potentially adverse effects in the environment. The mode of occurrence of elements in coal mining wastes strongly influence their behaviour during leaching and burning (Chuncaí et al., 2014; Eskenazy et al., 2010; Finkelman et al., 2018; Gürdal, 2008; Ribeiro et al., 2011; Ribeiro and Flores, 2021; Swaine and Goodarzi, 1995). The leaching processes occurring in the coal waste piles are the primary pathways for the trace elements entrance into the environment, depending on their concentration and mode of occurrence within the mineralogical constituents. In addition, during the combustion process in coal waste piles, the organically associated and more volatile elements may volatilize and, consequently, be emitted to the atmosphere and/or be adsorbed in the combustion by-products. Recent studies on coal related fires are particularly focused on experimental methods and mathematical modelling to predict the spontaneous combustion liability of coal (Onifade and Genc, 2020 and references therein). These authors concluded that prediction of the spontaneous combustion liability of coal is difficult because of the numerous factors involved and add that the understanding of the material properties is a pre-requisite for the experimental methods and modelling at the large-scale.

Considering that many coal deposits are investigated as alternative sources of some critical elements (Dai et al., 2016; Dai and Finkelman, 2018; Seregin and Finkelman, 2008) and looking at coal waste piles from another perspective, the recycling of these materials, from both burned and unburned coal waste piles, is in good agreement with European Union (EU) perspectives that identifies the recycling of mining waste as key sector in the potential source of secondary critical raw materials (European Commission, 2018). Additionally, the sustainable recovery of mining wastes contributes to mitigate environmental impacts. The EU identified 30 critical raw materials with extremely high level of external dependence, and strongly recommends the development of measures to increase recycling of by-products and residues (European Commission, 2020). Economic importance and supply risk are the two main parameters used to determine criticality for the EU.

Therefore, the investigation of coal waste piles as an alternative secondary source of critical raw materials and carbon-based materials is of value.

The Douro Coalfield (NW of Portugal), from Carboniferous (Upper Pennsylvanian [Lower Stephanian C]) age, embody the most important coal-bearing deposit in NW of Portugal (general orientation NW-SE; 53 km length; 30 to 250 m width;) (Eagar, 1983; Fernandes et al., 1997; Lemos de Sousa and Wagner, 1983; Pinto de Jesus, 2003; Wagner and Lemos de Sousa, 1983). The mining activities in Douro Coalfield started in 1795 until 1994 and the exploited anthracite A coal type (ISO, 11760, 2005) was principally used as fuel supply for power generation. The mining occurs mostly in underground excavation in two principal areas: São Pedro da Cova and Pejão, whose activities ended in 1972 and 1994, respectively (Custódio, 2004).

The coal waste piles, made up rejected and overburden material from mining operations in Douro Coalfield, are emplaced over the old mine sites and adjacent areas, materializing significant environment impacts. At least 20 coal waste piles were identified in previous studies (Ribeiro et al., 2011) but a systematic inventory of the existing waste piles in the Douro Coalfield was never made. Three of these waste piles near São

Pedro da Cova mining area started to burn in 2005 after ignition caused by forest fires and one of them is still burning nowadays, after more than 15 years. Previous investigations on both burning/burned and unburned coal waste piles from Douro Coalfield and the associated environmental problems were developed in previous research (Ribeiro et al., 2010a, 2010b, 2010c, 2011, 2012, 2013, 2015, 2017; Ribeiro and Flores, 2021; Espinha Marques et al., 2021; Mansilha et al., 2021). The burning coal waste piles from Douro Coalfield have been continuously the subject of several studies because they represent the first occurrence of coal related fires in Portugal. In addition, the coal waste piles are located very close to population centres or are included in forested areas; despite the environmental issues related with mining waste disposal for itself, the first situation amplify the concerns about the human health and the second brought concerns related with the proper management of forested areas since the ignition of coal waste piles are often caused by forest fires.

In 2017, two other coal waste piles started to burn in Pejão mining area, also after the ignition caused by forest fires that strongly affected the region. In these cases, as well as in burned coal waste piles from São Pedro da Cova mining, the process in each coal waste pile was very heterogeneous and the burning process did not affect the totality of the waste material. In these coal waste piles in Pejão, a plan to extinguish the combustion process was implemented by the company responsible for environmental recovery and monitoring of degraded mining areas in Portugal (EDM - Empresa de Desenvolvimento Mineiro), through remobilization and cooling with water mixed with a cooling agent. The remobilization caused the mixture of the mining waste material that underwent different combustion intensity and brought to the surface of the piles the reddish coloured material. This explains the spatial heterogeneity of the material within the waste piles.

The main objective of this study is the comprehensive characterization of the two burned coal waste piles in Pejão mining area that ignited in 2017. It is expected to contribute to the knowledge about the self-burning of coal waste piles, which is an uncommon phenomena associated with anthracite A coal mining, as is this case. In addition, it is also expected to provide information useful for the identification of potentially environmental impact related with coal mining waste disposal and combustion as well as for the potential of Douro Coalfield mining waste material as a secondary source of critical raw materials. For the accomplishment of these main goals, the specific objectives are as follow: (i) to determine the petrographic and geochemical composition of burned and unburned material from the coal waste piles in Pejão; (ii) to identify thermally induced changes resulting from the burning process, principally in the organic matter and in the mode of occurrence of organic and inorganic constituents; and, (iii) to evaluate the enrichment of trace elements in Douro Coalfield mining waste material.

2. Materials and methods

2.1. Sampling

The coal waste piles in Douro Coalfield are made of rejected and overburden material from mining operations and are composed, predominantly, of fragments of carbonaceous shales and lithic arenites with variable quantities of anthracite A (ISO 11760, 2005). Previous studies indicated that unburned coal waste piles in Douro Coalfield have a carbon content between 3.0 wt% and near 70.0 wt%, indicating a great heterogeneity amongst them; the burned waste pile material presented from less than 1.0 wt% to about 35.0 wt%, depending on combustion intensity (Ribeiro et al., 2011; Ribeiro and Flores, 2021).

Samples for this study were collected in two partially burned coal waste piles in Pejão mining area (Pj-A and Pj-B), where the combustion process was extinguished through remobilization of the waste material. Fig. 1 shows the location and an aerial image of Pejão mining area and the studied coal waste piles. In both cases the rejected and overburned material from coal mining was deposited in a hillside, which in the case



Fig. 1. Location of Pejão mining area and aerial image of the sampled coal waste piles Pj-A ($41^{\circ}02'28''\text{N}$, $8^{\circ}23'03''\text{W}$) and Pj-B ($41^{\circ}02'55''\text{N}$, $8^{\circ}23'41''\text{W}$) (from Google Earth).

of Pj-B is adjacent to the Douro River. The coal waste piles have an elongated form with 100 to 120 m length. Fig. 2 shows a detailed aerial image of the sampled coal waste piles, where it can be observed the heterogeneity in the material at the surface. It is possible to distinguish unburned and burned areas but these last areas include mixed burned material differently affected by combustion. Therefore, it is not possible to identify the advance and spatial distribution of the combustion process within the coal waste piles. However, it was possible to distinguish zones with material that underwent higher combustion intensity from those less affected (Fig. 2).

In coal waste pile Pj-A (Fig. 3) a total of 6 samples were collected (2 from unburned material and the others from the burned material). In coal waste pile Pj-B (Fig. 4), 3 samples of burned material and 1 sample of unburned material were collected. Sampling was performed during the extinguishment and remobilization of material in waste pile Pj-A. The coal waste pile Pj-B had been extinguished a few months before sampling.

In the laboratory, the samples were dried, homogenized, and quartered to get representative samples and after were crushed to <1 mm for petrographic analysis and <212 μm for geochemical analysis.

2.2. Methodologies

The comprehensive characterization of the coal waste material was achieved by petrographic and geochemical analysis. The petrographic characterization was performed on polished pellets through optical microscopy for the identification of the organic and inorganic components and for vitrinite mean random reflectance measurement. The preparation of whole rock polished pellets was done in accordance with standard ISO 7404-2 (2009). The ICCP nomenclature (ICCP 1998, 2001) was used for identification of the organic matter and determination of vitrinite mean random reflectance follows the standard ISO 7404-5 (2009). The identification of thermally affected particles followed the ICCP classification (Misz-Kennan et al., 2020). Petrographic observations were performed in a Leica 4000-M microscope equipped with a Discus-Fossil spectrophotometer system under standard conditions, white light and using oil immersion objectives. The petrographic analysis was performed at Institute of Earth Sciences, Porto (Portugal).

Scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX) analyses were performed in Materials Centre of the University of Porto to complement optical microscopy observations and



Fig. 2. Aerial image of the sampled coal waste piles (from Google Earth).



Fig. 3. Coal waste pile Pj-A. A) Burning area during waste material remobilization for cooling; B) Burned area with reddish coloured material and coal fire gas minerals precipitated in the surface of the waste material; C) Unburned waste material.



Fig. 4. Coal waste pile Pj-B. A) and B) General view of the burned area with reddish coloured material; C) General view of the unburned waste material.

to provide further information on minerals identification and elements mode occurrence. The analysis of selected samples on polished pellets included observation under secondary electrons and back scattered electrons detection modes and EDX analysis for the determination of chemical compositions. The SEM-EDX analysis were conducted with a FEI Quanta 400FEG environmental scanning electron microscope, equipped with a Genesis X4M energy dispersive X-ray analyser.

The geochemical analyses included: proximate analysis for the determination of ash and volatile matter (ISO 1171, 2010; ISO 562, 2010); ultimate analysis for determination of carbon (C), hydrogen (H), nitrogen (N) and total sulphur (St) using LECO S-2000 and LECO S-632 apparatus; and inductively coupled plasma emission spectrometry/mass spectrometry (ICP-ES/MS) for determination of the inorganic composition of major, minor and trace elements in the studied samples after digestion with an acid solution of H_2O -HF- $HClO_4$ - HNO_3 . Analysis of reference materials, duplicates and blanks was performed for quality assurance. The proximate and ultimate analyses were performed at *Instituto de Ciencia y Tecnología del Carbono* (INCAR-CSIC in Spain), and the ICP-ES/MS analyses were performed by Bureau Veritas Mineral Laboratories (Canada).

Geochemical data of other coal waste piles from Douro Coalfield (53 samples), as well as from coal (3 samples) and main overlying lithologies (3 samples), all collected in coal waste piles, were included and integrated with the results obtained in the present study. The chemical

composition of all samples was determined in the same laboratory and following the same analytical procedure. Coal waste samples were analyzed as whole rock and coal samples were analyzed after ashing. The above mentioned data is published by Ribeiro et al. (2011) and Ribeiro and Flores (2021). The chemical composition of world coals composition (WCC) and background of black shales (BBS) was considered for comparison (Ketrís and Yudovich, 2009).

3. Results and discussion

3.1. Waste material from Pejão mining area

3.1.1. Petrographic characterization

Figs. 5 and 6 show a petrographic broad view of the studied samples of each coal waste pile. The observation of the images allows the general characterization and the comparison between burned and unburned samples of the same waste pile (photomicrographs were taken under the same intensity of light). Fig. 5 shows that the unburned samples from Pj-A waste pile (Pj-A-2 and Pj-A-5) are darker and present organic particles along with abundant mineral matter; samples Pj-A-4, Pj-A-6 and principally Pj-A-1 present reddish colour showing that were thermally affected; at this scale, sample Pj-A-3 do not show signs of thermal effects and the organic particles are easily observed.

Fig. 6 shows that both the unburned and burned samples from Pj-B

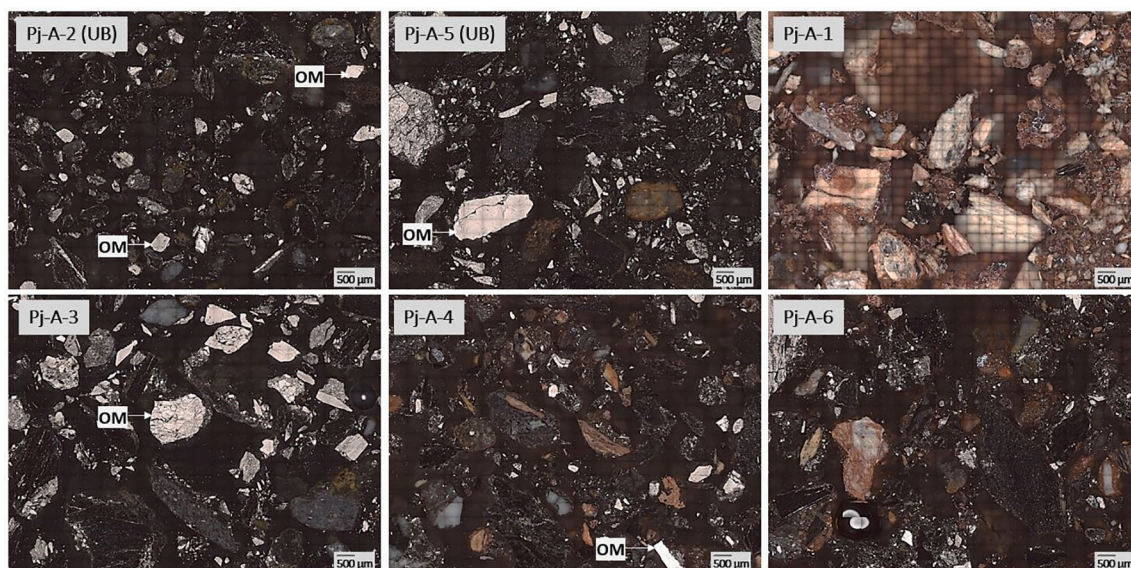


Fig. 5. Petrographic general view of burned and unburned (UB) samples from Pj-A waste pile (OM - organic matter).

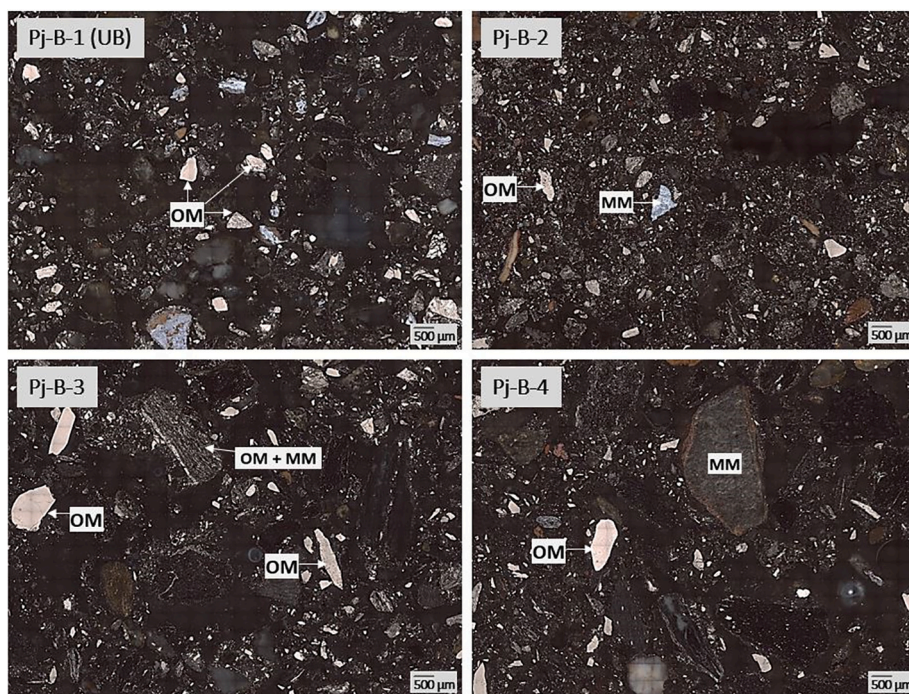


Fig. 6. Petrographic general view of burned and unburned (UB) samples from Pj-B waste pile (OM - organic matter; MM - mineral matter).

waste pile are essentially composed of mineral matter but organic particles are clearly observed. In burned samples (Pj-B-2, Pj-B-3 and Pj-B-4) the presence of iron oxides (particles with greyish blue or orange colors) is more evident, despite not having a reddish colour. At the outset, this may indicate less intense combustion process. Previous investigations reveal that the reddish waste materials collected in burning/burned coal waste piles in Douro Coalfield underwent more intense combustion process where higher temperatures were attained (based on the newly formed minerals; Ribeiro et al., 2015). Nevertheless, the reddish coloured material was observed in the field in both waste piles (Figs. 3 and 4).

Figs. 7 to 11 show detailed photomicrographs of the studied samples. The organic matter of samples from both coal waste piles is essentially composed of vitrinite (principally collotelinite and detrovitrinite), with

minor proportions of inertinite (mainly fusinite, semifusinite and inertodetrinite). The organic particles occur isolated and along with mineral matter.

The unburned samples from Pj-A coal waste pile (Fig. 7) include vitrinite and inertinite particles as isolated particles and detrital forms, sometimes embedded with mineral matter (Fig. 7A, E), and with signs of oxidation effects such as iron oxides enclosing organic particles (Fig. 7A), organic particles with cracks (Fig. 7B, C, D), and framboidal oxidized pyrite (Fig. 7D).

Figs. 8 and 9 show petrographic images of burned waste samples from Pj-A coal waste pile. While Fig. 8 includes the darker samples (Pj-A-3 and Pj-A-4), Fig. 9 includes images of the more reddish samples (Pj-A-1 and Pj-A-6), which are expected to be more thermally affected. Previous research demonstrates that the most thermally affected material from

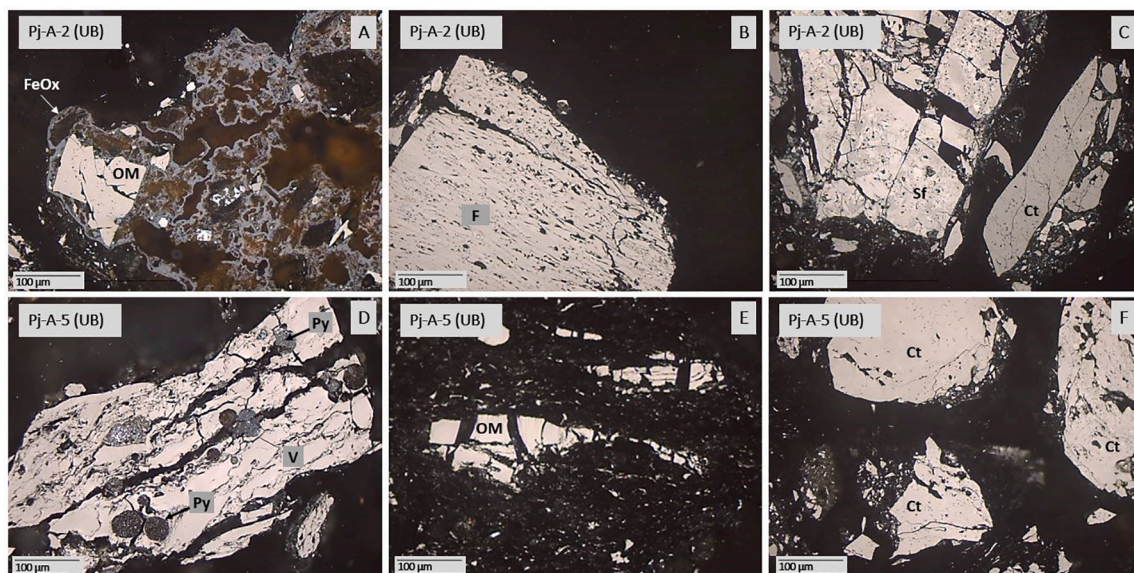


Fig. 7. Photomicrographs of unburned material from Pj-A waste pile. A) Iron oxides (FeOx) enclosing organic particles (OM); B) Fusinite (F); C) Semifusinite (Sf) and collotelinite (Ct); D) Vitrinite (V) with oxidized framboidal pyrite (Py); E) Organic matter (OM) embedded in mineral matter; F) Particles of collotelinite (Ct).

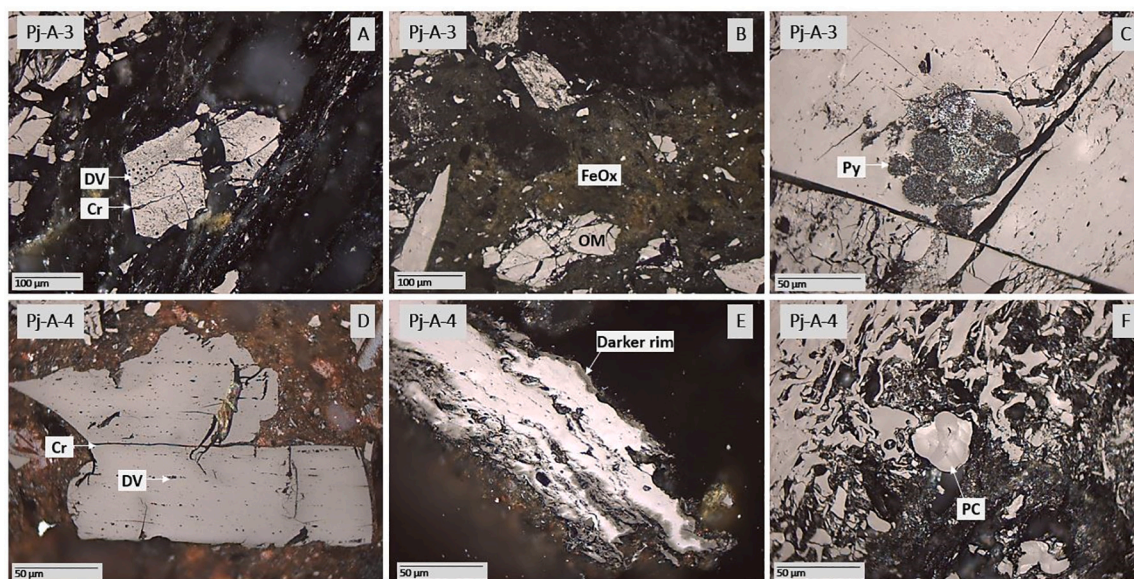


Fig. 8. Photomicrographs of burned material from Pj-A waste pile. A) Organic particle with cracks (Cr) and devolatilization vacuoles (DV); B) Organic particles (OM) enclosed by iron oxides (FeOx); C) Oxidized framboidal pyrite (Py); D) Organic particle with cracks (Cr) and devolatilization vacuoles (DV); E) Organic particle with dark reaction rims and plasticized edges; F) Pyrolytic carbon (PC).

Douro Coalfield, that is, the waste material that underwent higher temperatures present a reddish colour due to formation of iron oxides (magnetite, hematite and maghemite) (Ribeiro et al., 2015) and stronger changes in organic matter (Ribeiro et al., 2010a). Despite unaltered organic particles can still be observed, images in Fig. 8 evidence signs of thermal effects in organic and mineral particles, such as cracks (Fig. 8A, C, D), devolatilization vacuoles (Fig. 8A, D), formation of iron oxides (Fig. 8B), including oxidation of framboidal pyrite (Fig. 8C), dark reaction rims (Fig. 8D, E), plasticized edges (Fig. 8E) and formation of pyrolytic carbon (Fig. 8F). Fig. 9A shows that unaltered organic particles also occur in the most thermally affected samples, however they are less abundant in samples less affected. The occurrence of devolatilization vacuoles (Fig. 9B, E), cracks (Fig. 9E), dark reaction rims (Fig. 9B, D), formation of iron oxides (Fig. 9C) and occurrence of organic particles with lower reflectance and with plasticized edges (Fig. 9F) were also

observed.

In Fig. 10, photomicrographs of unburned waste from Pj-B waste pile (sample Pj-B-1) shows the occurrence of semifusinite (Fig. 10A), collotelinite (Fig. 10B, C) and iron oxides (Fig. 10D, E, F). The presence of iron oxides and organic particles with cracks (Fig. 10C) are indicative of oxidation processes occurring in the coal waste pile.

Fig. 11 shows photomicrographs of burned waste from Pj-B waste pile (Pj-B-2, Pj-B-3, and Pj-B-4) and organic particles thermally affected presenting: dark reaction rims (Fig. 11A, B, C, and H); devolatilization vacuoles (Fig. 11D, G), and plasticized edges (Fig. 11F). Oxidized framboidal pyrite was also noticed (Fig. 11E) as well as unaltered organic particles, as is the case of the fusinite in Fig. 11I.

The vitrinite reflectance of the unburned samples varies between 4.56% and 4.74% while the burned samples present reflectance varying between 4.12% and 4.56% evidencing the lowering of vitrinite

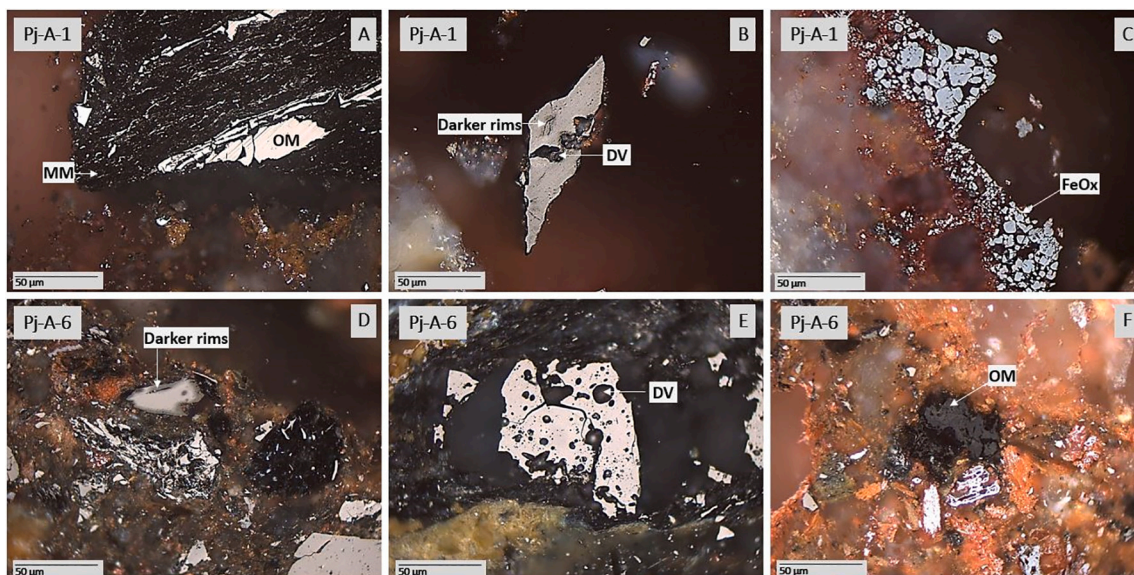


Fig. 9. Photomicrographs of more intensely burned material from Pj-A waste pile. A) Unaltered organic matter (OM) embedded in mineral matter (MM); B) Organic particle with devolatilization vacuoles (DV) and dark reaction rims; C) Iron oxides (FeOx); D) Organic particle with dark reaction rims; E) Organic particle with devolatilization vacuoles (DV) of different sizes indicating various phases in the devolatilization process; F) Organic particle (OM) with lower reflectance and with plasticized edges.

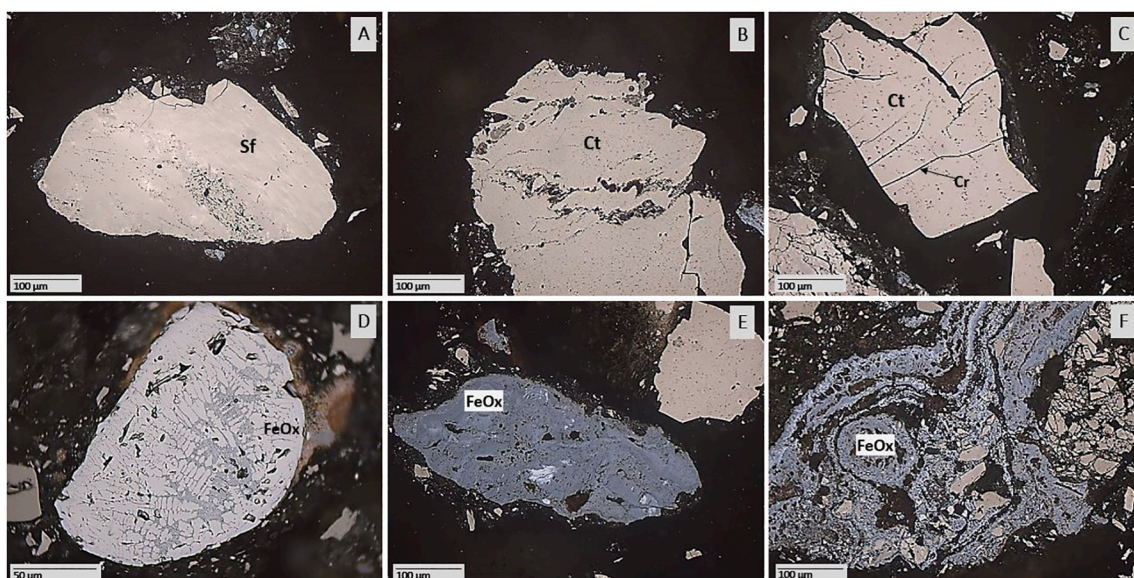


Fig. 10. Photomicrographs of unburned material from Pj-B waste pile (sample Pj-B-1). A) Semifusinite (Sf); B) Collotelinite (Ct); C) Collotelinite (Ct) with cracks (Cr) evidencing oxidation; D) E) and F) Iron oxides (FeOx).

reflectance due to the combustion process (Table 1). Mean random vitrinite reflectance of unburned samples are consistent with the expected for Douro Coalfield (anthracite coal rank; ISO 11760, 2005). The classification of thermally affected particles by Misz-Kennan et al. (2020) identifies the occurrence of paler in colour particles in which the mean vitrinite reflectance is higher comparing to the unaltered vitrinite particles (reflecting low heating rate). However, in the studied samples it was found lower vitrinite reflectance in thermally affected materials that is attributed to the high rank of Douro Coalfield (anthracite A), and to high heating rate and combustion temperature underwent by these materials. The lowering of vitrinite reflectance attributed to the combustion at high temperatures had already been identified by other authors (Taylor et al., 1998) and also in burned coal waste materials from anthracite mining in Douro Coalfield and El Bierzo Coalfield (Ribeiro

et al., 2010a; Ribeiro et al., 2016b, respectively). The presence of pyrolytic carbon also proves the combustion high temperatures (Kwiecińska and Pusz, 2016).

The SEM observations and EDX analysis of selected samples affected by burning process, performed to complement the petrographic analysis, reveal the occurrence of abundant aluminosilicates together with iron oxides (Fig. 12A, 12B, 12C); it was possible to observe framboidal pyrite as well as secondary iron oxides sometimes enclosing organic matter (Fig. 12A), that are assumed to form during the combustion process at high temperatures (Ribeiro et al., 2015). Fig. 12B and 12D show the occurrence of organic matter embedded in mineral matter; the organic particle in the centre in Fig. 12D (spectra OM-Z2) shows superficial heterogeneities that may be sign of thermal changes. These observations and EDX analysis corroborate the previous petrographic descriptions.

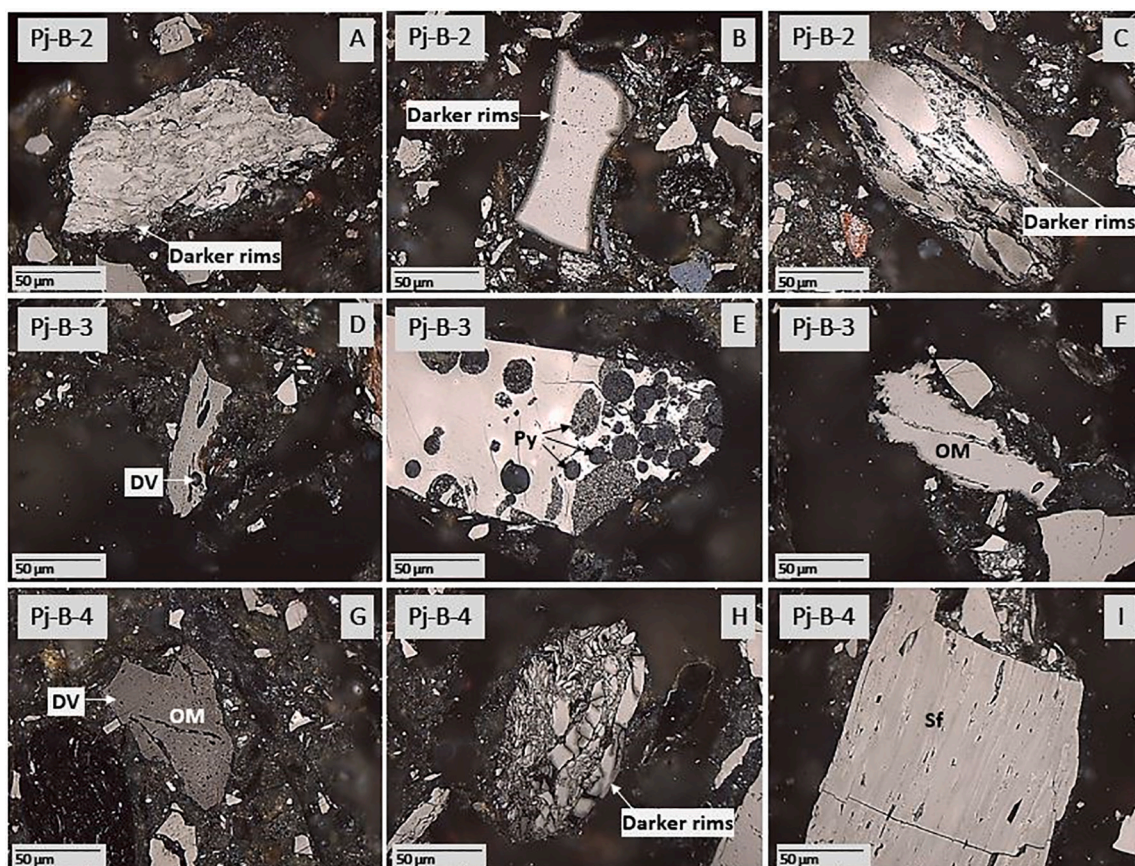


Fig. 11. Photomicrographs of burned material from Pj-B waste pile. A), B), and C) Organic particles with dark reaction rims; D) Organic particle with devolatilization vacuoles (DV); E) Oxidized framboidal pyrite (Py); F) Organic particle (OM) with plasticized edges; G) Organic particle (OM) with lower reflectance and devolatilization vacuoles (DV); H) Organic particle with dark reaction rims; I) Semifusinite (Sf).

Table 1

Vitrinite mean random reflectance (Rr) of the studied samples, number of measurements in each sample (N) and standard deviation (SD).

	Rr (%)	N	SD
Pj-A-2 (UB)	4.56	104	0.452
Pj-A-5 (UB)	4.74	104	0.570
Pj-A-1	4.31	63	0.487
Pj-A-3	4.46	102	0.409
Pj-A-4	4.38	104	0.527
Pj-A-6	4.26	111	0.422
Pj-B-1 (UB)	4.60	105	0.513
Pj-B-2	4.12	102	0.756
Pj-B-3	4.56	102	0.385
Pj-B-4	4.25	100	0.380

UB - unburned material.

3.1.2. Geochemical characterization

The ash yield and elemental composition of the studied coal waste samples are presented in Table 2. The ash yield (on dry basis, d) of the unburned samples varies between 73.09 wt% and 77.80 wt%. The ash yield of the burned samples presents a great heterogeneity, varying between 63.17 wt% and 99.24 wt%, and the mean value is 81.65 wt%. The higher ash yield in the majority of burned samples is attributed to the burning processes that leads to the partial consumption of C and concentration of inorganic matter. The exceptions are attributed to the heterogeneous nature of the materials composing the coal waste piles. The most thermally affected samples (Pj-A-1 and Pj-A-6) present the higher ash yields, indicating that the organic matter was more intensely affected during combustion. For sample Pj-A-1 the content of C, H, N and O was not determined because the high ash yield of this sample. The C

content (on dry ash-free basis, daf), as expected and in accordance with ash yield, is generally lower in the burned samples. The elemental composition of the samples exhibits great heterogeneity, as predictable for this type of materials, composed of a mixture of coal and the coal seams bearing lithologies. The concentration of these elements does not reveal any trend when considering the differences between burned and unburned material. Sample Pj-A-1 has an ash yield >99% and the lowest St most likely due to the C consumption during combustion.

The chemical composition of major, minor and trace elements in the studied samples is presented in Table 3, together with data from Douro Coalfield materials: other coal waste piles (DCWP), coal (DC_{Coal}) and main overlain lithologies (DC_{Litho}) for comparison (Ribeiro et al., 2011, 2021). Data for ash composition of world hard coals (WCC) and BBS were also added (Ketris and Yudovich, 2009). Considering major and minor elements, Al, Fe, and K are the most abundant (>1%), and Ca, Mg, Na, P, S, and Ti have lower concentrations (<1%). This is consistent with the mineralogical constituents (e.g. aluminosilicates and iron oxides) identified by petrographic analysis. Major differences between the studied samples are noticed for Al, Fe, and S concentration in materials from Pj-B, and for Al, Fe, K, and S concentration in materials from Pj-A.

Generally, the concentration of major and minor elements in the studied samples is similar to the mean concentration of the same elements in other DCWP and in DC_{Litho}. When compared with chemical composition of DC_{Coal}, the waste material presents lower concentrations, except for S in all samples and Fe in some samples (Table 3).

Fig. 13, illustrating the concentration of trace elements and sum of rare earth elements (REE), reveals that the chemical composition of samples is very similar. Amongst samples from Pj-B, major differences are observed for Cd, Cu, Mn, and Pb (Fig. 13A). Differences in the chemical composition of samples from Pj-A are more noticeable which is

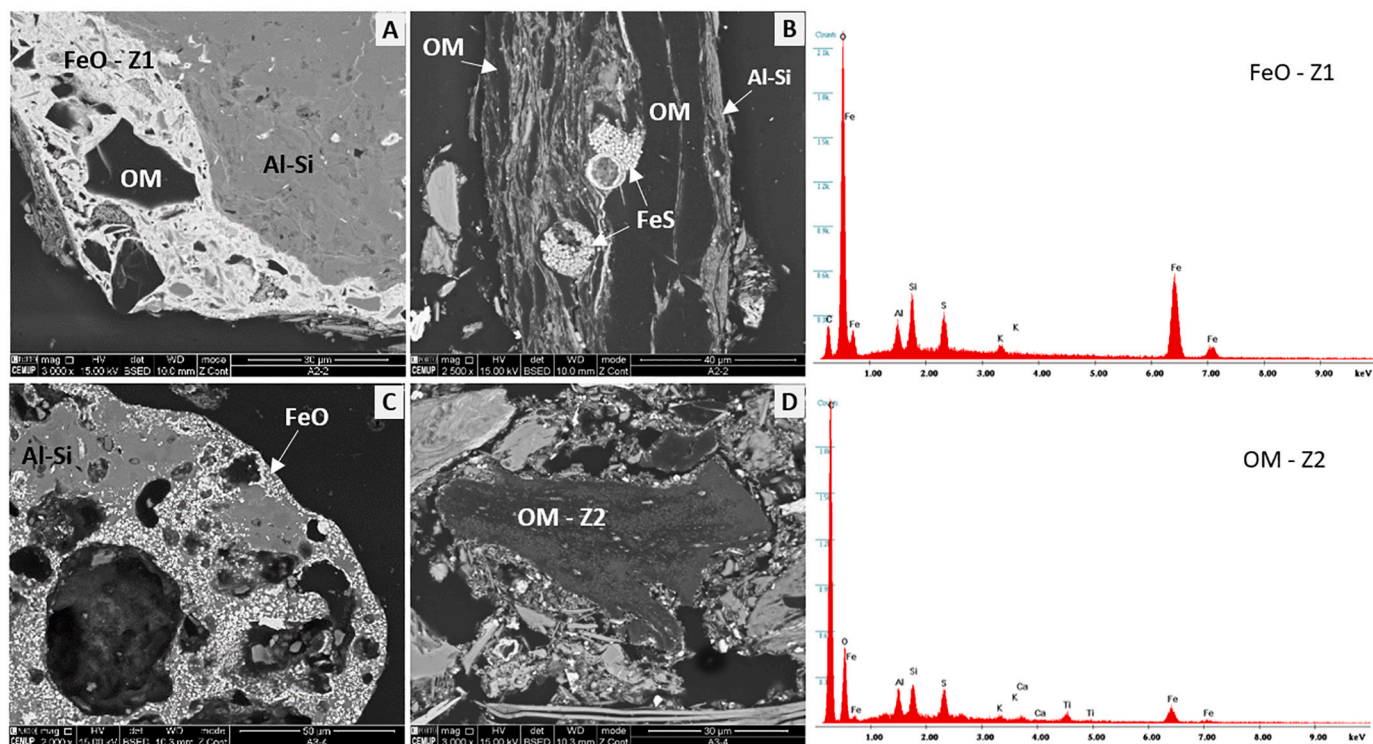


Fig. 12. SEM images of samples Pj-B-4 (A, B) and Pj-A-4 (C, D). A) Aluminosilicates (Al—Si) and iron oxides (EDX spectrum FeO - Z1) enclosing organic matter (OM). B) Mineral matter (aluminosilicates) with embedded organic matter (OM) and framboidal pyrite (FeS). C) Aluminosilicates (Al—Si) with iron oxides (FeO). D) Organic particle (spectrum OM - Z2) apparently affected by the combustion.

Table 2
Ash yield and elemental composition of the studied coal waste samples (values in wt%).

	Ash (d)	C (daf)	H (daf)	N (daf)	O (daf)	St (d)
Pj-A-2 (UB)	77.80	76.44	3.74	2.39	16.04	0.31
Pj-A-5 (UB)	73.09	93.35	3.27	1.82	0.11	0.39
Pj-A-1	99.24	—	—	—	—	0.11
Pj-A-3	63.17	72.88	2.61	1.47	21.75	0.48
Pj-A-4	84.62	75.29	3.97	2.99	13.72	0.62
Pj-A-6	85.71	70.40	4.48	3.08	18.33	0.53
Pj-B-1 (UB)	76.16	67.99	3.69	2.43	22.65	0.77
Pj-B-2	75.91	73.97	3.36	2.28	17.60	0.67
Pj-B-3	79.74	66.83	3.60	2.32	25.52	0.35
Pj-B-4	83.13	69.65	4.39	2.96	21.04	0.33

UB - unburned; d - dry basis; daf - dry ash free basis.

due to the fact that intense and moderate thermally affected mining waste material was collected, as already described. The most significant differences are observed in sample Pj-A-1 that is the most thermally affected sample; this sample has a lower concentration of Bi, Cd, In, Pb, Sb, Se, Sn, and Tl than the other samples (Table 3; Fig. 13). The decrease in the concentration of these elements is primarily attributed to volatilization at high temperatures. On the other hand, Ba, Cr, Cu, Rb, Sc, Sr, and V have high concentration in this sample when compared with other Pj-A samples. The high concentration of Pb in samples Pj-B-1 (UB) and Pj-B-2 stands out from the other samples.

Trace elements concentration in the studied samples are generally lower than that reported for DC_{Coal}, and is in good agreement with chemical composition of DCWP and DC_{Litho}, except for As, Cu, and Mo which have substantial higher concentration in the studied samples (Table 3).

Regarding the comparison with the maximum values reported for BBS (Table 3), the concentration of Cs and Li in the studied samples is generally 2 to 4 times higher. The elements Be, Rb, Th, and Pr have

concentration slightly above from those reported for maximum of BBS in some samples. When comparing the results with the ash composition of world hard coals (WCC) the elements Cs, Li, and Rb also present concentration slightly above in the studied samples (Table 3). The enrichment in Cs, Li and Rb was already described for Douro Coalfield mining waste and was attributed to the contribution of granitic rocks that sourced the basin (Ribeiro et al., 2010a). The Pb concentration in samples Pj-B-1 and Pj-B-2 is significantly higher considering both the BBS and the WCC.

3.2. Overview about mining waste material from Douro Coalfield

3.2.1. Geochemical composition and thermally induced changes

Table 4 integrate the data about the chemical composition of the Pejão waste material (Pj-A and Pj-B) with material from other DCWP as well as with DC_{Coal} and main overlain lithologies (DC_{Litho}). The analysis of the results of this study and the previous research has demonstrated that the mining waste material in the different waste piles is heterogeneous, principally considering petrographic features and C content. However, despite some differences in the inorganic chemical composition, the samples of waste material have similar composition, with major differences being noticed only in the most thermally affected samples, recognized based on field and petrographic observations (Ribeiro et al., 2010a), and on the mineralogical composition and magnetic properties (Ribeiro et al., 2015). Table 4 presents the mean, maximum and minimum of elements concentration in a total of 63 samples of waste material from DCWP. It was also included the mean of elements concentration in unburned waste material (44 samples), in burned waste material (19 samples) and in selected most thermally affected waste material (5 samples).

Data in Table 4 and Fig. 14 validate that the mean chemical composition of waste material (DCWP) is generally between the chemical composition of the DC_{Coal} and of the DC_{Litho} overlaying the coal seams, but closer to the DC_{Litho}. This is to be expected since the waste

Table 3

Geochemical composition of the studied samples from Pejão (major and minor elements in wt% and trace elements in ppm). Data from DCWP (53 samples), from DC_{Coal} (3 samples) and DC_{Litho} (3 samples) (Ribeiro et al., 2011; Ribeiro and Flores, 2021), as well as data from WCC and BBS (Ketris and Yudovich, 2009) were added.

	Pj-A-2 (UB)	Pj-A-5 (UB)	Pj-A-1	Pj-A-3	Pj-A-4	Pj-A-6	Pj-B-1 (UB)	Pj-B-2	Pj-B-3	Pj-B-4	DCWP (n = 53)	DC _{Coal} (n = 3)	DC _{Litho} (n = 3)	WCC	BBS
Al	8.36	7.57	10.9	4.07	8.81	8.11	7.54	7.97	9.08	9.01	9.22	11.68	9.19	n.a	n.a
Ca	0.08	0.13	0.04	0.01	0.17	0.17	0.03	0.07	0.09	0.08	0.07	0.32	0.05	n.a	n.a
Fe	4.12	4.22	3.35	2.64	4.94	5.20	7.97	5.65	3.69	4.29	3.44	4.45	2.66	n.a	n.a
K	2.52	1.97	3.29	1.73	2.54	2.22	2.14	2.23	2.52	2.49	2.32	2.55	2.47	n.a	n.a
Mg	0.39	0.35	0.31	0.09	0.33	0.83	0.18	0.20	0.29	0.29	0.24	0.46	0.46	n.a	n.a
Na	0.40	0.45	0.46	0.30	0.43	0.44	0.31	0.33	0.46	0.47	0.39	1.00	0.41	n.a	n.a
P	0.06	0.06	0.03	0.03	0.06	0.06	0.05	0.09	0.06	0.06	0.07	0.22	0.03	0.15	0.93–2.2
S	0.23	0.30	0.13	0.22	0.55	0.51	0.73	0.56	0.27	0.27	0.27	0.07	0.10	n.a	n.a
Ti	0.29	0.21	0.58	0.18	0.26	0.25	0.18	0.25	0.28	0.27	0.38	0.58	0.40	0.53	1.5–4.6
Ag	0.21	0.22	0.14	0.17	0.21	0.17	0.25	0.27	0.15	0.17	n.a	n.a	n.a	0.6	0.40–2.4
As	62.7	36.4	10.3	38.9	47.5	57.2	67.4	94.0	38.3	43.7	42.7	142	11.0	46.0	10–80
Ba	502	406	685	289	523	450	382	572	550	532	555	1187	667	980	270–800
Be	6.00	3.00	4.00	2.00	4.00	3.00	5.00	6.00	4.00	6.00	3.87	12.0	3.33	12.0	1.0–3.0
Bi	0.70	0.55	<0.04	0.38	0.53	0.55	0.58	0.71	0.62	0.51	0.69	1.77	0.22	7.50	0.0–4.0
Cd	0.08	0.38	<0.02	0.05	0.09	0.10	0.05	<0.02	0.09	0.06	0.22	1.06	0.12	1.20	2.0–12
Co	12.6	18.6	3.40	5.70	6.20	9.20	8.50	3.90	6.60	5.60	5.11	73.3	8.6	37.0	10–30
Cr	89.0	85.0	140	64.0	90.0	113	90.0	83.0	91.0	91.0	132	184	85.7	120	50–160
Cs	17.3	13.1	32.2	11.3	19.0	15.2	19.2	22.7	21.4	18.6	27.8	78.3	18.9	8.0	2.0–7.0
Cu	51.9	54.8	79.1	53.5	44.8	48.5	108	43.1	48.2	52.9	33.6	131.2	8.85	110	35–150
Ga	23.2	20.7	9.00	19.6	24.3	24.4	21.1	23.5	25.4	26.2	25.4	36.4	23.3	36.0	9.0–25
Hf	2.85	2.60	1.97	1.73	2.17	2.17	2.20	2.92	3.10	3.17	3.23	3.01	3.89	9.0	2.5–6.0
In	0.10	0.09	<0.01	0.07	0.11	0.09	0.09	0.09	0.11	0.09	n.a	n.a	n.a	0.20	0.7
Li	107	100	113	104	100	101	75.8	92.6	128	125	169	497	155	82.0	15–50
Mn	342	465	76.0	55.0	132	212	197	72.0	141	122	126	313	233	430	200–800
Mo	2.47	3.63	2.95	3.16	2.61	2.39	3.06	3.04	2.40	2.36	3.18	25.8	0.69	14.0	6.0–60
Nb	8.93	5.78	15.9	4.89	7.00	5.99	5.53	9.75	8.71	7.25	13.9	22.6	16.9	22.0	7.0–15
Ni	32.8	55.3	49.7	17.5	23.3	40.0	30.5	18.0	27.3	25.2	30.1	483	39.0	100	40–140
Pb	46.2	36.4	1.99	34.6	35.1	37.1	288	275	40.2	42.2	37.6	88.6	36.6	55.0	10–40
Rb	136	121	201	95.9	143	116	140	143	147	139	139	164	121	110	40–120
Re	0.004	0.01	<0.002	0.004	<0.002	0.003	<0.002	0.01	0.01	0.01	n.a	n.a	n.a	n.a	0.2–3.5
Sb	11.0	7.49	1.26	5.71	6.04	6.57	8.38	15.0	5.55	7.13	8.60	8.76	5.28	7.50	2.0–11
Sc	13.6	12.8	15.8	4.40	12.4	12.5	10.5	11.9	13.5	14.0	13.1	20.8	14.0	24.0	7.0–20
Se	2.20	2.30	0.60	1.40	1.40	1.10	1.40	2.10	1.10	1.30	n.a	n.a	n.a	10.0	3.0–30
Sn	4.00	2.90	0.50	2.30	3.80	3.50	6.40	5.40	4.20	4.30	5.39	10.2	4.97	8.00	2.0–10
Sr	104	91.0	113	50.0	80.0	82.0	66.0	114	93.0	94.0	109	568	103	730	100–300
Ta	0.70	0.50	1.30	0.40	0.50	0.50	0.50	0.70	0.70	0.60	0.88	1.4	0.90	2.00	0.5–1.0
Te	0.07	0.07	<0.05	<0.05	<0.05	0.07	0.09	0.09	0.09	0.09	n.a	n.a	n.a	n.a	1.3–3.0
Th	11.6	11.1	12.3	5.60	11.0	9.20	12.2	14.2	13.7	12.5	12.4	15.0	10.3	23.0	4.0–11
Tl	1.81	1.06	0.07	0.85	1.67	1.56	1.61	1.83	1.82	1.75	n.a	n.a	n.a	4.60	0.5–10
U	5.00	4.50	4.50	3.60	4.00	3.70	4.60	5.00	5.40	5.00	5.70	10.4	4.07	15.1	4.0–25
V	112	109	186	84.0	116	124	93.0	109	116	118	122	321	118	170	100–400
W	1.40	0.80	2.10	0.70	1.20	1.30	1.30	1.20	1.20	1.10	2.57	6.60	2.10	7.0	0.0–15
Y	11.6	12.1	12.8	4.40	8.50	7.30	9.20	10.9	12.4	10.7	10.9	23.5	7.00	57.0	15–40
Zn	72.6	129	33.2	40.2	64.7	73.7	56.0	41.4	76.3	66.0	45.6	215	65.2	170	60–300
Zr	106	92.2	73.0	64.7	79.0	78.9	79.1	107	105	104	112	103	132	0.60	60–190
REE	161	145	147	89.3	141	109	146	190	172	161	166	285	138	388	83.8–197
LREE	149	132	132	84.1	131	101	136	178	159	148	18.4	256	128	331	75.0–178
HREE	12.1	12.9	15.0	5.20	10.3	8.80	9.80	12.2	13.5	12.7	153	28.8	9.30	57.3	8.8–19.4

UB - unburned; LREE - light REE; HREE - heavy REE; n.a - data not available.

piles are made of the rejected and overburden from coal mining (composed essentially of fragments of carbonaceous shales and lithic arenites with variable amounts of C). The exceptions are Co, Hf, Mn, Nb, Ni and Zn that have lower concentrations in DCWP than in DC_{Coal} and DC_{Litho}.

From an environmental perspective, potentially toxic elements with higher concentration in DCWP than in DC_{Litho} (representing the best approximation of the regional background) may be of concern since the waste material is exposed to natural conditions that favour oxidation, percolation of precipitation waters and remobilization of elements. Considering the studied samples, potentially toxic elements with concentration notably higher than in DC_{Litho} are As, Cd, Cu, and Mo, together with Fe and S. Therefore, potential environmental impacts of coal mining waste disposal in Douro Coalfield are related with these hazardous elements, that may affect soils and waters in surrounding environments, and in consequence the human and other forms of living health (Garbarino et al., 2018).

Comparing the mean chemical composition of unburned samples

(Mean UB) with burned (Mean B) and with the most thermally affected samples (Mean Intense B) it is noticed that the concentration of the majority of elements increase in the burned material (Table 4), certainly due to the C consumption and loss of other elements by volatilization. The concentration of elements As, Cd, Co, Mn, Pb, Sb, Sn, and Zn decrease in burned material, principally and progressively in the most thermally affected samples (Fig. 14), which is attributed to partial volatilization of these elements at high combustion temperatures. The volatilization of these elements in a coal combustor was investigated by Yan et al. (2001) that found that As, Cd, Pb, Sb, Sn, and Zn volatilize at low to intermediate temperatures while Co and Mn are hardly vaporized, depending on combustion conditions and coal type. According to these authors, during combustion of high rank coal, Sb may volatilize at temperatures lower than 300 °C; Cd, Pb, Sn, and As volatilize at temperatures lower than 650 °C; Zn volatilize at temperatures lower than 950 °C; Co and Mn volatilize at temperatures lower than 1500 °C. This indicates that this range of temperatures may had been achieved during combustion in the waste piles, which is consistent with the newly

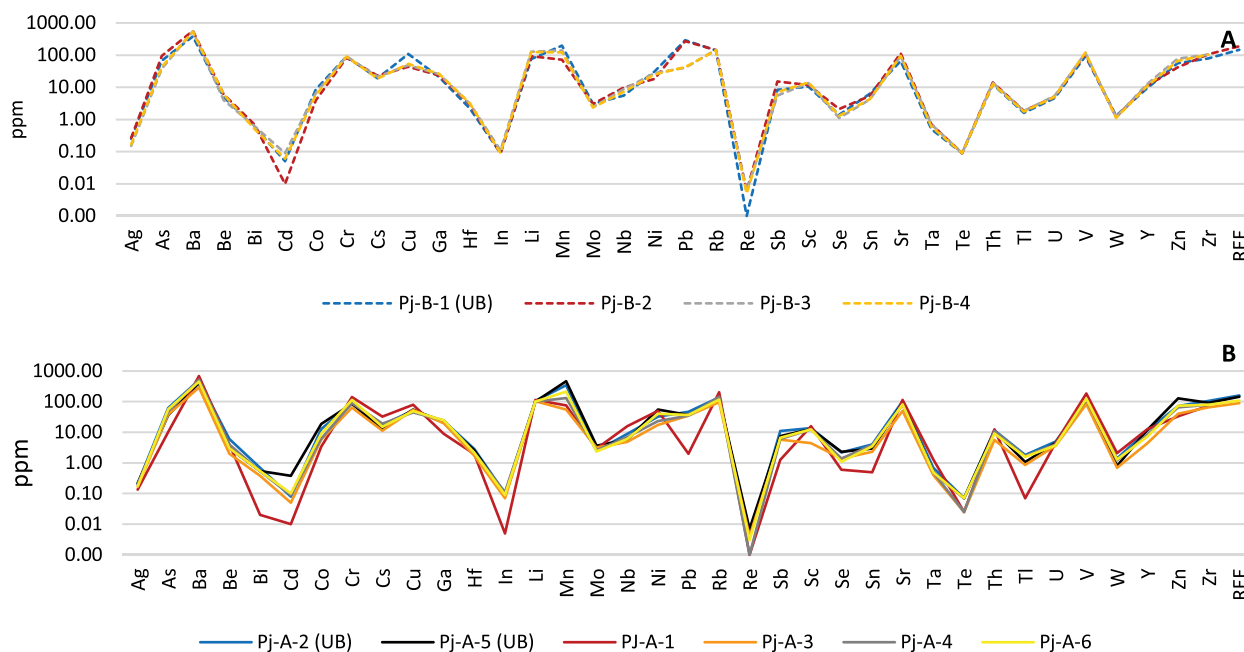


Fig. 13. Trace elements concentration and sum of REE in the studied samples. A) Samples from Pj-B waste pile. B) Samples from Pj-A waste pile.

formed minerals found in the most affected samples (Ribeiro et al., 2015).

3.2.2. Elements mode of occurrence

The recognition of elements mode of occurrence in coals is important because their behaviour during weathering and combustion depends on concentration and chemical form. Statistical methods, such as correlation coefficients and cluster analysis, are commonly used for indirect identification of elements mode of occurrence (Eskenazy et al., 2010; Finkelman et al., 2019).

To investigate the elements mode of occurrence in coal waste material from Douro Coalfield, Pearson's correlation coefficients were calculated based on inorganic elements concentration, ash yield and C content of the 63 samples of DCWP. The SEM-EDS results as well as data about the mineralogical composition of coal mining wastes from Douro Coalfield (Ribeiro et al., 2010a, 2011, 2015) were also taken into account.

Considering the Pearson's correlation coefficients, the positive correlation of elements with ash yield allows the identification of inorganic affinities while the positive correlation with C is indicative of elements' organic affinity. Table 5 shows the correlation coefficients between ash yield and C with selected elements.

The significant positive correlation with ash was verified for Al and K ($p < 0.05$), thus representing the aluminosilicates of the mineral fraction. Other elements typically associated with aluminosilicates present positive correlation with ash but also with Al and K. The occurrence of abundant aluminosilicates was identified by petrographic and SEM-EDX analyses in Pejão waste piles (this study) and in other DCWP (Ribeiro et al., 2010a, 2011, 2015).

On the other hand, S displays a negative correlation with ash and Al, and positive with C indicating its occurrence, at least partially, in association with organic matter. In addition, S have a significant positive correlation with As, Mo, and Pb ($p < 0.05$). These elements are known for their principal occurrence in association with sulfides in hard coals, but also with organic matter (Finkelman et al., 2018). The weak but positive association of S with Fe corroborates their partial association in sulphides. The elements As, Co, Cu, Mn, Ni, Sb, and Zn also have significant positive correlation with Fe ($p < 0.05$ significance) indicating their association with Fe related minerals such as iron oxides and sulphides that were also identified by petrographic observations, SEM-EDX

and XRD in materials from Douro Coalfield (Ribeiro et al., 2010a, 2011, 2015). The significant positive correlation between Ca, Fe, and Mn indicates their association in carbonates (e.g. siderite), whose occurrence was also identified by XRD in materials from DCWP (Ribeiro et al., 2015).

The significant positive correlation between the lithophile elements Cs, Li, and Rb indicates their association, most likely related with the granitic rocks that sourced the basin that, as already mentioned, explains their enrichment in materials from Douro Coalfield and higher concentration in the most thermally affected samples. According to Finkelman et al. (2018), Cs, Li, and Rb in hard coals occur mostly in association with silicates. The elements Nb, Th, U, and REE display significant positive correlation with Cs, Li, Rb, and also with Al, thus indicating their association with mineral fraction.

3.2.3. Coal and coal mining wastes from Douro Coalfield as a secondary source of critical raw materials

To evaluate the enrichment of chemical elements in DCWP and in DC_{Coal} , the concentration coefficients (CC) of trace elements were calculated based on the BBS and WCC established by Ketris and Yudovich (2009). The CC outlines the enrichment or depletion of elements being determined by the ratio between element concentration in coal waste and coal samples and the element concentration defined for the BBS (maximum) and WCC (for hard coals). The enrichment of the elements based on CC may be classified according with Dai et al. (2015, 2016) as follows: unusually enriched $CC > 100$; significantly enriched $CC > 10$; enriched $5 < CC < 10$; slightly enriched $2 < CC < 5$; within the average $0.5 < CC < 2$; depleted $CC < 0.5$. To evaluate the DC_{Coal} , three coal samples and the WCC for hard coal ashes were considered while, to evaluate the enrichment of DCWP, the CC were calculated based mean of coal waste samples and on the maximum established for BBS and on WCC for hard coals. Fig. 15 displays the CC determined for DCWP (Fig. 15A) and for DC_{Coal} (Fig. 15B).

Considering the mean chemical composition of 63 samples of DCWP (Fig. 15A), the CC calculated based on BBS reveal a slight enrichment in Cs and Li while the other elements are within the average values or depleted. The CC calculated based on WCC indicate that the elements Cs and Li are significantly enriched ($CC > 10$), the elements Cr, Pb, Rb, and Sb are enriched $5 < CC < 10$, and the elements As, Ba, Cu, Ga, Hf, Nb, Sc, Sn, Ta, Th, U, V, W, Zr, and REE are slightly enriched $2 < CC < 5$.

Table 4

Geochemical composition of samples from DCWP, including from Pj-A and Pj-B (mean, minimum, and maximum concentration of DCWP; mean of unburned samples - Mean UB, mean of burned samples - Mean B, mean of the more intense burned samples - Mean Intense B), as well as from DC_{Coal} and DC_{Litho} (Ribeiro et al., 2011, Ribeiro and Flores, 2021).

		DCWP (n = 63)			Mean UB (n = 44)	Mean B (n = 19)	Mean Intense B (n = 5)	DC _{Coal} (n = 3)	DC _{Litho} (n = 3)
		Mean	Min	Max					
Al	(%)	9.0	2.3	12.2	9.0	9.2	10.5	1.7	9.2
Ca		0.1	0.02	0.4	0.1	0.1	0.1	0.3	0.4
Fe		3.6	0.2	10.6	3.7	3.5	3.2	4.5	2.7
K		2.3	0.5	3.3	2.3	2.4	2.6	2.6	2.5
Mg		0.3	0.1	0.8	0.3	0.2	0.2	0.5	0.5
Na		0.4	0.1	0.7	0.4	0.5	0.6	1.0	0.4
P		0.1	0.01	0.4	0.1	0.1	0.1	0.2	0.03
S		0.3	0.04	1.1	0.3	0.3	0.4	0.1	0.1
Ti		0.4	0.1	0.6	0.4	0.4	0.5	0.6	0.4
As	(ppm)	43.8	19.0	114	45.3	40.4	39.3	142	11.0
Ba		543	182	913	530	569	606	1187	667
Be		3.9	2.0	6.0	4.0	3.9	4.2	12.0	3.3
Bi		0.7	0.2	1.8	0.7	0.6	0.8	1.8	0.2
Cd		0.2	0.1	0.9	0.2	0.2	0.1	1.1	0.1
Co		5.6	0.8	18.6	5.6	5.5	4.5	73.3	8.6
Cr		125	22.0	282	119	137	150	184	85.7
Cs		26.4	9.8	58.4	25.7	28.0	39.2	78.3	18.9
Cu		37.5	12.6	108.3	36.4	40.3	40.0	131	8.8
Ga		24.9	5.7	33.4	24.8	25.0	24.3	36.4	23.3
Hf		3.1	0.8	5.4	3.3	2.8	2.8	3.0	3.9
Li		159	11.4	374	161	154	161	497	155
Mn		136	6.0	1802	160	90.9	74.6	313	233
Mo		3.1	2.0	10.4	2.9	3.7	4.9	25.8	0.7
Nb		13.0	2.7	32.8	12.1	15.0	20.0	22.6	16.9
Ni		30.4	3.8	89.9	29.2	33.3	37.0	483	39.0
Pb		44.9	18.6	288	46.6	40.9	31.5	88.6	36.6
Rb		139	32.0	201	137	144	164	164	121
Sb		8.4	1.1	76.4	9.3	6.3	4.0	8.8	5.3
Sc		13.0	4.5	19.1	12.9	13.0	14.0	20.8	14.0
Sn		5.1	0.6	15.9	5.3	4.8	4.0	10.2	5.0
Sr		105	45.0	325	92.1	131	183	568	103
Ta		0.8	0.1	2.6	0.8	1.0	1.3	1.4	0.9
Th		12.3	5.1	21.9	12.3	12.1	13.8	15.0	10.3
U		5.5	2.4	9.0	5.6	5.3	6.5	10.4	4.1
V		121	48.0	186	117	128	140	321	118
W		2.4	1.0	5.6	2.3	2.5	3.4	6.6	2.1
Y		10.8	5.1	21.8	10.8	10.7	13.0	23.5	7.0
Zn		48.7	12.3	129	49.7	46.6	32.5	215	65.2
Zr		109	26.6	198	113	99.0	101	103	133
LREE		150	64.9	269	148	155	183	256	128
HREE		18.2	7.5	30.4	18.0	18.6	21.7	28.8	9.3
REE		163	70.0	290	161	167	198	285	138

n = number of samples.

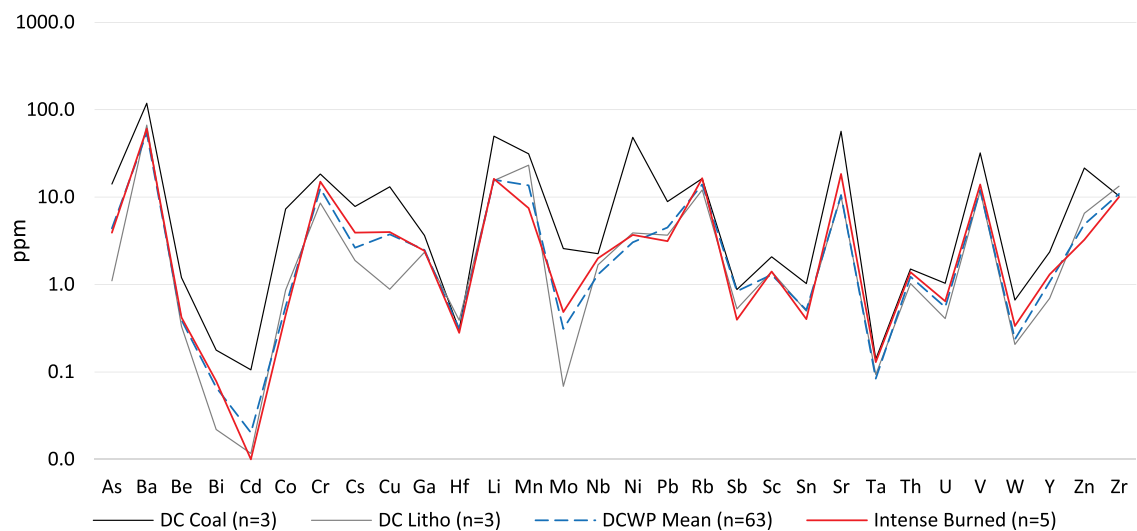


Fig. 14. Chemical composition of DC_{Coal}, DC_{Litho}, mean of DCWP and mean of the most intensely burned samples.

Table 5
Pearson's correlation coefficients between ash yield and C with selected elements.

	Ash	C	Al	Ca	Fe	K	S	Ti	As	Cd	Co	Cs	Cu	Li	Mn	Mo	Nb	Ni	Pb	Rb	Sb	Th	U	Zn	
C	-0.51																								
Al	0.72	-0.58																							
Ca	0.11	0.08	-0.04																						
Fe	0.39	0.03	0.11	0.46																					
K	0.85	-0.44	0.73	-0.11	0.24																				
S	-0.25	0.31	-0.15	0.09	0.19	-0.13																			
Ti	0.49	-0.60	0.77	-0.25	0.34	0.48	-0.19																		
As	-0.06	0.16	-0.16	0.10	0.45	-0.04	0.28	-0.30																	
Cd	-0.03	-0.26	0.01	0.03	-0.16	0.01	-0.10	0.13	0.00																
Co	0.28	0.19	0.05	0.38	0.52	0.14	0.02	-0.18	-0.07	0.04															
Cs	0.13	-0.29	0.51	-0.10	-0.14	0.11	-0.13	0.54	-0.05	-0.10	-0.11														
Cu	0.31	0.24	0.03	0.18	0.64	0.22	0.06	-0.18	0.38	-0.18	0.39	-0.16													
Li	0.30	-0.40	0.52	0.12	0.01	0.12	-0.27	0.50	-0.12	0.11	0.11	0.72	-0.09												
Mn	0.13	0.01	-0.10	0.70	0.69	-0.09	-0.03	-0.39	0.30	0.03	0.36	-0.17	0.39	-0.05											
Mo	-0.01	-0.09	0.02	0.03	-0.02	-0.05	0.32	0.13	0.05	-0.01	0.07	-0.01	0.00	-0.01	-0.06										
Nb	0.25	-0.46	0.56	-0.19	-0.38	0.23	-0.14	0.80	-0.31	0.04	-0.17	0.49	-0.21	0.32	-0.32	0.40									
Ni	0.46	-0.17	0.17	0.21	0.43	0.29	-0.13	0.05	-0.11	0.12	0.65	-0.22	0.32	0.08	0.26	0.24	0.00								
Pb	-0.07	0.35	-0.13	-0.10	0.33	-0.09	0.38	-0.21	0.38	-0.20	0.02	-0.04	0.41	-0.13	-0.02	0.05	-0.08	-0.12							
Rb	0.65	-0.40	0.82	-0.21	0.06	0.83	-0.01	0.67	-0.04	-0.07	-0.07	0.50	0.08	0.33	-0.24	0.05	0.45	0.04	0.01						
Sb	0.14	-0.09	0.04	0.24	0.41	0.15	-0.03	-0.24	0.14	0.12	0.27	-0.30	0.17	-0.04	-0.02	-0.14	-0.29	0.28	0.02	-0.10					
Th	0.32	-0.29	0.62	0.18	0.02	0.25	-0.07	0.55	-0.15	0.02	0.10	0.46	-0.01	0.40	-0.01	0.27	0.70	0.09	0.08	0.50	-0.02				
U	0.12	-0.35	0.45	0.01	-0.29	0.09	-0.23	0.56	-0.16	0.06	-0.13	0.54	-0.17	0.34	-0.12	0.20	0.78	-0.06	-0.04	0.33	-0.22	0.74			
Zn	0.36	0.13	0.02	0.36	0.57	0.18	-0.12	-0.22	0.19	0.25	0.78	-0.21	0.45	0.14	0.41	-0.15	-0.35	0.59	-0.01	-0.11	0.40	-0.07	-0.21	-0.08	
REE	0.19	-0.24	0.45	0.16	-0.05	0.10	-0.05	0.46	-0.22	0.01	0.13	0.56	-0.12	0.44	-0.01	0.37	0.70	0.04	0.07	0.35	-0.06	0.90	0.74		

Bold numbers mark correlations significant at $p < 0.05$.

However, the CC based of the ash of WCC only reveals the Cs and Li slight enrichment. This information is systematized in [Table 6](#). The remaining (Be, Bi, Cd, Co, Mn, Mo, Ni, Sr Y, and Zn) are within the average values or depleted.

Considering the enrichment or depletion of trace elements in DC_{Coal} ([Fig. 15B](#)), samples show relevant variability. The element Cs is significantly enriched in one sample, Cs, Li, and Ni are enriched in at least one sample, and As, Co, Mo, Ni, Pb, and V are slightly enriched in at least one sample. The inconsistent behaviour can be due to the variable factors that control the geological processes affecting the different sectors of Douro Coalfield ([Pinto de Jesus, 2003](#); [Moura et al., 2016](#)), since the coal samples were collected from different sectors of the basin. In previous studies on coal from Douro Coalfield by [Moura et al. \(2016, 2018\)](#), the enrichment /depletion behaviour of trace elements in the different stratigraphic and sedimentary facies of the basin were investigated. [Moura et al. \(2016\)](#) identified a differentiated enrichment/depletion behaviour in coals from the different sectors and seams of the basin, which is consistent with the findings in this study.

Considering the elements slightly to significantly enriched in DC_{Coal} and DC_{WP} ([Table 6](#)), if on the one hand some are considered critical raw materials by the EU ([European Commission, 2020](#)) (Ba, Ga, Hf, Li, Nb, Sb, Sc, Ta, V, W, and REE), on the other, As, Co, Cr, Cu, Mo, Ni, Pb, and U are of concern from an environmental point of view ([Orem and Finkelman, 2003](#); [Swaine and Goodarzi, 1995](#)). Mercury was found to be unusually enriched in some samples of coal from Douro Coalfield ([Moura et al., 2018](#)), adding further to the environmental problems. Additionally, it was also identified the production of graphene sheets and carbon nanotubes as a consequence of the self-burning of coal waste materials in Douro Coalfield ([Ribeiro et al., 2010c](#)). Carbon materials are known to be of interest from a technological and economic point of view and natural graphite is included in the list of critical raw materials.

The above mentioned indicates that some inorganic elements in the Douro Coalfield materials have the potential to impact the surrounding environment through leaching and mobilization, but others inorganic elements and carbon materials may be of economic interest. Therefore the reutilization of coal waste materials as a secondary source of critical raw materials could be economically relevant and will allow the mitigation of environmental impacts caused by their deposition. [Dai and Finkelman et al. \(2018\)](#) also found that the extraction and utilization of critical elements from coal and its combustion byproducts could result in a number of economic and environmental benefits.

4. Conclusions

The petrographic, mineralogical and geochemical composition of burned and unburned material from Pejão coal waste piles (Pj-A and Pj-B) allow the identification of thermally induced changes caused by combustion. The petrographic observations reveal that the organic matter (isolated particles and within mineral matter), is principally composed of vitrinite, with minor proportions of inertinite. Evidences of thermally induced changes in burned samples include dark reaction rims, cracks, devolatilization vacuoles, plasticized edges, pyrolytic carbon and lower vitrinite reflectance, despite the presence of unaltered particles. The mineral matter is composed of abundant aluminosilicates, and also sulphides and iron oxides that are more abundant in burned samples. SEM-EDX analysis corroborates some of the petrographic observations. The lowering of vitrinite reflectance, the presence of pyrolytic carbon, and the newly formed iron oxides point out high combustion temperature. The differentiated intensity of the petrographic thermal effects observed in organic particles demonstrates that the combustion temperature attained within each coal waste piles was heterogeneous. The geochemical composition of the studied samples is generally within the expected for Douro Coalfield coaly materials (between DC_{Coal} and DC_{Litho} , and close to the chemical composition of other DC_{WP}). More noticeable differences are observed for the most thermally affected sample.

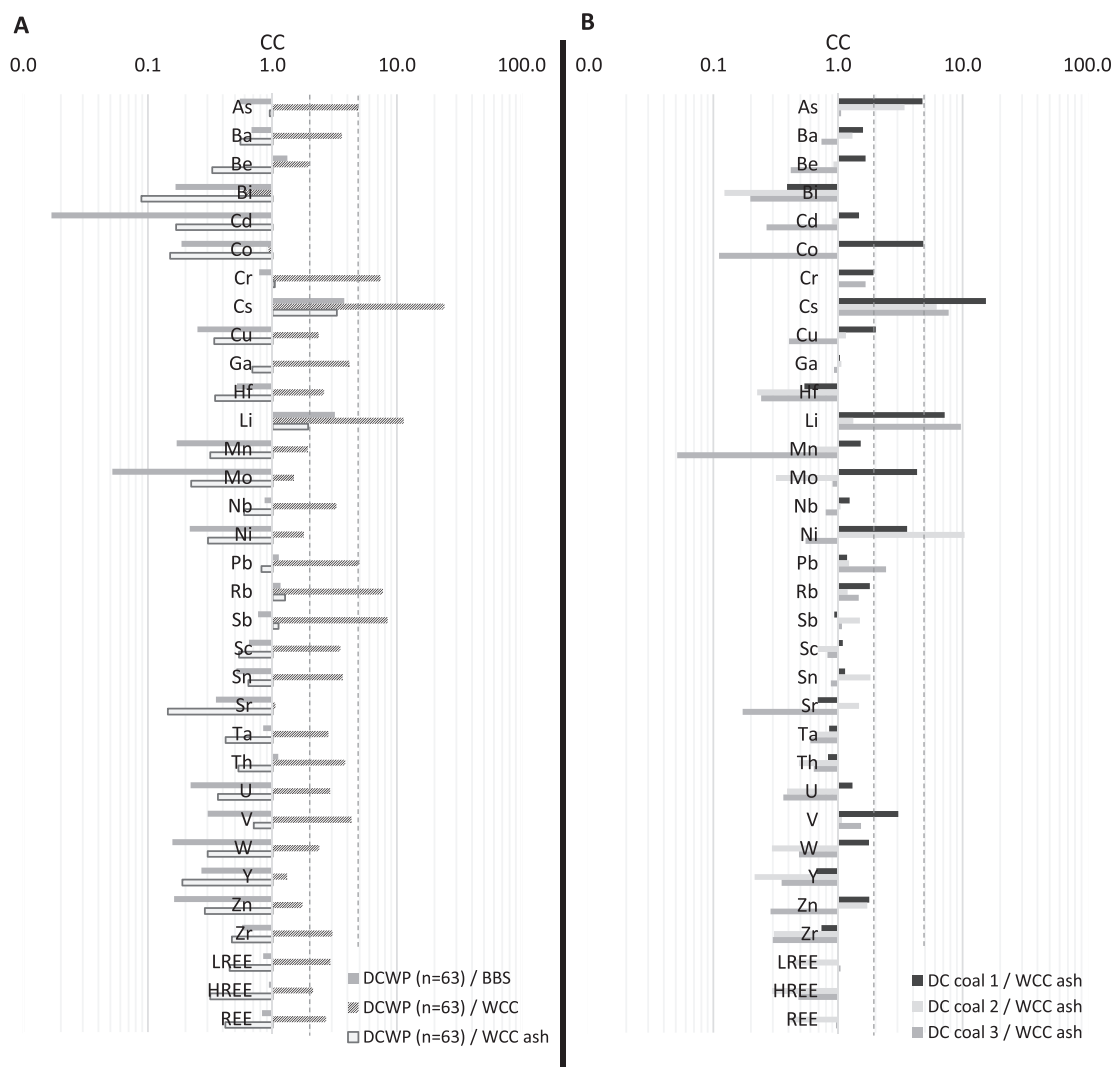


Fig. 15. Concentration coefficients (CC) of trace elements and of the sum of REE, LREE and HREE in DCWP (A) and DC_{Coal} (B) relatively to BBS and WCC (Ketris and Yudovich, 2009).

Table 6
Classification of trace elements enrichment in DCWP and DC_{Coal}.

DCWP/BBS	Slightly enriched 2 < CC < 5	Cs, Li
DCWP/WCC	Significantly enriched CC > 10	Cs, Li
	Enriched 5 < CC < 10	Cr, Pb, Rb, and Sb
	Slightly enriched 2 < CC < 5	As, Ba, Cu, Ga, Hf, Nb, Sc, Sn, Ta, Th, U, V, W, Zr, and REE
DCWP/WCC _{ash}	Slightly enriched 2 < CC < 5	Cs
DC _{Coal} /WCC _{ash}	Significantly enriched CC > 10	Cs
	Enriched 5 < CC < 10	Cs, Li, Ni
	Slightly enriched 2 < CC < 5	As, Co, Mo, Ni, Pb, V

Considering the new data from this study and data about other DCWP (making a total of 63 samples), the mean chemical composition of waste material is generally between the chemical composition of the DC_{Coal} and of the DC_{Litho} overlaying the coal seams. The potentially toxic elements As, Cd, Cu, and Mo, together with Fe and S, present higher concentration in DCWP than in DC_{Litho} and therefore are of concern

when considering the environmental impacts caused by coal waste disposal that favour oxidation, percolation of precipitation waters and remobilization of elements. The decrease of As, Cd, Co, Mn, Pb, Sb, Sn, and Zn concentrations in burned material is attributed to partial volatilization of these elements at high combustion temperatures (between 300 °C and 1500 °C), at least pontually, corroborating the petrographic analysis and previous studies on burned waste material from Douro Coalfield.

From the elements slightly to significantly enriched in Douro Coalfield materials, Ba, Ga, Hf, Li, Nb, Sb, Sc, Ta, V, W, and REE, are considered critical raw materials by the EU, while As, Co, Cr, Cu, Mo, Ni, Pb, and U are environmentally sensitive and may cause negative impacts in surrounding areas. The reutilization of Douro Coalfield materials as a secondary source of critical raw materials, including inorganic elements and carbon materials, has the potential to be economically interesting, allowing at the same time the mitigation of environmental impacts caused by their deposition. The differences between CC considering WCC and WCC ash are pertinent for investigation on extraction techniques. This study and the comprehensive characterization of coal waste material, including determination of elements concentration and modes of occurrence, is fundamental and serves as a basis for research dedicated to establishment of the best techniques for environmentally and economically viable re-processing and extraction of secondary raw

materials.

CRedit authorship contribution statement

Joana Ribeiro: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Isabel Suárez-Ruiz:** Conceptualization, Methodology, Writing – review & editing. **Deolinda Flores:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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