New data on the geochemistry of coals from the Douro Carboniferous Basin (Portugal)

Novos dados geoquímicos dos carvões da Bacia Carbonífera do Douro (Portugal)

H. Moura#1,2, A.D. Pinto de Jesus2, J. Ribeiro3, I. Suárez-Ruiz3, D. Flores2, P.P. Cunha1

Abstract: This research aims at an integrated study regarding the geochemical composition of selected coals from the Douro Carboniferous Basin, through proximate and ultimate analysis as well as the major and trace elements composition and their concentration coefficients (CC). The results indicate that the proximate and ultimate analysis data agree with the coal rank and show variable ash yields. The elements abundance demonstrates that the enrichment/depletion is variable but Zn, Pb, Sb and Cs enrichment is more or less transversal, which is considered to be a result of magmatic fluids circulation. According to trace element CC, the Douro Carboniferous Basin exhibit values considered enriched, wherein mercury exhibits an unusual enrichment (CC > 100) in a sample from the TSU B1 unit in S. Pedro da Cova. The geochemical markers of these coals corroborate the interpretation of duplication of the sedimentary succession, suggested by previous sedimentological and stratigraphic studies.

Keywords: Coal, concentration coefficients, Douro Carboniferous Basin, geochemical composition, trace elements.

1. Introduction

The characterization of coals is relevant from a geological point of view, mainly the concentration in trace elements and the relationship with geological events that occurred during the basin history, as well as for technological and industrial coal use, mainly for energy supply or for the production of metallurgical coke (Suárez-Ruiz and Creling, 2008). Furthermore, coals may contain trace elements with industrial significance such as U, Ge, Ga, Sc and rare earth elements (REE). Nowadays the demand for REE and yttrium (REY) is greater than the supply, and coal deposits can be an alternative to the conventional deposits (Dai et al., 2010, 2016, and references therein). Moreover, coal is rich in some harmful elements such as mercury, which during the technological and industrial processes are emitted to the atmosphere. In addition to the relevance of the energy and mining industries, as well as the technological market, studies like this can reveal new information about mineralizations (Suárez-Ruiz et al., 2012).

The Douro Carboniferous Basin (DCB) is the most important coal basin in Portugal and the coal of this coal-bearing sequence is classified as high rank A (anthracite A) according to the ISO 11760 (2005). The coal was exploited for many years (1795-1994) in two main mining areas, S. Pedro da Cova and Pejão, principally as fuel for power generation.

The present study focuses on the characterization of the geochemical composition of coals from the DCB in order to determine the enrichment/depletion of mercury and other trace elements, such as REY. These coals may represent an economic resource or a possible environmental issue, depending on the enriched elements, and taking into account their concentrations and modes of occurrence in raw coal, since it can give information for the beneficiation of coals for further technological and industrial uses. The large volumetric waste piles resulting from the exploitation of the coals from this basin can also be a material to be beneficiated and recycled for further reuse.

2. Geological setting

The DCB is located in northwestern Portugal mainland, with general orientation NW-SE. This is the major Carboniferous Basin present in the Douro-Beira Carboniferous Trough (Sulco Carbonífero Dúrico-Beirão - SCDB) occurring in the Central
Iberian Zone, a narrow strip extending for 53 km with a width rarely greater than 500 m (Pinto de Jesus, 2003).

In this basin, the base of the Paleozoic record rests by an angular discordance over the Complexo Xistograváquico (CXG, Beira Group, upper Precambrian-lower Cambrian). The top of the basin sedimentary infill is cut by an important reverse fault that placed the Lower Paleozoic formations of the reverse limb of the Valongo anticline over the Carboniferous sequence (Fig. 1). The Carboniferous sedimentary record indicates an intramontane basin of the Upper Pennsylvanian (Lower Stephanian C) with alluvial-palustrine/lacustrine-fluvial and deltaic deposits containing coal seams interbedded (Pinto de Jesus, 2003).

The stratigraphy and the sedimentary facies of the DCB (Fig. 1) were described by Pinto de Jesus (2003).

TSU A – (Complex; TSU A1 and TSU A2) - The base of the sequence includes breccias associated with the transport from the active tectonic margins of the basin.

TSU B – (Simple; TSU B1 and TSU B2) - This unit consists of pelitic and coal-bearing facies. Coal and carbonaceous mudstone facies change to silt and clay, occasionally with lenticular bodies of sandstone. Both facies, pelitic and organic, were formed by vertical accretion as can be conclude by the presence of floral remains and micaceous clasts occurring always parallel to the stratification and no paleosols were found. So, the sedimentary deposits present horizontal lamination, a structure typical of lacustrine low energy aquatic environments.

TSU C – (Simple; TSU C1 and TSU C2) - Consists of a fluvial braided system with flow parallel to the near SW basin margin. The TSU C1 unit is composed by fluvial lithofacies associations, with conglomerates progressing to sandstones and upwards into siltstones in a multistory-multichannel fluvial braided system with SE-NW flow, as evidenced by the lithologies spatial distribution and sedimentary structures.

TSU D – (Simple; TSU D1 and TSU D2) - Present lacustrine/deltaic facies at the base resulting in a lenticular pelitic and coal-bearing sedimentation, due to a reduction of the tectonic activity and, consequently, a loss of transport energy. Therefore, the palustrine sedimentation takes place on the entire basin, progressing into a lacustrine sedimentation as a result of the increasing water depth.

The sedimentary series suffered duplication as a result of a tectonic context causing the sectioning of the basin; thereby the coal seams TSU B2 and TSU D2 are the duplication of the seams TSU B1 and TSU D1, respectively (Pinto de Jesus, 2003) (Fig. 1).

3. Materials and methodologies

For this research a set of five anthracite samples were used, being four of them from previous studies (Lemos de Sousa, 1978). The geochemical analysis included proximate and ultimate analysis and the determination of chemical composition in major and trace elements. For the analysis, all samples were ground to pass the 212 μm sieve.

Proximate analysis includes moisture and volatile matter contents and ash yield determined under standardized conditions (ISO 589, 2008; ISO 562, 2010; ISO 1171, 2010; respectively). The moisture content is used only to calculate the other chemical parameters in dry and dry ash-free bases, according to the ISO 1170 standard. Ultimate analysis (carbon, hydrogen, nitrogen and total sulfur) were performed using a LECO S-2000 for C, H, N and a LECO S-632 for total sulfur (S). The oxygen content was obtained by difference \([O,db = 100 - (Ash,db + C,db + H,db + N,db + St,db)]\). The chemical composition of samples on major and trace elements and the mercury concentration was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) and by inductively coupled plasma-mass spectrometry (ICP-MS).

4. Results and discussion

I. Ultimate and Proximate Analysis

The results of the proximate analysis were reported in table 1. Coals from the DCB reveal a medium to high ash yield (9.88% to 43.24 %, weight, db). The volatile matter content is low (from 3.99 % to 14.90 %, weight, daf), which is in accordance with the rank of the studied samples. The ultimate analysis displays high C content (83.62 % to 94.28 %, daf) and very low H (1.30 % to 1.99 %, daf), N (0.85 % to 1.01 %, daf) and O (2.64 % to 9.35 %, daf) contents, which is in agreement with the rank. Regarding the total sulfur content, the values vary slightly (0.69 % to 3.36 %, db), having samples from TSU B1 from S. Pedro da Cova and Pejão higher and similar values (3.36 % and 3.31 %, respectively).

II. Major and Trace Elements

The abundance on major and trace elements of the DCB samples, when compared with the average values of the world hard coals (Ketris and Yudovich, 2009), show that some of them are enriched in certain elements. The abundance of enriched elements occurs in a greater number of elements in two samples, namely TSU B1 from S. Pedro da Cova and Pejão, while the other samples exhibit a lower number of enriched elements.
Regarding the major elements, the studied samples display a high content of Al in the samples TSU B1 from S. Pedro da Cova and Pejão and TSU D2 from Pejão, pointing out the presence of clay minerals. A high content of Fe and St is also observed in the samples TSU B1 from S. Pedro da Cova and Pejão indicating the presence of pyrite. Regarding the Ca content, it is generally low in all samples although carbonate minerals were identified, except in sample TSU B1 from S. Pedro da Cova.

Concerning the trace elements, generically, the samples are enriched in: Ag, As, Co, Cr, Cs, Cu, Ga, Hg, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sn, Sr, Th V, W, Y, Zn, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er and Yb. Within the enriched trace elements, it is important to note the contents of Ag, As and Co for the samples TSU B1 from S. Pedro da Cova and Pejão, as they present much higher values than those considered for the average of world hard coals reported by Ketris and Yudovich (2009). The same is valid for the contents of Hg in the samples TSU B1 from S. Pedro da Cova and Pejão and TSU D2 from Pejão. The Cs and Sb contents are also very high in the samples TSU B1 from S. Pedro da Cova and Pejão, respectively.

### III. Concentration Coefficients

The concentration coefficient (CC) is the ratio of trace element concentration in studied coal samples versus the respective value established for the worldwide hard coals by Ketris and Yudovich (2009). The enrichment/depletion pattern of the elements in coals reported by Ketris and Yudovich (2009). The same is valid for the worldwide hard coals (0.5 < CC < 2) are Ga, Mo, Rb, Sc, Se, Sn, Th, V, W and Y. A depletion (CC < 0.5) is observed for the other elements, including Ti, Ba, Be, Bi, Hf, Sr, Ta, Th and U.

Concerning the REEs (Fig. 3), only the CC of Sm reveals a slightly enrichment (2 < CC < 5). The remaining REEs exhibit concentration values within the average for world hard coals (0.5 < CC < 2). The Ho, Tm and Lu are depleted (CC < 0.5) in these coals.

In summary, in samples TSU B1 from S. Pedro da Cova and Pejão some of the elements are enriched comparing with the values established for world hard coals and, in opposition, samples TSU D2 from S. Pedro da Cova and Pejão and the sample from the Eastern Basin (S. Pedro da Cova) present depletion on the majority of the elements.

### IV. Abundance and Genetic Consequences

The DCB, as previously reported, presents a different enrichment depending on the sample. The samples TSU B1 from S. Pedro da Cova and Pejão exhibit the same geochemical markers, since they have higher content of Fe and St, and the contents of some of the trace elements are almost identical, including Ag, As, Cd, Co and Cu.

The remaining samples (TSU D2) from S. Pedro da Cova and Pejão and the sample from the Eastern Basin (S. Pedro da Cova) are not so enriched. The sample from the Eastern Basin (S. Pedro da Cova) occurs stratigraphically between TSU D2 and the sequences of the Lower Paleozoic, by a fault contact and the coal seams of this package are very mylonitized.

It is noticed that there is a more obvious enrichment in the lower coal seams, namely seam TSU B1 and probably also in the duplicated seam TSU B2. This enrichment is probably due to magmatic fluids and percolating waters enriched in these elements resulting from the intrusion that generated granitoid rocks in the region, that lead to the coalification of the coal to the anthracite rank. In addition to the higher enrichment in seam TSU

### Table 1. Proximate and ultimate data of the studied coals from DCB.

<table>
<thead>
<tr>
<th>Seam</th>
<th>Mine</th>
<th>Ash (%)</th>
<th>VM (%)</th>
<th>C (%)</th>
<th>N (%)</th>
<th>H (%)</th>
<th>O (%)</th>
<th>St (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSU B1</td>
<td>S. Pedro da Cova</td>
<td>17.58</td>
<td>19.40</td>
<td>83.62</td>
<td>0.96</td>
<td>1.99</td>
<td>9.35</td>
<td>3.36</td>
</tr>
<tr>
<td>TSU B1</td>
<td>Pejão</td>
<td>43.24</td>
<td>55.07</td>
<td>5.93</td>
<td>0.68</td>
<td>5.71</td>
<td>5.56</td>
<td>2.29</td>
</tr>
<tr>
<td>TSU D2</td>
<td>S. Pedro da Cova</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>TSU D2</td>
<td>Pejão</td>
<td>16.40</td>
<td>5.07</td>
<td>94.28</td>
<td>0.85</td>
<td>1.30</td>
<td>2.74</td>
<td>0.69</td>
</tr>
<tr>
<td>Eastern Basin</td>
<td>S. Pedro da Cova</td>
<td>9.88</td>
<td>3.99</td>
<td>93.60</td>
<td>1.01</td>
<td>1.91</td>
<td>2.64</td>
<td>0.76</td>
</tr>
</tbody>
</table>

VM = volatile matter; C = carbon; H = hydrogen; N = nitrogen; St = total sulfur; db = dry basis; daf = dry ash-free basis *data not available

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**Figure 2.** Concentration coefficients of trace elements of the studied coals from DCB, normalized by average trace element concentrations in the world hard coals (Yudovich and Ketris, 2005).

**Figura 2.** Coeficientes de concentração dos elementos traço dos carvões estudados da BCD, normalizados através das concentrações médias de elementos traço nos carvões mundiais de grau médio e grau superior (Yudovich e Ketris, 2005).
B1, some elements display very high contents, in particular Hg in sample from S. Pedro da Cova, showing also the higher REEs contents. This factor can be an indicator that the crustal stretching may have been greater than initially thought permitting the circulation of the magmatic fluids. Wang et al. (1999) reported enrichment for some trace elements as a result of a granite intrusion for the Late Permian anthracites in the Coalfield Meitan (Hunan Province, Southern China). It is therefore concluded that the igneous minerals from the hydrothermal fluids were the main responsible for the enrichment of trace elements in the coals from the DCB.

5. Conclusions

The coals from the Douro Carboniferous Basin were characterized from a geochemical point of view. The enrichment/depletion of trace elements was discussed as well as the establishment of the relationship between the enrichment of elements present in coals and its geological context.

The proximate and ultimate analysis data is in agreement with the rank of the coals and presents variable ash yields. The study of the geochemical composition revealed that some coals from the DCB can be considered enriched on trace elements according to their CC, especially mercury in sample TSU B1 from S. Pedro da Cova, which exhibits an unusual enrichment (CC > 100).

It would be interesting to investigate a higher number of coal samples from DCB, in order to prove and identify the existence of different geochemical markers in each coal seam, and therefore to support the interpretation of the sedimentary succession tectonic duplication.

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