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Physicochemical Properties and REE Distribution of the Northwest and Central Greece Coal Deposits: A Review †

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Abstract: This review presents a mineralogical and physicochemical comparison of coal seams located in the regions of Northwest and Central Greece. The comparison extends to the fly ash derivatives from the coal combustion for energy production, in the cases where data are available. Coal occurrences from Northwest Greece tend to exhibit higher content of rare earth elements (REE) compared to those of Central Greece. Moreover, fly ash products show similar trends in Light-REE compared to their coal parent rocks. The observed REE distribution seems to be correlated with the occurrence of specific minerals such as allanite, monazite, as well as with Fe-contents.

Keywords: lignite; fly ash; maceral; rank; REE

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1. Introduction

In Greece, lignite combustion used to be the primary power generation process, satisfying over 30% of the national generation and corresponding to 19% of the Total Primary Energy Supply (TPES) during 2016. However, nowadays, and as following the EU policies intends to be a front-runner in diminishing the reliance on domestic lignite, the contribution of lignite-fired power plants in the energy sector is rapidly decreasing, although they still play a significant role in the stability of the electricity system [1].

Nevertheless, in this energy-transition phase, new opportunities that were overlooked in the past, as well as challenges, have arisen concerning the potential value of domestic lignite deposits, and their industrial wastes/derivatives. Among the various factors that contribute to any decision making processes regarding the prospect and/or exploitation of any raw material, knowing the properties of the raw material in question is the primary step.

In this context, this paper presents a synthetic review comparison of previously published in scientific journals, or partially published in technical research data reports on petrographical, mineralogical and physicochemical features from selected coal basins in Northwest and Central Greece. The study areas include the following basins: (1) Mesohellenic Trough, (2) Dimitras-Karperos-Grevena basin, (3) Kastoria basin, (4) Ptolemais basin, (5) Amyntaio basin, (6) Lavas-Servion basin and (7) Prosillio-Trigoniko basin from the Northwest region of Greece, and the Almyros basin in Central Greece (Figure 1a).

The aim is to discuss the similarities and differences between the aforementioned regions in terms of their essential properties, and to provide an initial record of the REE distribution when data are available.

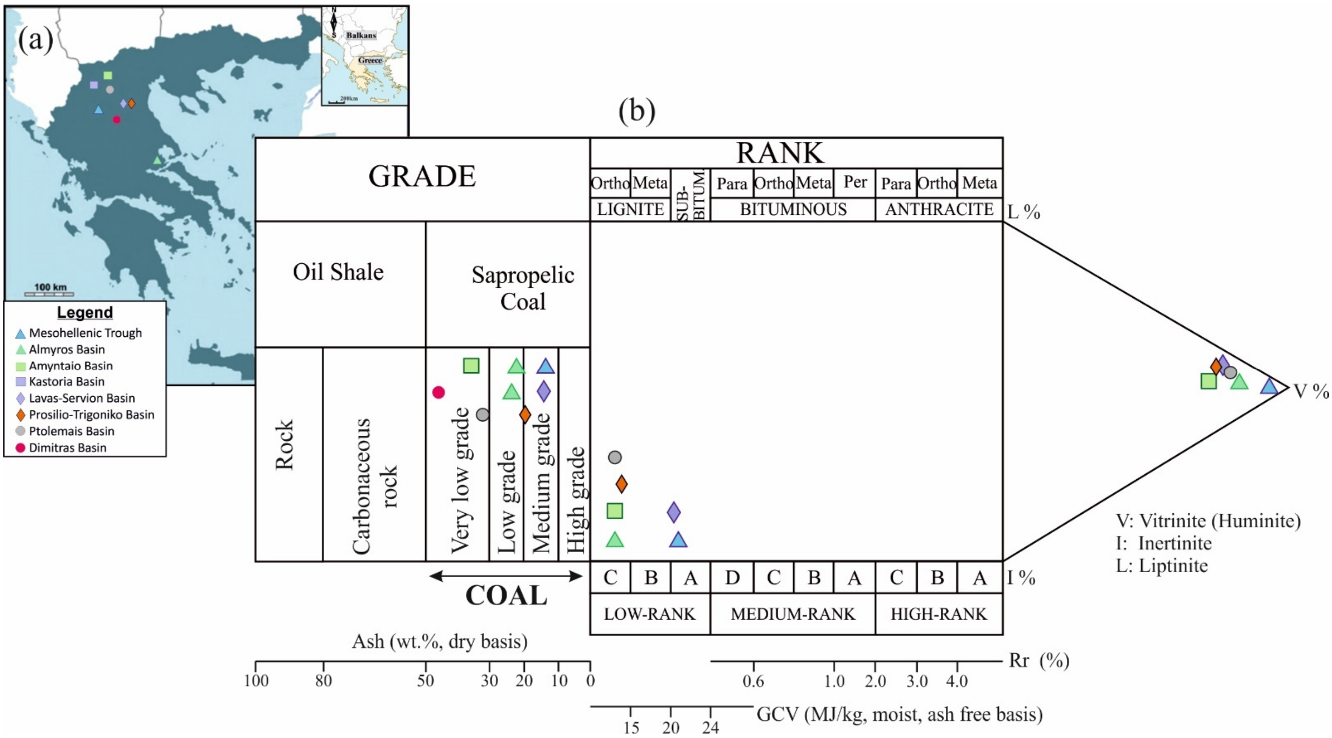

Figure 1. (**a**) Map of Greece indicating the studied coal basins; (**b**) ECE-UN classification of the reviewed coal basins [2].

2. Geological Setting

The lignite-bearing sequences investigated in this study were deposited in two main tectonic phases; the older one is related to the formation of the Mesohellenic Trough as a back-arc sedimentary basin that evolved during the Late-Oligocene to Miocene period [3–6] within the stratigraphic units of this basin, where thin coal layers or lenses were developed under deltaic and fluvial-lacustrine regimes. The second and main phase of coal formation in Greece is related to the post-Alpine extension phase (Late Miocene to Late Pliocene) that produced several intermontane basins in a NW-SE direction, occurring across the main axis of Mainland Greece (Figure 1a). These intermontane basins, from a North to South direction, include the Kastoria, Amyntaio-Ptolemais [7,8], Lavas-Servion, Prosilio-Trigoniko [9,10] and Dimitras basins, as well as the Almyros basin further to the SE, and host thick lignite seams [11], intercalating primarily with marls and clays, deposited mostly under lacustrine regimes and secondary under fluviatile ones.

3. Methodology

This review is based on an evaluation of data published in international journals, as well as in publicly accessible repository domains. Data were collated, evaluated, processed and presented in Harker (binary) diagrams, ternary diagrams, REE-chondrite normalized diagrams, and multi-trace primitive mantle element diagrams.

4. Results and Discussion

4.1. Proximate, Ultimate Analysis and Coalification

Regarding the proximate analysis data, the reported coals are mainly characterized by medium to high ash yields in their exploitable (proven and/or probable) reserves, with the coals of Tsotili in Mesohellenic Trough, Prosilio and Lava displaying average values ≤ 15 wt% (dry basis), whereas the rest display between 15–25 wt% (db), with the Amyntaio lignites being the most inferior (reaching even 40 wt%, db) (Table 1, Figure 1b).

The volatile matter parameter ranges from 25 to 40 wt% (dry ash free basis) in Almyros, Mesohellenic Trough, Prosilio and Lava to >50 wt% in the Ptolemais basin. Subsequently, fixed carbon yields are above 40 wt% (dry ash free basis) in the Mesohellenic Trough, between 20–40 wt% in Almyros, Ptolemais, Prosilio and Lava, and below 20 in Amyntaio. In terms of heating value, the highest values (>5000 kcal/kg) are recorded in coals from the Mesohellenic Trough and Lava, and the lowest (1700 kcal/kg) in Amyntaio. The features of the proximate data indicate that the grade of the studied coals range from medium to very low, and the coalification rank ranges from Low Rank A–B for Mesohellenic Trough and Lava (sub-bituminous) to low rank C (lignite) for the rest of the basins (Figure 1b, [2]).

Elementary C, H, N, O and S average data of the studied coal samples are presented in Table 1. Total sulphur values of coals from Northwest and Central Greece range between 0.7 and 1.70%, being classified as low to medium-S coals [12]. Coals from the Lavas basin exhibit the highest average content of C among the lignites of Northwest Greece, whereas those from Amyntaio exhibit the lowest. Additionally, in both the Almyros and Lava basins the xylite-rich lithotype are more carbon-enriched in C than in the matrix. Plotting the O/C and H/C on a van Krevelen diagram (Figure 2a) confirms this differentiation among the xylite-rich and matrix lithotypes; additionally, it is evident that Lava coals (falling almost in the sub-bituminous field) are of higher rank than the Ptolemais and Amyntaio, whereas the matrix lithotype of Almyros is the least coalified.

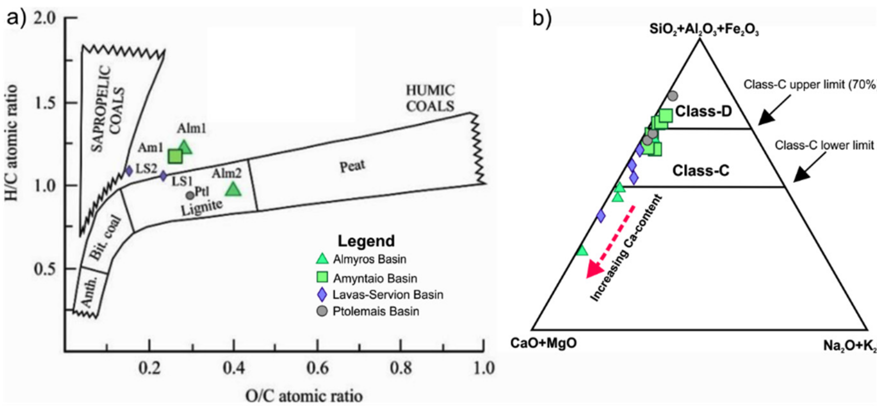

Figure 2. (**a**) Van Krevelen classification diagram of O/C vs. H/C atomic ratios plots for the coal deposits under study; (**b**) Ternary classification diagram for coal fly ashes.

Table 1. Averaged physicochemical qualitive data of the coal seams from the Mesohellenic Trough (MT; [13,14]), Almyros (Alm; [11,15]). Amyntaio (Am; [7,16]; Dimitras (D; [17]). Kastoria (K; [13]), Lavas-Servion (LS; [18]), Prosilio (P; [19,20]) and Ptolemais (Pt; [21,22]).

	MT1	Alm1 [a]	Alm2 [a]	Am1	D	K	LS1 [b]	LS2 [b]	P	Ptl
Moisture (wt%)	9.1	50.0	52.6	54.3	50.0	48.3	46.7	21.5	42.3	44.3
Ash (wt%, db)	13.5	22.0	26.4	36.0	46.4		15.9	16.9	19.8	32.1
VM (wt%, daf)	41.8	32.1	24.7	27.3	30.2		30.5	41.1	34.5	55.9
Cfix (wt%, daf)	48.5	23.7	20.4	17.3	19.8		22.7	36.0	23.1	34.2
GCV(kcal/kga.r.)	5415	2600	1960	1723	1850	1770	2820	5560	2870	2404
S_{Total} (wt%,db)	0.8	1.7	1.5	0.9	1.0	-	0.7	1.1	0.7	1.1
C (wt%, db)		52.6	44.8	40.8			58.2	63.8		45.1
H (wt%, db)		4.3	3.2	4.2			5.0	5.9		3.0
N (wt%, db)		0.5	1.1	2.8			1.2	0.3		1.0
O (wt%, db)		19.3	23.9	14.2			18.6	12.1		17.9

[a]: Alm1: west site, Alm2 east site; [b]: LS1: matrix lithotype, LS2: xylite-rich lithotype.

4.2. Organic Petrographical and Mineralogical Data

The maceral analysis data of the reviewed coal deposits [11,22] indicate the dominance of huminite group with detrohuminite being the most frequent subgroup. Only in the xylite-rich lythotypes, telohuminite is the major maceral sub-group. Macerals of the liptinite and inertinite groups occur on average with combined values less than 20 vol%. These petrographical features indicate that the almost exclusive accumulation of humic coals originates mostly from herbaceous plants, with minor arboreal contributions (Figure 1b) (e.g., [23,24]).

In terms of mineralogical composition, Lavas-Servion coals contain quartz, mica and kaolinite, siderite, pyrite, gypsum, calcite and magnetite [25,26]. The lignite of the Ptolemais basin contains silicates in the form of quartz, feldspars and clays, carbonate minerals (calcite, dolomite, aragonite, siderite) and sulphides and sulphates (pyrite, gypsum, anhydrite). In the Amyntaio basin, the major minerals are quartz, kaolinite, siderite, and diaspore, with the secondary occurrence of calcite and gypsum [26]. In the Almyros basin, the main mineralogical assemblages are of quartz, feldspars, gypsum and calcite [11]. The contained minerals reflect primarily the marginal lithologies of the palaeopeatlands, as well as the intense detrital influx during peat formation, which results in the elevated ash yields. Furthermore, the mineral matter type controls the type and the chemistry of the bottom and fly ashes produced during coal combustion.

4.3. Classification and Geochemical Features of Fly Ashes

Based on the C-618 classification of fly ashes (ASTM; [27]), fly ashes from Amyntaio and Ptolemais fall into Class-D and Class-C, respectively (Figure 2b). Nevertheless, the vast majority of NW Greece fly ashes are classified as Class-C. Fly ashes from the Almyros basin are poor in SiO_2, Al_2O_3 and Fe_2O_3 and rich in CaO contents, whereas their plots lie closer or within the Class-C field (Figure 2b; [28]).

4.4. REE and Trace Elements in Coal Samples

Available data from lignite samples from the Lavas-Servion (NW Greece [29]) and Almyros (C. Greece [11,30]) basins for trace element and Rare Earth Element (REE) concentrations are presented (see Supplementary Material Tables S1 and S2). REE patterns of Lavas-Servion lignites exhibit a high fractionation between light rare earth (LREE) and heavy rare earth (HREE) elements. They also present strong negative Eu anomalies (Eu_N/Eu^* = 1.17–1.31), negative Nd anomalies and positive Tb anomalies. $(La/Sm)_N$ ratio ranges from 3.33 to 3.59, whereas $(La/Yb)_N$ ratio ranges from 7.81 to 8.15.

Coal samples from the Almyros basin exhibit steep patterns decreasing from LREE to HREE. They also exhibit strong negative Hf, Ho, Tm and Lu anomalies with positive Sm, Dy, Er and Yb anomalies. Eu_N/Eu^* ratio is extensively variable (0.88 to 1.31). $(La/Sm)_N$ and $(La/Yb)_N$ ratios range from 2.50 to 3.33 and 5.43 to 10.87, respectively (Figure 3a). Lignites from the Lavas-Servion basin exhibit higher REE contents compared to those of Almyros basin.

Coal occurrences from Lavas-Servion basin exhibit a wide range of V (V: 30.40–95.10 ppm) and Ba values (Ba: 46.90–101.80 ppm), whereas Zn contents are quite high (Zn: 56.90–88.50 ppm). Coal occurrences from Almyros basin display a wide range of Cr and V contents (Cr: 57.20–136.00 ppm; V: 60.40–134.00 ppm). In addition, Ba and Sr values are quite high ranging from 123.20 to 156.50 ppm and 142.80 to 194.20 ppm.

Analysis of the data presents sub-parallel patterns of multitrace elements in the Lavas-Servion and Almyros basins (Figure 3b), characterized by strong positive Th, Pb and Ta anomalies. In addition, they exhibit slightly positive P and Sm anomalies and slightly negative Zr anomalies. Sr presents negative anomalies in Lavas-Servion lignites and positive anomalies in Almyros lignites.

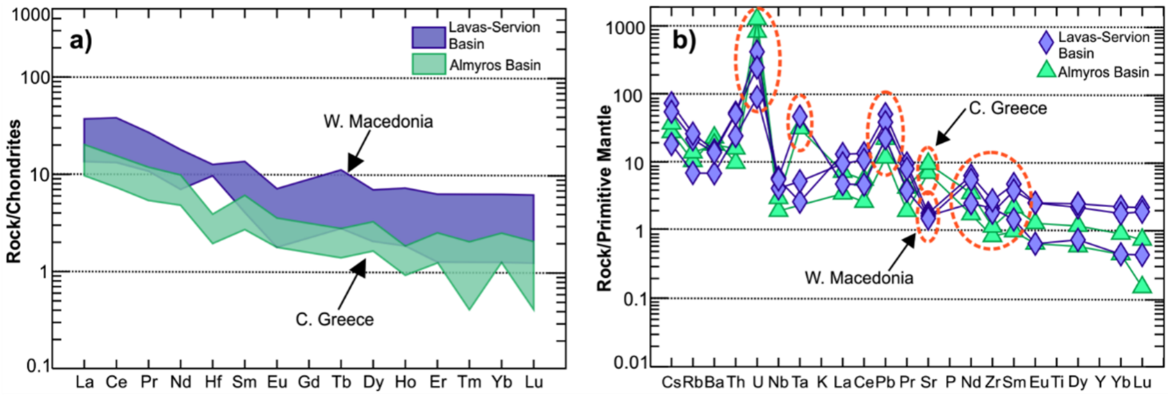

Figure 3. (**a**) Chondrite normalized-REE patterns (Normalization factors after McDonough and Sun, [31]) from coal samples from Lavas-Servion and Almyros basins (data from Supplementary Materials Table S2), (**b**) Primitive mantle-normalized patterns for samples from Lavas-Servion and Almyros basins (Normalization factors after McDonough and Sun, [31]).

The occurrence of significant detrital mineral components such as monazite, allanite, zircon and xenotime is a major factor that controls the REE-enrichment in coal samples [32,33]. Monazite is usually associated with high REE values and negative Eu anomalies. Lavas-Servion coal exhibits quite elevated REE contents and negative Eu anomalies. Th values are positively correlated with IREE contents (IREE-Th: 17.33–2.00 ppm; 49.85–4.40 ppm; 40.13–4.20 ppm). An alternative hypothesis for the strong Eu anomalies can be associated with the occurrence of plagioclase grains. The positive Nd anomalies of Lavas- Servion coal also support the presence of REE-bearing monazite, which is an Nd-bearing mineral. Sr anomalies are associated with the occurrence (positive anomaly) or the absence (negative anomaly) of plagioclase grains, indicating that fly ashes from the Almyros basin are plagioclase-bearing, whereas those from the Lavas-Servion basin lack plagioclase grains.

Uranium exhibits strong positive anomalies in the multitrace element patterns of Figure 3a. The occurrence of U in coal is usually associated with the amount of organic matter, and occasionally with the presence of U-bearing minerals [34–36]. Although detailed studies of Greek coals and related ashes regarding U affinity are limited, evidence for organic affiliation are provided for Megalopolis lignite and a bituminous coal layer in the Parnassos area [37,38].

4.5. REE and Trace Elements in Fly Ashes

Class-C fly ashes usually tend to be more abundant in REE, compared to the other types, due to the substitution of Ca^{+2} and Fe^{+3} by trivalent LREE and HREE, respectively, being highly comparable with fly ashes derived from the Powder River Basin and Jungar coals [32]. Moreover, there is a significant relationship between the Fe-oxides components in fly ash, formed from glass devitrification during coal combustion and the REE abundance [32,39–41].

These results can explain the higher REE Chondrite Normalized patterns of coal fly ash samples from the Lavas-Servion basin (Class-C), compared to those of their parent coal (Figure 4). The REE-bearing minerals of the coal fly ash are usually hosted within the Si-Al glass matrix, which offers them a low leaching efficiency [36,42]; a similar pattern has been reported for coals in Greece regarding the behaviour of REE in laboratory produced ashes [38], as well as for selective trace element enrichments (e.g., Th, Yb) from lignite occurrences in the region of Lofoi (Florina basin) [43]. The total REE and Th in coal fly ash samples range from 164.1 to 418.8 ppm and 6.2 to 10.7, respectively, whereas Ce is strongly enriched. This is indicative of the presence of monazite within the coal fly ash samples, whereas the occurrence of REE-bearing allanite cannot be excluded.

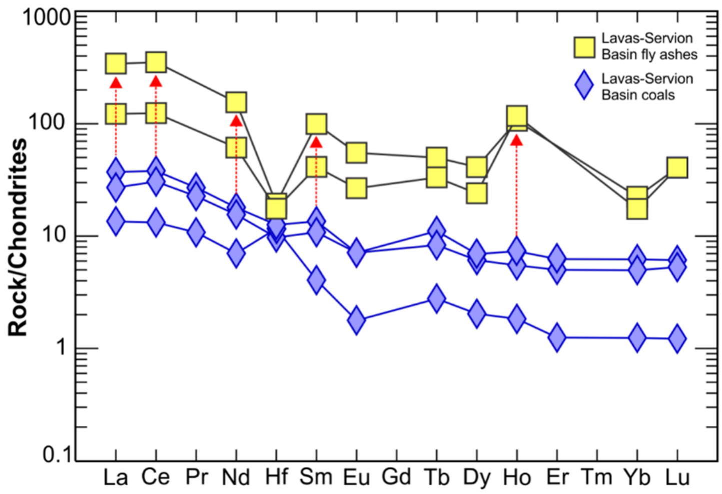

Figure 4. Chondrite normalized-REE patterns (Normalization factors from McDonough and Sun, [31]) from coal samples from Lavas-Servion and Ptolemais basins.

5. Conclusions

Physicochemical properties of coal seams derived from the regions of northwest and central Greece are investigated against the coalification grade of the respective coals. Both areas are characterized by the predominance of huminite group minerals. Inorganic mineral components include quartz, feldspars, sulphides, sulphates, micas, carbonates and Fe-oxides in various and unequal amounts between the different basins. Coal occurrences from NW Greece exhibit higher Rare Earth Element (REE) contents compared to those of Central Greece. This can be attributed to the occurrence of allanites, Fe-oxides and especially monazite, confirmed by the strong negative Eu anomalies and the higher Th values in samples from the Lavas-Servion basin. According to the ASTM classification, coal seams are mainly classified as C-Class CaO rich coals. In terms of coalification, the reported coals range from sub-bituminous in Mesohellenic Trough, Lava and Prosilio to lignites in Ptolemais, Amyntaio, the less mature being in Almyros.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/materproc2021005103/s1, Table S1: Averaged Trace element content for the xylite-rich and matrix lignite deposits of the Almyros basin [11,30]) and the Lavas-Servion basin [29]; Table S2: Averaged Rare Earth Element (REE) content (ppm) for the xylite-rich and matrix lignite deposits of the Almyros basin [1,2] and the Lavas-Servion basin [3].

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