

The Drama Lignite Deposit, Northern Greece: Insights from Traditional Coal Analyses, Rock-Eval Data, and Natural Radionuclides Concentrations

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In the present study the results of traditional methods for characterizing 25 lignite samples, representing a continuous sequence of the Drama deposit, Northern Greece, are presented. The moisture, the volatile matter, and the ash contents are high, while the sulfur content remains at low levels. Rock-Eval analysis was performed on the same samples. The T_{\max} values obtained do not correlate with coal type and rank and are higher than those expected for lignites. The reflectivity values are lower than 0.2%. In values $< 0.5\%$ R_m and $> 1.5\%$ R_m , T_{\max} does not correlate with R_m . It is also noticed that the difference in hydrogen contents is not related to the T_{\max} values as would be expected. The concentrations of ^{238}U , ^{235}U , ^{226}Ra , ^{210}Pb , ^{228}Ra , ^{228}Th , and ^{40}K , determined in samples D2 and D5, are similar to those reported in the literature for Greek lignites. The concentrations of uranium-series isotopes are among the higher for lignites worldwide.

Keywords Drama, Greece, lignite, radionuclides, Rock-Eval pyrolysis

More than 60 basins in Greece formed during Neogene and Quaternary times include coal deposits. The rank of the coal varies from peat up to the subbituminous coal stage. The most abundant type of coal in Greece is lignite. Lignite deposits formed from the Miocene to the Pleistocene in mires of intramontane and paralic basins, such as the basins of Ptolemais, Florina, and Drama in Northern Greece and the basin of Megalopolis in Southern Greece. The proved lignite

Received 5 March 1999; accepted 20 May 1999.

The present work has been made possible thanks to the Institute of Geology and Mineral Exploration (IGME). I warmly thank J. Broussoulis and P. Yiakkoupis of IGME for providing the core samples and for fruitful discussions. The author is especially indebted to François Marquis and Jean Espitalié for the Rock-Eval pyrolysis analyses and for their advice during the interpretation of the results. I am particularly grateful to Asst. Prof. M. Manolopoulou for the radioactivity measurements and for her valuable help in the comprehension of the results. The assistance of Asst. Prof. T. Soldatos and Lecturer A. Koroneos is highly appreciated. I wish also to thank Prof. S. Valceva, University of Sofia, Bulgaria, for having assisted me through helpful discussions, and Asst. Prof. K. Christanis, University of Patras, Greece, for his critical review and suggestions for improvement of this article.

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reserves are estimated up to 6,750 Mt without adding the 4,300 Mm³ of the Philippi peat, about 150 km in the east of Thessaloniki, Northern Greece. The economically recoverable lignite reserves reach 3,900 Mt, approximately 58% of the total. The calorific value is very low: 1400 kcal/kg in Ptolemais–Amynteo, only 900 kcal/kg in Megalopolis. The ash content is always high, in contrast to the sulfur content which is always low. Opencast mining takes place in the basins of Ptolemais, Amynteo, and Megalopolis. The annual production exceeds 60 Mt, of which 98% is used for electricity generation. The total installed capacity of the power plants is 4,833 MW. A number of publications have referred to the geology, petrology, mineralogy, and geochemistry of Greek peats and lignites, such as those of Cameron et al. (1984), Christanis (1983, 1987, 1994), Kaouras (1989), Goodarzi et al. (1990), Gentzis et al. (1990, 1996, 1997), Broussoulis et al. (1991), Kalkreuth et al. (1991), Fowler et al. (1991), Kaouras et al. (1991), Antoniadis (1992), Antoniadis et al. (1992), Botis et al. (1993), Valceva & Georgakopoulos (1993), Valceva et al. (1995), Filippidis et al. (1996), Sakorafa & Michailidis (1997), and Antoniadis & Rieber (1997). The present article integrates conventional analyses of lignites from the Drama deposit with a pure geochemical analysis—Rock-Eval pyrolysis—and methods of measurement of the quantity of the naturally occurring primordial radionuclides which will be released, to some extent, to the environment after the lignite combustion.

Geological Setting

The 700-km² intramontane basin of Drama is a tectonic graben formed since the Miocene by post-alpidic tectogenesis (Figure 1). Tectonic movements during the Early-Middle Pleistocene separated the Drama basin from the Serres graben in the west. Pre-Neogene metamorphic and igneous rocks of the Rhodope massif, such as gneisses, schists, marbles, and granites, constitute the margins of the Drama basin (Melidonis, 1969, 1981). The Neogene-Quaternary formations of the basin consist of clay, mud, sand, conglomerate, marl, peat, and lignite. The lignite deposit extends all over the central plain area of the Drama basin. In the Lower Pleistocene, a lacustrine environment gradually developed in a large part of the basin. Lacustrine, calcareous gyttja was deposited, constituting the floor of the lignite deposit and occurring in many other marginal parts of the basin. As the lake gradually shallowed, extended peat-forming mires, covered by herbaceous vegetation, formed. It was on these peat-forming mires that the genesis of Drama lignites started 1 million years ago (Van Der Wiel & Wijnstra, 1987). Over most of the basin, clastic material from alluvial fans deposited at different times. The extensions of the fans in the area of the Drama lignite deposit separate the limno-telmatic deposits into three distinct lignite seams (A, B, and C; see Figure 2). The formation of the Drama lignite in a limno-telmatic environment is confirmed by petrographic and palynological investigations (Kaouras et al., 1991). Maximum growth of all three lignite seams is found in the area of Agia Paraskevi (Figure 1). Seam C is not developed in the north of the village of Nerofraktis; seam B is not developed as far north as the village of Koudounia, and seam A seems to extend further to the north. The minable lignite reserves are estimated to exceed 1,430 Mt, with more than 1,060 Mt belonging to seam A, which is the thicker and more extensive one. The Drama lignite deposit has not been exploited yet.

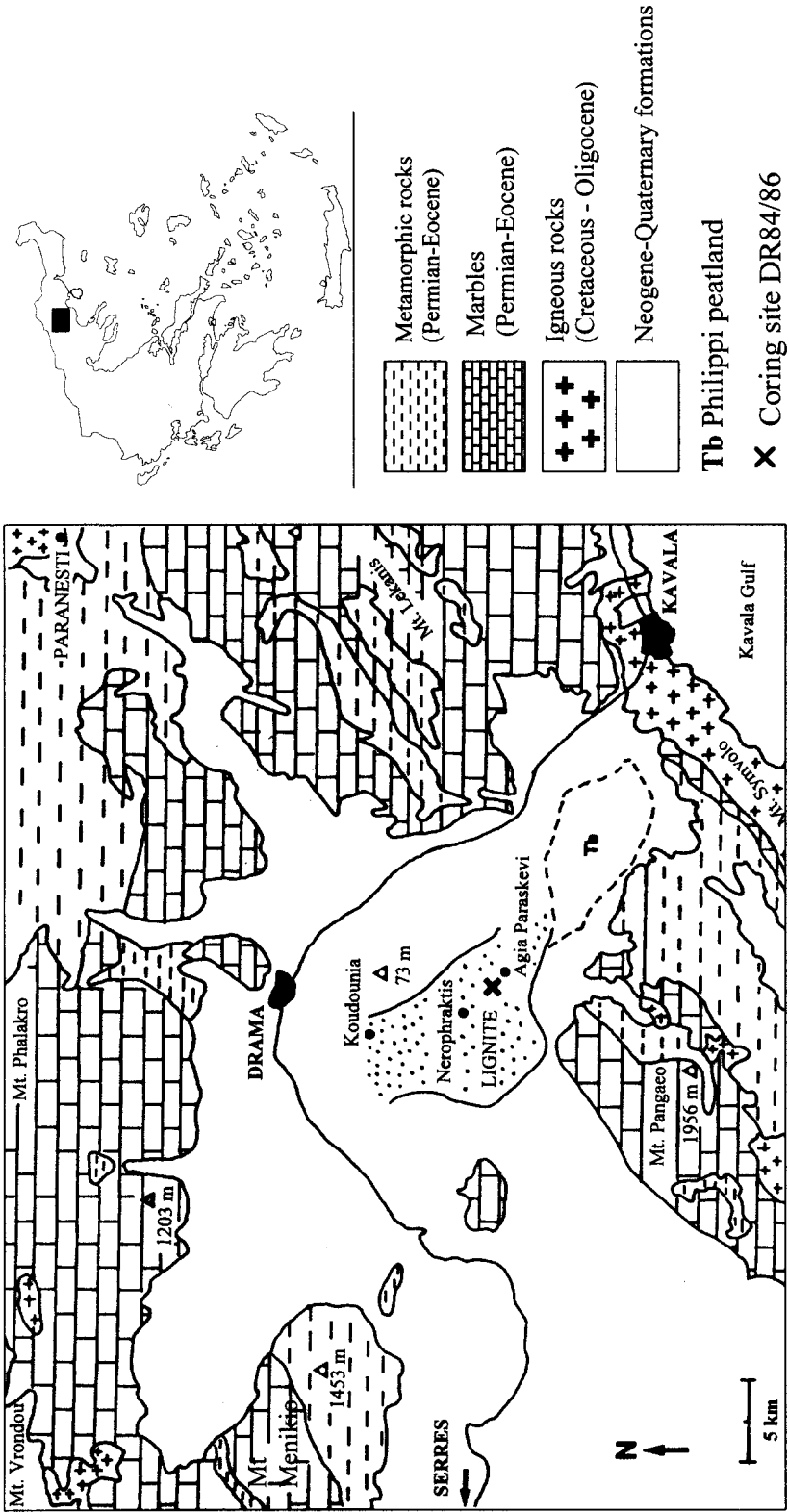


Figure 1. Simplified geological map of Drama basin (after Melidonis, 1969).

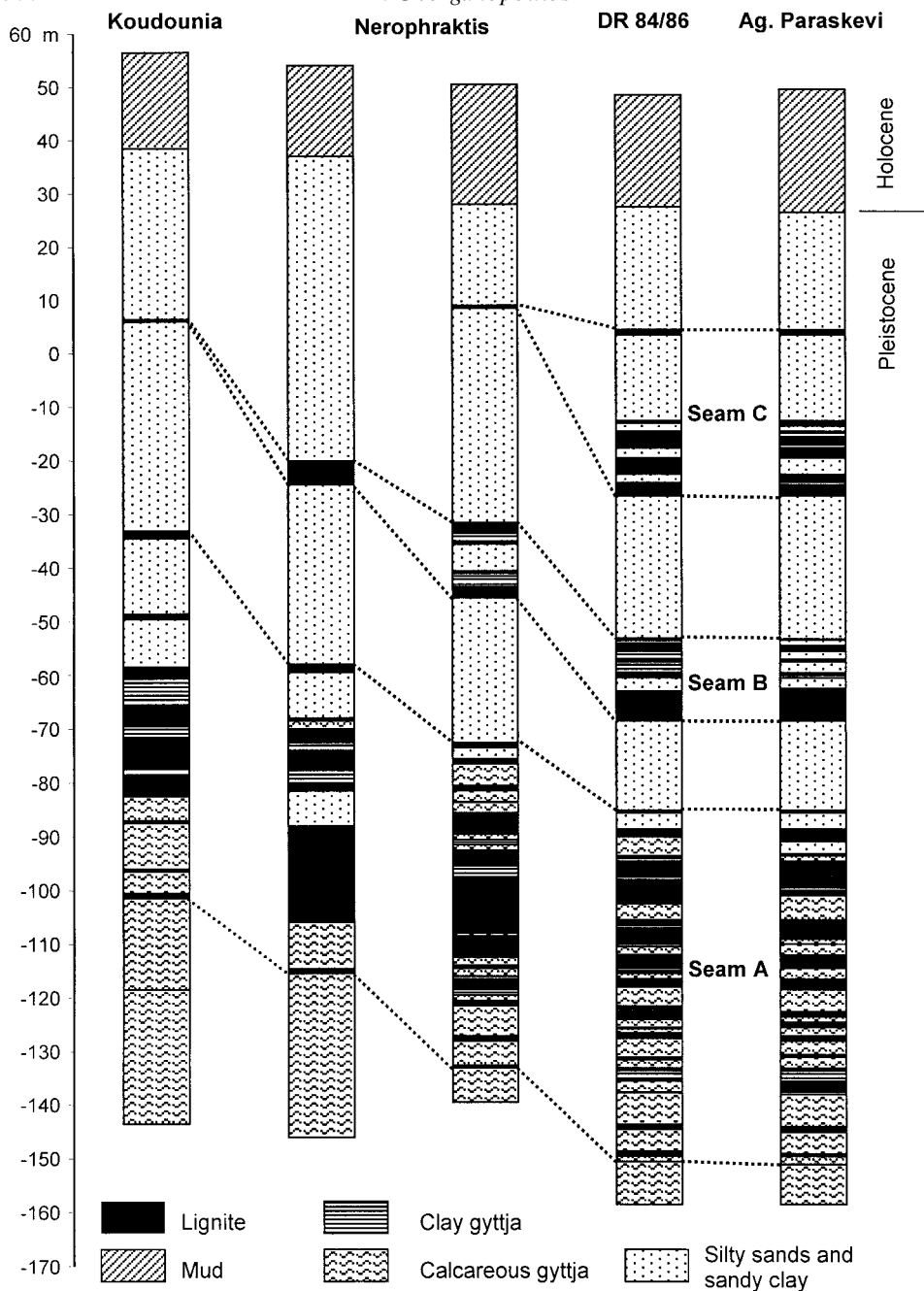


Figure 2. Generalized profiles of the Drama lignite deposit (after Filippidis et al., 1996).

Samples and Analytical Methods

Twenty-five lignite samples representing a continuous sequence of the Drama deposit were obtained from the DR 84/86 core. The coring site is located about 1.2 km in the north of Agia Paraskevi village (Figure 1). Drilling and sampling was carried out by the Institute of Geology and Mineral Exploration (IGME), Athens.

Each sample represents a seam interval 0.2 to 1.6 m thick. Figure 2 shows the stratigraphic and areal extent of the sampled lignites. The samples were air-dried after being crushed in coarse fragments. Then the samples were crushed to pass a 1-mm sieve. The number and thickness of each sample is given in Table 1. Proximate and ultimate analyses were performed according to ISO standards. The moisture, the ash content (on a dry basis), the volatile matter (on a dry and dry, mineral matter-free basis), the carbon content (on a dry basis), and the total sulfur and organic sulfur content were determined. The calorific value was determined by thermogravimetric analysis using an isothermal bomb calorimeter. Polished sections of the samples were prepared for microscopic observation. The lignite samples were mounted in epoxy resin and then ground and polished according to the standard method (Stach et al., 1982). The reflectance was determined in immersion oil at a monochromatic light ($\lambda = 546$ nm). Reflectance measurements were taken on eu-ulminite A (dark). Fluorescence spectra analysis has not been carried out.

Organic Geochemistry: The Rock-Eval Pyrolysis Method

The Rock-Eval pyrolysis method uses a special device in which coals or rocks with organic substance are subjected to sustained pyrolysis under an inert atmosphere, which allows faster study of the organic matter and its stage of evolution. The main part of the instrument is a small oven in which a pulverized rock sample (about 100 mg) is heated in a helium atmosphere (Espitalié et al., 1977). In the case of coals, the recommended sample size of 100 mg may overload the flame ionization detector (FID) (Peters, 1986). In previous studies 5-mg aliquots were used (Fowler et al., 1991; Sykes et al., 1994). In the present study, between 10 and 16 mg of lignite were used. This amount of sample provides good results for both TOC and S_2 values. After a few minutes' purge for traces of air, the device heats the sample progressively from 180°C up to 600°C at a constant rate of 15°C/min. During the assay, the hydrocarbons, which are free in the sample at the time of sampling, are first volatilized at a moderate temperature. The quantity of these hydrocarbons is recorded as a function of time by means of a flame ionization detector (FID), giving a first peak (S_1). The second peak (S_2) is representative of the hydrocarbons and hydrocarbon-like compounds generated by thermal cracking and other reactions of the organic matter (lignite in our case). The organic matter pyrolysis also generated oxygen-containing volatiles, i.e., carbon dioxide (CO_2) and water. The measurement of CO_2 (S_3 peak) is limited to the range 180–390°C, in order to include the main stage of CO_2 generation from organic matter and to avoid other sources of CO_2 (decomposition of carbonates, bicarbonates, etc.). From S_1 and S_2 the microprocessor determines the total production index (TPI), which is the ratio $S_1/(S_1 + S_2)$. S_1 , S_2 , S_3 are calculated in milligrams of products (hydrocarbons, CO_2) per gram of sample. A fourth parameter is the temperature, T_{max} (in degrees Celsius) at which the maximum rate of generation of hydrocarbons occurs (top of the S_2 peak). This parameter is used mostly for evaluation of the maturation stage. For the purposes of this study, the Oil Show Analyzer (O.S.A.) version of Rock-Eval analyzers was used. In the Oil Show Analyzer the determination of the total organic carbon (TOC) is not optional, as in the case of the ROCK-EVAL II apparatus, and is realized in place of the analysis of the CO_2 coming from the organic matter cracking (S_3 peak). From the above-mentioned parameters the hydrogen index (HI) and the oxygen index (OI) are calculated by means of S_2 , S_3 ,

Table 1

Proximate and ultimate analyses and calorific values (kcal/kg) for the Drama lignites (% dmmf is percent on a dry, mineral matter-free basis; % d.b. is dry basis at standard conditions; % a.r. is as-received basis)

Sample	Lignite seam	Depth beneath surface (m)	Ply thickness (m)	Moisture (% a.r.)	Ash (% d.b.)	Volatile matter (% d.b.)	Net calorific value (d.b.)	Volatile matter (% dmmf)	Net calorific value (dmmf)	Fixed carbon (% dmmf)	Total sulfur (% d.b.)	Volatile sulfur (%)
D.1	C	45.00	0.90	59.0	44.0	40.0	2660	69.1	4790	31.00	4.00	1.7
D.2	C	62.20	0.80	66.0	31.3	42.0	3587	64.3	5143	37.50	2.00	0.4
D.3	C	63.50	0.80	68.0	27.6	44.9	3645	65.8	5298	35.60	2.70	0.5
D.4	C	64.70	0.60	65.0	27.0	47.2	3600	65.3	5100	35.50	2.50	0.4
D.5	C	68.60	0.90	63.8	45.8	36.2	2731	67.4	5231	33.90	1.30	0.1
D.6	C	75.00	0.70	66.0	26.2	45.1	3756	61.4	5123	40.20	1.90	0.4
D.7	B	102.70	0.50	59.0	43.6	38.0	2980	68.2	5306	33.30	2.30	0.4
D.8	B	106.60	0.80	65.0	33.8	41.8	3476	63.2	5550	36.80	2.70	0.7
D.9	B	109.40	0.70	62.0	47.9	35.8	2879	69.6	5467	30.10	2.90	1.1
D.10	B	113.05	0.50	69.0	31.2	44.6	3765	64.3	5378	36.30	3.60	0.7
D.11	B	113.55	1.05	68.5	26.1	47.0	3935	63.8	5460	35.80	3.30	0.5
D.12	B	117.10	1.00	68.0	23.4	45.7	4120	62.1	5541	39.20	3.00	0.2
D.13	A	134.90	0.80	64.0	42.9	38.2	2813	67.3	5012	32.50	4.00	0.6
D.14	A	144.50	0.50	61.8	27.2	43.6	3757	66.0	5602	35.70	3.40	0.9
D.15	A	148.00	0.50	63.3	28.9	42.0	3549	64.7	5678	35.10	1.90	0.4
D.16	A	150.80	0.70	57.7	41.9	37.3	2927	66.9	5248	31.80	3.80	1.9
D.17	A	156.70	0.30	66.0	41.0	21.5	2200	50.2	4934	47.20	2.20	0.3
D.18	A	159.50	0.50	55.0	45.1	36.2	2712	65.4	5400	34.60	2.90	0.9
D.19	A	163.00	1.00	61.0	42.9	36.4	3154	68.9	5786	32.60	5.00	1.1
D.20	A	166.60	0.50	62.9	40.5	24.0	2070	58.1	5142	44.90	1.90	0.3
D.21	A	174.20	0.30	60.0	42.1	37.8	3009	68.7	5598	34.10	4.20	1.2
D.22	A	183.00	0.30	54.9	45.3	34.3	2445	68.0	5345	33.30	3.40	1.2
D.23	A	186.30	0.30	55.0	48.4	31.1	2278	69.6	5432	30.80	3.90	0.6
D.24	A	187.60	0.50	54.6	46.1	31.4	2615	67.8	4986	32.00	3.00	0.4
D.25	A	200.40	0.50	62.0	37.2	41.1	3549	64.9	5619	35.70	4.20	1.2

and TOC content. They are respectively expressed in milligrams of HC per gram of TOC and in milligrams of CO₂ per gram of TOC. The oxygen index and the S₃ peak are not included in the Oil Show Analyzer measurements. The Rock-Eval pyrolysis analyses were performed at the Laboratory of Organic Geochemistry, Institut Français du Pétrole, Rueil-Malmaison, France.

Radioactivity

Two lignite samples (D2 and D5) were selected to measure the quantities of the naturally occurring radionuclides. The samples were homogenized, packaged to preclude radon emanation, and then counted for natural gamma radiation on a low-background, high-purity Ge detector, linked to an appropriate data acquisition system (Manolopoulou, 1990; Manolopoulou & Papastefanou, 1992). Therefore, the concentrations of ²³⁸U, ²³⁵U, ²²⁶Ra, ²¹⁰Pb, ²²⁸Ra, ²²⁸Th, and ⁴⁰K (in Bq/kg) were determined. The radioactivity measurements were performed at the Nuclear Physics Department, Aristotle University of Thessaloniki.

Results and Discussion

Chemical Analyses

Results from traditional proximate and ultimate analysis and calorific values of the Drama lignites are reported in Table 1. The studied lignites are characterized by low values of fixed carbon (30.10–47.20%) and high ash contents (23.4–48.4%, on a dry basis). The as-received moisture varies within the range 54.6–69%. After combustion in the boiler, residual mineral matter must be disposed off in the form of ash (Unsworth et al., 1991). Such disposal always has an economic penalty, which will be severe for the Drama deposit, as the ash content of all Drama samples is quite high. The volatile matter, on a dry basis, ranges from 21.5% to 47.2%, while on a dry, mineral matter-free basis, it varies between 50.2% and 69.6%. Such volatile matter contents are considered high, but are within the range of low-rank coals such as lignites. The total sulfur content varies for seam C from 1.3% to 4.0%, whereas the values for the volatile sulfur are from 0.1% to 1.7%. For seam B, the total sulfur content varies from 2.3% to 3.6%, with values of volatile sulfur from 0.4% to 1.1%. Finally, for seam A, total sulfur values vary from 1.9% to 5.0%, whereas volatile sulfur values vary from 0.3% to 1.9%. Generally, the volatile sulfur amounts in average approximately 20% of total sulfur (the difference from the total sulfur remains in ash). In the present study the “net” calorific value of the samples is given. It differs most significantly from the “gross” value due to the fact that the lignite samples have a high moisture content. The “net” calorific value is quoted to a dry and to a dry, mineral matter-free basis, after recalculation. The average net calorific value on a dry basis for seam C is 3,330 kcal/kg, for seam B is 3,526 kcal/kg and for seam A is 2,852 kcal/kg. On a dry, mineral matter-free basis the values are 5,114, 5,450, and 5,367 kcal/kg, respectively.

Rock-Eval Pyrolysis

The results of Rock-Eval pyrolysis are presented in Table 2. Rock-Eval pyrolysis has been applied to coal samples (Teichmüller & Durand, 1983; Durand & Paratte, 1983; Bertrand, 1984; Verhayen et al., 1984; Georgakopoulos, 1984; Peters, 1986;

Table 2
Rock-Eval data for Drama lignite samples

Sample	Lignite seam	Depth (m)	Sample weight (mg)	Rate (°C/min)	S1 (mg/g of sample)	S2 (mg/g of sample)	T_{max} (°C)	H.I.	TOC (%)	SI/TOC	RC (%)	RC/TOC
D.1	C	45.00	14.8	15	0.20	19.05	420	113	16.79	1.19	15.19	0.90
D.2	C	62.20	12.2	15	0.40	82.86	427	186	44.61	0.90	37.70	0.85
D.3	C	63.50	13.5	15	0.51	77.85	420	172	45.19	1.13	38.69	0.86
D.4	C	64.70	14.1	15	0.14	39.14	442	150	26.08	0.54	22.82	0.87
D.5	C	68.60	12.0	15	0.66	31.50	442	136	23.22	2.84	20.55	0.89
D.6	C	75.00	12.6	15	0.31	40.07	446	107	37.43	0.83	34.08	0.91
D.7	B	102.70	13.1	15	0.30	71.29	422	164	43.50	0.69	37.56	0.86
D.8	B	106.60	9.4	15	0.10	36.59	437	74	49.56	0.20	46.51	0.94
D.9	B	109.40	12.9	15	0.46	65.19	436	193	33.71	1.36	28.26	0.84
D.10	B	113.05	15.9	15	0.37	55.72	429	151	36.93	1.00	32.27	0.87
D.11	B	113.55	12.2	15	0.57	65.90	419	154	42.77	1.33	37.25	0.87
D.12	B	117.10	13.4	15	0.07	40.07	427	97	41.25	0.17	37.92	0.92
D.13	A	134.90	12.3	15	0.32	46.74	431	127	36.86	0.87	32.95	0.89
D.14	A	144.50	10.2	15	0.29	68.52	416	158	43.42	0.67	37.71	0.87
D.15	A	148.00	12.1	15	0.49	51.57	436	154	33.46	1.46	29.14	0.87
D.16	A	150.80	16.9	15	0.76	62.54	430	189	33.12	2.29	27.87	0.84
D.17	A	156.70	11.2	15	0.53	21.51	440	149	14.40	3.68	12.57	0.87
D.18	A	159.50	10.3	15	0.09	41.94	441	210	20.01	0.45	16.52	0.83
D.19	A	163.00	15.3	15	0.19	62.41	441	193	32.32	0.59	27.12	0.84
D.20	A	166.60	12.5	15	0.40	27.92	443	111	25.11	1.59	22.76	0.91
D.21	A	174.20	12.0	15	0.16	46.00	446	143	32.18	0.50	28.35	0.88
D.22	A	183.00	10.2	15	0.09	53.33	434	146	36.55	0.25	32.12	0.88
D.23	A	186.30	12.0	15	0.00	24.58	438	112	21.89	0.00	19.85	0.91
D.24	A	187.60	10.2	15	0.00	22.25	439	82	27.26	0.00	25.41	0.93
D.25	A	200.40	10.8	15	0.27	36.11	428	115	31.51	0.86	28.49	0.90

Kalkreuth & Macauley, 1987; Boudou et al., 1990; Fowler et al., 1991; Marquis et al., 1992; Suggate & Boudou, 1993; Sykes et al., 1994; Bostick & Daws, 1994; Newman et al., 1997), and it was evident that a very cautious interpretation of the results should be made. Typically, the application of pyrolysis experiments on different coal samples has been undertaken to confirm the idea that coals may provide a source of oil and gas accumulations. The most volatile compounds (guest bitumen) appear in the first P_1 peak. The area S_1 of this peak is very low for all Drama samples. Similar low values have already been reported for a large coal series (Teichmüller & Durand, 1983). As Teichmüller and Durand (1983), Bostick and Daws (1994), and others have also noted, S_1 is small in coals and does not increase with increasing rank. Furthermore, peats and lignites have much higher S_1 values than bituminous coals (Suggate & Boudou, 1993). The hydrocarbon-like products and related volatile bitumens, formed by thermal cleavage from the organic matter, appear in the second peak P_2 . For the upper seam C, the values of S_2 (in mg HC/g) vary from 19.05 to 82.86. For seam B, the values of S_2 vary from 36.59 to 71.29, whereas for the lower seam A, the values vary between 21.51 and 68.52. These S_2 values indicate that only minor hydrocarbon expulsion occurs from the Drama lignites. The T_{\max} values for all samples vary between 416 and 446°C. Some samples show high T_{\max} values, although all samples are obtained from only a 160-m-deep well and are of the same low rank. In general, for terrestrial organic matter in the early stages of evolution the T_{\max} values vary between 395 and 420°C. It must also be noticed that the differences in the mineral matter content of the samples do not influence the T_{\max} values. For the samples showing high T_{\max} value, the latter does not correlate with both coal type and rank. According to Newman et al. (1997), any relationship between coal type and T_{\max} is erratic at the lowest coal rank (high-volatile bituminous B) they have investigated. Therefore, it can be concluded that the relationship between T_{\max} and coal type is also erratic for lignites. In all samples the reflectivity values are lower than 0.2% (Table 3). Between 0.5% R_m ($T_{\max} \approx 425^\circ\text{C}$) and 1.5% R_m ($T_{\max} \approx 475^\circ\text{C}$), the correlation between R_m and T_{\max} is fairly linear. In values $< 0.5\%$ R_m and $> 1.5\%$ R_m , T_{\max} increases more quickly than R_m (Teichmüller & Durand, 1983). Some scattering is also noticeable: this is not only due to uncertainties of measurements, but also due to different significances of R_m and T_{\max} : R_m is measured on huminite (eu-ulminite A), while T_{\max} is measured on whole coal (huminite + liptinite + inertinite). In a previous work, Kaouras et al. (1991) presented a petrographic and palynological study, conducted on a set of samples from one borehole of the Drama lignite deposit. The authors established that the macerals of the huminite group in 9 samples vary from 61.49% to 81.72%, those of the liptinite group from 8.42% to 31.76%, and those of the inertinite group from 6.01% to 24.72%. These values point out that T_{\max} cannot correlate perfectly with R_m . In other words, T_{\max} is influenced by the petrographic composition, besides the rank, the latter determined on the basis of huminite reflectance. The hydrogen index values vary from 107 to 186 for seam C, from 74 to 193 for seam B, and from 82 to 210 for seam A. It is noticed that the differences in hydrogen contents are not related to the T_{\max} values as would be expected. Apart from that, the values of T_{\max} and those of the depth are not related to each other. The Oil Show Analyzer device determines total organic carbon (TOC) in weight percent of sample, by summing up the pyrolyzed organic carbon (deduced from the total amount of hydrocarbons $S_1 + S_2$) with the residual organic carbon (RC) obtained after oxidation. In Figure 3, the

Table 3
Mean random reflectances (% R_m , oil) measured on eu-ulminites A
of the Drama lignite samples

Sample	Seam	Depth (m)	Random reflectance in oil (%)
			Eu-ulminite A
D.1	C	45.00	0.20 ± 0,02
D.2	C	62.20	0.12 ± 0,03
D.3	C	63.50	0.13 ± 0,05
D.4	C	64.70	0.13 ± 0,03
D.5	C	68.60	0.17 ± 0,05
D.6	C	75.00	0.19 ± 0,03
D.7	B	102.70	0.20 ± 0,03
D.8	B	106.60	0.15 ± 0,02
D.9	B	109.40	0.17 ± 0,03
D.10	B	113.05	0.11 ± 0,02
D.11	B	113.55	0.13 ± 0,03
D.12	B	117.10	0.14 ± 0,03
D.13	A	134.90	0.14 ± 0,03
D.14	A	144.50	0.12 ± 0,01
D.15	A	148.00	0.17 ± 0,02
D.16	A	150.80	0.13 ± 0,02
D.17	A	156.70	0.17 ± 0,02
D.18	A	159.50	0.17 ± 0,02
D.19	A	163.00	0.12 ± 0,01
D.20	A	166.60	0.14 ± 0,02
D.21	A	174.20	0.14 ± 0,02
D.22	A	183.00	0.14 ± 0,03
D.23	A	186.30	0.17 ± 0,03
D.24	A	187.60	0.17 ± 0,02
D.25	A	200.40	0.18 ± 0,03

Rock-Eval TOC values are related to fixed carbon as determined by proximate analysis for the Drama lignite samples. For a part of the samples the values are almost the same, but for the rest there is a significant difference. It is difficult to provide a satisfactory explanation about this phenomenon. The total organic carbon can be divided into two fractions: the first, connected to the hydrocarbons that are released during the cracking of the coal, is found in the pyrolyzate. The second fraction is the residual carbon (RC) or "dead carbon," which constitutes the inert carbon that reacts only in oxidation. These two carbon forms were studied by Gransch and Eisma (1970), who originally proposed the "carbon ratio" (C_R/C_T). The residual carbon C_R (or RC) is related to the abundance of polyaromatic nuclei. The volatile fraction C_T minus C_R (C_T being the total organic carbon) is related to the abundance of aliphatic chains and oxygen-containing functional groups which are lost during pyrolysis. For the same type of organic matter the ratio C_R/C_T increases with the degree of maturation, reaching approximately the

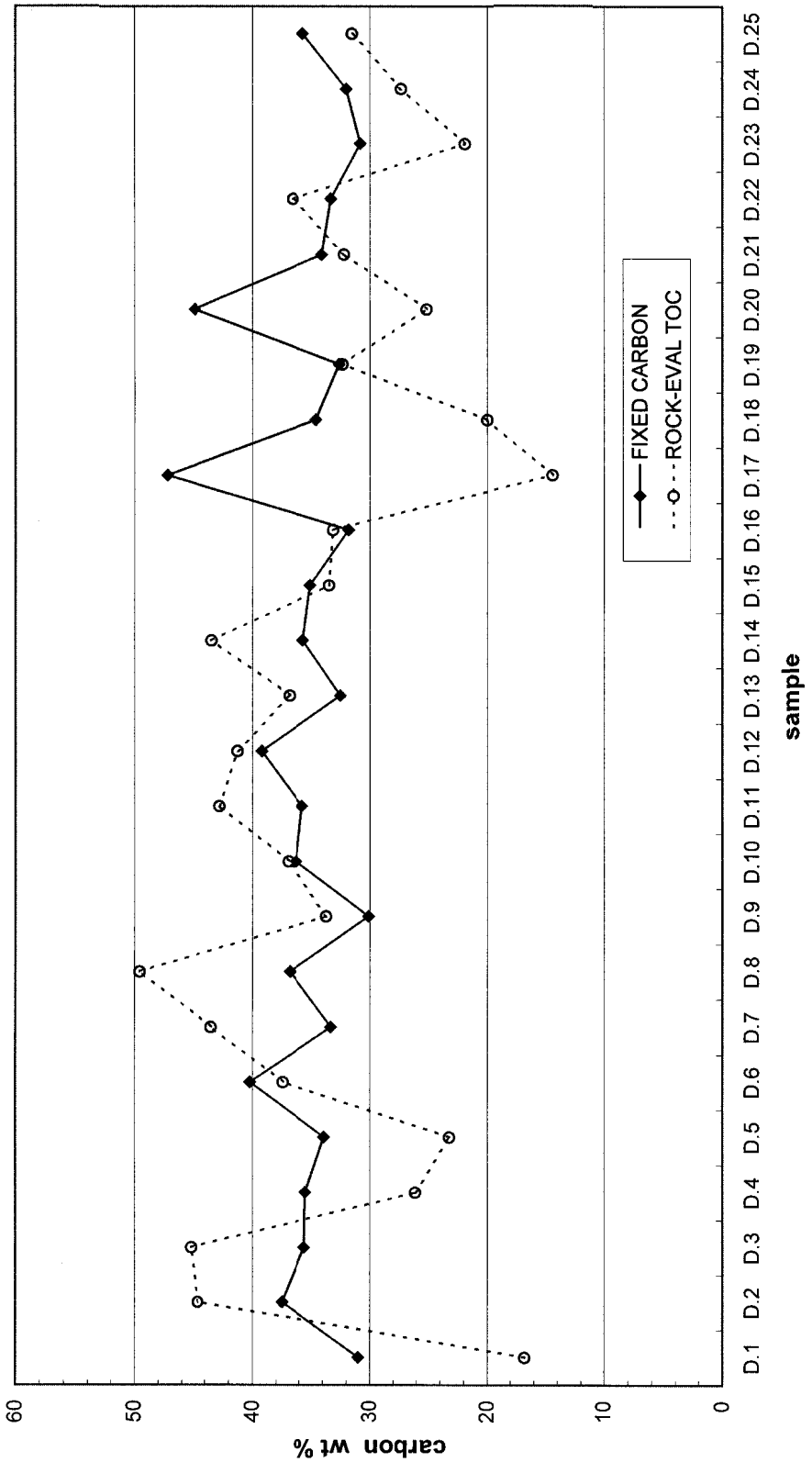


Figure 3. Relationship between Rock-Eval TOC values with fixed carbon content as determined by proximate analysis for the Drama lignite.

value 1 in the case of graphite. In addition, high C_R/C_T values may be obtained from type III organic matter or coals, even at low stages of maturation. In the Drama samples, the values of the carbon ratio vary from 0.83 to 0.94. Independent of the methodology that is used, the difference between TOC and C_R corresponds to the carbon that is liberated during pyrolysis, termed C_p . Therefore, the relation: $C_T - C_R = C_p$ is formed. During pyrolysis this C_p is liberated in the form of hydrocarbons, CO, and CO₂. The quantities of CO are very low and can be ignored (Souron et al., 1975). The quantity of carbon that is related to the CO₂ liberated during pyrolysis is, of course, larger than the quantity of carbon that is related to the CO, but still remains at very low levels. In the case of recent sediments originating from higher plants, the quantity of carbon related to the CO₂ constitutes just 8% of the total organic carbon. In the case of lignites (as in the Drama case), this percentage falls to 4%, whereas for type III rock samples in the beginning of the mature stage it is 2% (Souron et al., 1975). From the above it is clear that the greatest part of the volatile organic carbon (C_p) is related to the hydrocarbons liberated during pyrolysis cracking and is represented by the S₂ peak, leading to an excellent correlation between S₂ area and TOC - RC difference.

Natural Radionuclides

Table 4 presents the concentrations of ²³⁸U, ²³⁵U, ²²⁶Ra, ²¹⁰Pb, ²²⁸Ra, ²²⁸Th, and ⁴⁰K (in Bq/kg), determined in samples D2 and D5, both obtained from seam C. Concentrations of U and Th are also calculated in ppm, while the concentration of K is calculated in weight percent. The results show a similar distribution of the naturally occurring radionuclides between the two samples. It seems that radioactive equilibrium exists between ²³⁸U and ²²⁶Ra and also between ²²⁶Ra and ²¹⁰Pb. This fact means that the rate of formation of the radioactive daughter product is equal to the rate of decay. According to Coles et al. (1978), secular equilibrium does exist

Table 4
Concentrations of ²³⁸U, ²³⁵U, ²²⁶Ra, ²¹⁰Pb, ²²⁸Ra, ²²⁸Th, and ⁴⁰K for samples D2 and D5 obtained from the upper seam C of the Drama lignite deposit

	D2		D5	
	Bq/kg	± 1 σ	Bq/kg	± 1 σ
²³⁸ U	121.0	14.0	95.0	12.0
²³⁵ U	6.5	2.1	4.8	0.9
²²⁶ Ra	125.3	2.6	108.4	1.3
²¹⁰ Pb	160.0	15.0	118.0	12.0
²²⁸ Ra	16.9	1.2	20.7	0.7
²²⁸ Th	14.5	1.3	19.7	0.8
⁴⁰ K	106.0	6.8	103.0	3.4
U (ppm)	9.80	12.0%	7.70	12.0%
Th (ppm)	3.90	5.5%	5.00	2.6%
K (%)	0.34	6.4%	0.33	3.3%

± 1 σ: standard deviation.

between all the nuclides of the uranium series chain in the coals. This radioactive equilibrium does not exist between ^{238}U and ^{226}Ra in the Ptolemais lignites (^{238}U : $^{226}\text{Ra} = 1.7 \pm 0.4$), whereas it does exist between ^{226}Ra and ^{210}Pb (^{226}Ra : $^{210}\text{Pb} = 1.0 \pm 0.2$) (Manolopoulou, 1990; Manolopoulou & Papastefanou, 1992). The mean isotopic ratio ^{238}U : ^{235}U for the two samples investigated is 19.4 ± 3.7 (Bq) and is in fairly good agreement with the natural one, 21.44 ± 0.02 (Bq). In general, the concentrations of natural radionuclides in types of coal are less than those in the earth's crust. The average activity concentrations in coal are 20 Bq/kg of ^{238}U , 20 Bq/kg of ^{232}Th , and 50 Bq/kg of ^{40}K , and all the decay products of ^{238}U and ^{232}Th are in radioactive equilibrium with their precursors (UNSCEAR, 1982). Lignite radioactivity has been very scarcely covered by the international bibliography. Therefore a comparison is undertaken between the results of the present study and those reported by several authors concerning higher-rank coals. A very comprehensive study by Gentzis and Goodarzi (1997) reports on the concentration of radionuclides in subbituminous coals used exclusively for power generation in Alberta, Canada. The authors compare the radioactivity measured in coals from the Highvale Mine and the Whitewood Mine with the same concentrations in other Canadian feed coals (Evans et al., 1985), in Australian coals, and in coals from the United States and the United Kingdom (Smith, 1987). They have found that the activity of ^{232}Th ranges from 10 to 40 Bq/kg, whereas the range in Australian coals is from 11 to 69, in the U.K. coals from 7 to 19, and in the U.S. coals from 4 to 21 Bq/kg. For ^{226}Ra the activity ranges from 10 to 40 Bq/kg, whereas the range in Australian coals is from 19 to 24, in the U.K. coals from 8 to 22, and in the U.S. coals from 9 to 59 Bq/kg. For ^{210}Pb the authors have found an activity range from 10 to 40 Bq/kg, very similar to those of Australian coals (16–28) and lower than those of U.S. coals (4–52). From all the above values it is clear that, in the case of Drama, the radium-226 and uranium-238 concentrations are within the higher range for world coals. Uranium and its daughter nuclides are associated with the organic material of lignites (coal matrix), while thorium and its daughter nuclides as well as potassium are associated with inorganic materials (ash matrix). The different behavior between the two isotopes of radium, ^{226}Ra and ^{228}Ra in the studied lignites, is probably due to the fact that ^{226}Ra has higher mobility in the coal matrix than ^{228}Ra , which is associated (as its parent ^{232}Th) with aluminosilicates. Radium-226 (and its precursor ^{238}U) has bimodal behavior either in the volatile form of uraninite or in the silicate form of coffinite $[\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}]$ (Coles et al., 1978; Manolopoulou & Papastefanou, 1992). Obviously, the small number (2) of lignite samples which were investigated for the concentrations of naturally occurring radionuclides does not permit significant conclusions to be made, but similar concentrations are also referred for the Ptolemais lignites, in which U has predominantly an organic mode of occurrence (Manolopoulou, 1990).

Conclusion

The present study was carried out to determine the quality parameters which reflect thermal value and any deleterious tendencies it may have for process efficiency and/or the environment. Traditional analyses such as proximate, ultimate, and calorific value do not show substantial variability among the three lignite seams of the Drama deposit. The moisture, the volatile matter, and the ash contents are always high, while the sulfur content of Drama lignites always remains

at low levels. A specific technique involving a pyrolysis process (Rock-Eval pyrolysis) has been used together with conventional methods. Rock-Eval analysis was not designed for coal characterization, and has not been evaluated rigorously for reproducibility in this regard. This method has been applied only a very few times in lignite studies, therefore, these results may be very interesting.

The T_{\max} of release of gaseous species under inert atmosphere (hydrocarbons, H_2) or under oxidizing atmosphere (H_2O , CO_2 , SO_2 , ...) allow a widening of the rank domain to be assessed, compared to the T_{\max} of the Rock-Eval pyrolysis, which concerns only the domain of 0.5 to 1.5% R_m .

The S_1 as well as S_2 values determined from the Rock-Eval pyrolysis for the set of Drama samples demonstrate that:

1. S_1 and S_2 correlate with coal type and rank, while T_{\max} does not.
2. Rock-Eval S_2 indicates only minor hydrocarbon expulsion from Drama lignites.
3. Comparison of the Rock-Eval analysis data (TOC) with those of the proximate analysis (fixed carbon) reveals that sometimes the Rock-Eval technique underestimates and some times it overestimates the carbon content.

Interpretation of the results of the Rock-Eval analysis is important for the evaluation of the petroleum-source potential of coals, but is of no value for lignites since they have no petroleum-source potential. However, this analytical method, although unconventional for lignites, combined with some other, also unconventional analytical methods, is valuable in relation to coal utilization (in hydroliquefaction, gasification, combustion, etc.).

The concentrations of the naturally occurring radionuclides, which to some extent will be released to the environment after the combustion of the lignite, are among the higher for lignites worldwide. As Coles et al. (1978) have reported, a part of ^{238}U which is associated with silicates or which is mineralized as coffinite in the lignite (coal matrix) remains with the bottom ash, whereas the ^{238}U part associated with the uraninite (UO_2) in the coal matrix forms volatile compounds, such as UO_3 . Ra-226 also forms volatile compounds such as $Ra(OH)_2$ and later condenses out on the finer fly ash particles (fly ash matrix).

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