



Organic petrographical, mineralogical and geochemical features of the Achlada and Mavropigi lignite deposits, NW Macedonia, Greece

Nikolaos Koukoulas^{a,*}, Stavros P. Kalaitzidis^b, Colin R. Ward^c

^a Centre for Research and Technology Hellas, Institute for Solid Fuels Technology and Applications, Mesogeion Ave. 357-359, GR-15231 Halandri, Athens, Greece

^b Geological Services, BHP Billiton Mitsubishi Alliance, Central Queensland Office, Peak Downs Mine, Moranbah, QLD 4744, Australia

^c School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney, NSW 2052, Australia

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ABSTRACT

The Achlada and Mavropigi lignite deposits in northern Greece provide the main coal source for the next generation of Greek power plants. A comparative characterization of these two lignite deposits is presented, covering the coal rank and the features of the maceral components, based on detailed coal petrography, and the mineralogical and geochemical features of the coals and their ashes, based on XRF and XRD analyses. The data are used to interpret the palaeoenvironments of the lignite beds, as well as factors that may affect their burnout behavior.

Both deposits have a lignite C rank. The Mavropigi lignite is mainly a matrix lignite lithotype, whereas the Achlada deposit consists both of matrix and xylite-rich lithotypes. The Achlada lignite was formed in a fluvial environment, mainly in the abandoned channels of a meandering river system during flooding periods; hence it is enriched in inorganic matter, with ash values > 30 wt.%. The Mavropigi lignite formed in a reed-marsh environment under limno-telmatic conditions, and displays ash values < 30 wt.%.

The inorganic matter of the two deposits is different in composition due to the contrasting environments, and these differences should be taken into account in optimizing their utilization for power production. A preliminary assessment indicates that the Achlada lignite may have more favorable slagging and fouling properties than the Mavropigi lignite, although experimental studies are required for more solid conclusions to be reached.

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1. Introduction

The power generation sector in Greece depends mostly on lignite-fired plants that provide almost 60% of the domestic power supply (Kavouridis and Koukoulas, 2008). There are more than 60 basins across the country that host lignite seams. These have been studied extensively during the last 40 years (e.g. Koukoulas, 1998; Christanis, 2004), and many are exploited or are potentially exploitable by the Power Public Corporation of Greece for electricity generation. In recent years new lignite deposits in northwest Greece have been developed or evaluated in order to maintain lignite supplies to the power stations; two of those new fields are the Achlada field in the Florina Basin and the Mavropigi field in the Ptolemais Basin (Fig. 1).

Knowledge of the quality parameters of lignite is essential not only for elucidating the depositional environment but also for planning rational utilization and obtaining efficient burnout from boiler installations (Diessel, 1992; Speight, 1994; Kolovos et al., 2002; Suárez-Ruiz and Ward, 2008). Crucial studies for the characterization of the coal are

proximate and ultimate analyses, and the determination of the mineralogical, geochemical and organic petrographic characteristics. Geochemical data can also be utilized to predict the slagging and fouling tendencies; slagging refers to the deposition of ash in the radiative section of a utility boiler, whereas fouling refers to ash deposition in the convective-pass region of a utility boiler (Erickson et al., 1995).

In this paper the petrographical, mineralogical and geochemical features of the Achlada and Mavropigi lignite deposits are presented, in order to provide the first integrated characterization of the lignites supplying the next generation of Greek coal-fired power plants. The deposits have not been yet studied in detail, and the results reported here cover a relatively minor part of the resource extensions. However, they are based on representative sampling programs carried out in each of the deposits.

2. Geological setting

The lignite deposits discussed in the present paper (Fig. 1) occur in the Ptolemais-Florina Graben, a major feature that extends in a NW–SE direction across north-western Greece (Kilias and Mountrakis, 1989). The margins and the basement of the graben consist of crystalline rocks and Mesozoic formations of the Pelagonian Zone and

* Corresponding author. Tel.: +30 210 6501771; fax: +30 210 6501598.

E-mail address: koukoulas@certh.gr (N. Koukoulas).

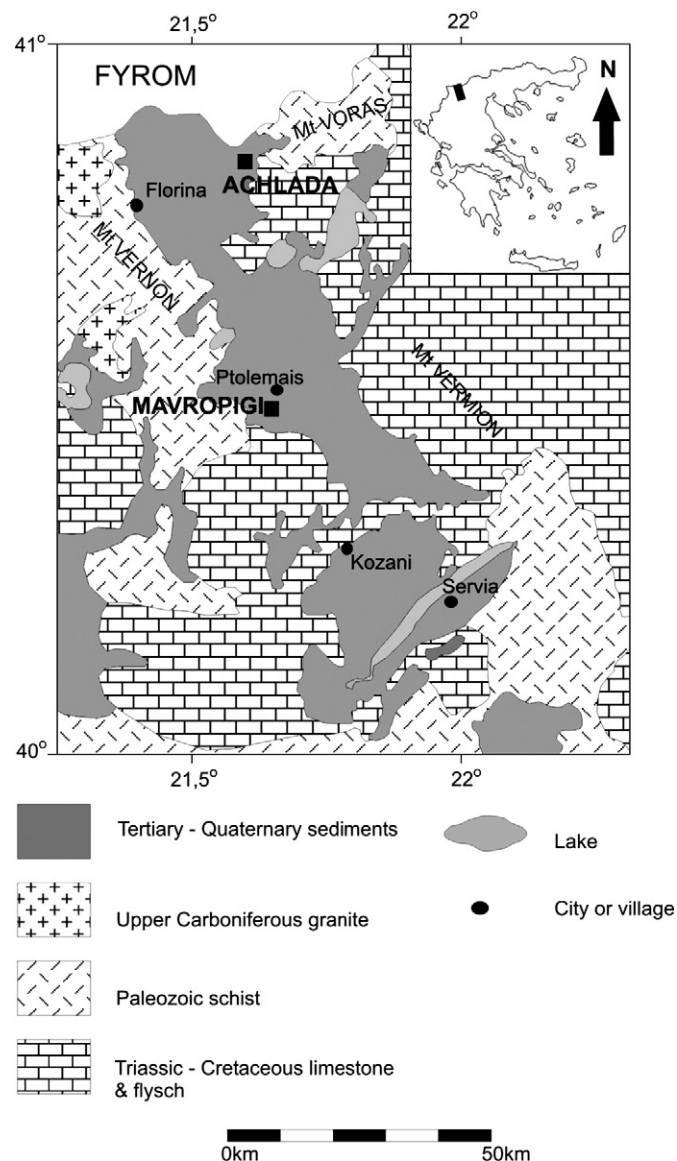


Fig. 1. Location of Achlada and Mavropigi lignite deposits within the context of the Ptolemais-Florina Graben.

the Axios Zone. The basin itself is filled with Tertiary and Quaternary sediments up to 1000 m thick. The upper part of the basin fill includes Miocene to Pliocene sand, sandy clay, lignite and marl, mainly of fluvial to lacustrine origin. A group of normal faults oriented NW–SE, NE–SW and ENE–WSW to E–W were activated during the Neogene, forming the different sub-basins within the Ptolemais-Florina Basin (Pavlidis and Moutrakis, 1987; Koukouzas, 2007).

The lignites of the Ptolemais–Florina Graben are classified into two main lithotypes: the Ptolemais type, which is a matrix or “earthy” lignite, and the Komnina type, which is a xylite-rich lignite. The Achlada deposit belongs to the Middle Miocene Komnina lignite sequence, whereas the Mavropigi lignite deposit is part of the Early Pliocene Ptolemais lignite sequence (Anastopoulos and Koukouzas, 1972; Koukouzas, 2007).

The Achlada lignites were developed mainly in abandoned channels and on the floodplain of a meandering river system. The Mavropigi lignite deposit, however, was developed in a lacustrine environment that occupied the broader area of the Ptolemais Basin during Pliocene times. The lignite beds formed at the lake margins under limno-telmatic conditions favorable for gelification (Antoniadis et al., 2006). Peat accumulation was susceptible to intermittent

moderate to high flooding events and, as a result, the lignites display variable ash yields. The lignite-forming periods alternated with extensive flooding events marked by marly sediments. Although the Mavropigi Field contains matrix lignite (Ptolemais type), deposition took place in lakes similar to those that had earlier produced the xylite-rich lignite in the Achlada Basin.

The distribution of lignites provides an indication that a huge lake extended from Monastir via Florina, Ptolemais, Lava and Prosilio to a point near Ellassona–Sarantaporo. The lake was shallow in Late Miocene times. The peat-forming vegetation in the mires was not arborescent, but was associated with extensive deposition of diatoms (Koukouzas, 2007). Tectonic movements took place in the Early Pliocene, resulting in the development of several horsts. Volcanic activity continued during the Late Pliocene, when the Mavropigi lignites were accumulating. No diatoms were deposited in the overburden sediments of the Pliocene lignites, however, since the conditions were different to those of Miocene times.

3. Methodology

Five samples from Achlada and six from Mavropigi were collected from the bench slopes of the respective mines using channel sampling; each sample represents an independent lignite layer (Fig. 2, Table 1). At both sites, the lithological features were macroscopically described and the lignite lithotypes identified according to guidelines established by the International Committee for Coal and Organic Petrology (ICCP, 1993). Samples with more than 10% by volume woody tissues were logged as xylite-rich material.

Proximate analyses were performed at the facilities of the Centre for Research Technology Hellas/Institute for Solid Fuels Technology and Applications (CERTH/ISFTA) according to procedures set down by American Society for Testing and Materials (ASTM) Standards D 3174 (1989a), D 3302 (1989b) and D 388 (1992c). The samples were crushed to <200 µm, and moisture (105–110 °C) and ash yield (815 °C) were determined. Volatile matter was determined using a TGA-2000 automatic multiple sample thermo-gravimetric analyzer, heating the material at 930 °C [ASTM D 3175 (1989)]. Gross calorific values were determined using a Parr 2040 calorimeter. Ultimate analysis was carried out using LECO C-H-N 1000 and LECO CS elemental analyzers. The major element concentrations of the lignite ashes were determined at the University of New South Wales (Australia) from fused borosilicate disks (Norris and Hutton, 1969) using a Philips PW-2400 wavelength-dispersive X-ray fluorescence (XRF) spectrometer.

Polished blocks 30 mm in diameter were prepared according to ISO 7404-2 (1985) and examined using a LEICA DMRX microscope at the Department of Geology, University of Patras. Point counting for maceral analysis (500 counts) was conducted under both white reflected light and blue-light excitation, and the macerals described following the Stoppel-Heerlen terminology (ICCP, 1963, 1971; Taylor et al., 1998; ICCP, 2001; Šýkorová et al., 2005). Additionally, the mean reflectance of ulminite in the samples was determined according to ASTM D2798-04 (2004).

Representative portions of the lignite samples were ground to fine powder, and were subjected to low-temperature oxygen-plasma ashing using an IPC 4-chamber asher at the University of New South Wales, as outlined in Australian Standard 1038, Part 22 (Standards Australia, 2000). The mass percentage of low-temperature ash (LTA) was determined in each case. Each LTA was analysed by X-ray powder diffraction using a Philips PW-1830 diffractometer with CuKα radiation (scanning step 0.04° 2θ and 2 second acquisition time). Quantitative analyses of mineral phases in each LTA were made from the X-ray diffractograms using Siroquant™, commercial interpretation software (Taylor, 1991) based on the Rietveld XRD analysis technique (Ward et al., 2001).

The clay fraction (less than 2 µm effective diameter) of each LTA sample was isolated by ultrasonic dispersion in water with sodium

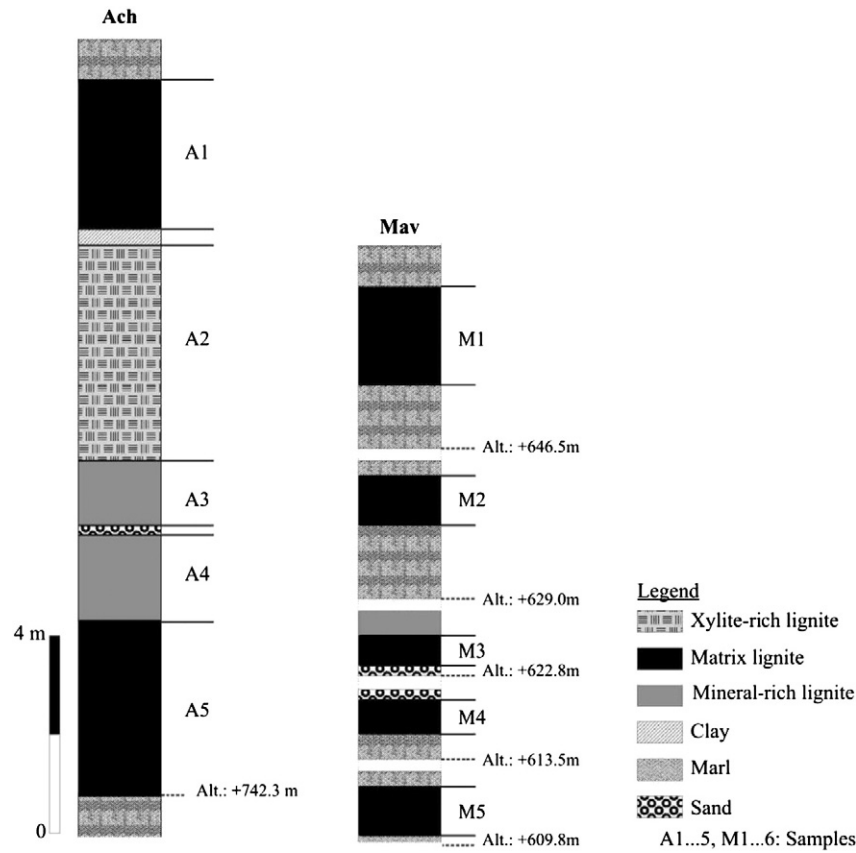


Fig. 2. Lithological columns of the sampling sections in the Achlada and Mavropigi lignite deposits.

hexametaphosphate (Calgon) and subsequent settling. The clay fractions were concentrated, settled as oriented-aggregates on glass slides (Gibbs, 1971), and investigated further by X-ray diffraction after glycol and heat treatment. The relative proportions of the different clay minerals in this fraction for each sample were determined from the relevant peak intensities as described by Griffin (1971).

4. Results

4.1. Lithological features

The lithological features of the studied seams are presented in Fig. 2. In the Mavropigi deposit, the lignite is mainly of matrix lithotype and is hosted within marl or sand layers; the thickness of the

lignite seams ranges between 0.6 and 2 m. In the Achlada deposit both matrix and xylite-rich lithotypes occur, with the total thickness of the lignite seams ranging up to ~15 m. The seams are hosted within clayey, marly and sandy sediments.

4.2. Proximate analysis and reflectance measurements

Moisture, ash yields, volatile matter, fixed carbon and gross calorific values are presented in Table 1. In general, the Achlada lignites display higher ash percentages (>36 wt.% on dry basis) than the Mavropigi lignites (12.5–34.6 wt.%). The volatile matter values range between 54.2 and 74.6 wt.% (on dry, ash-free basis) for Achlada and are 60.3–68.7 wt.% (daf) for the Mavropigi samples. The gross calorific value (GCV) of the Achlada lignite is generally low, ranging

Table 1

Description of samples from Mavropigi and Achlada deposits and results of proximate analysis (MM: mineral matter, M: total moisture in as received basis, vm: volatile matter, C_{fix} : fixed carbon) and determination of gross calorific value (GCV) (db: on dry basis, daf: on dry, ash-free basis, and m-af: moist, ash-free basis).

Sample	Lithotype	M wt.% (ar)	Ash wt.% (db)	VM wt.% (db)	C_{fix}^a wt.% (db)	GCV MJ/kg (db)	VM wt.% (daf)	C_{fix} wt.% (daf)	GCV MJ/kg (daf)	GCV MJ/kg (m-af)
<i>Achlada</i>										
A1	Matrix, MM-rich lignite	20.9	41.9	37.7	21.4	15.3	64.9	36.8	26.4	20.9
A2	Xylite-rich lignite	31.9	41.4	37.2	21.4	16.2	63.5	36.5	27.7	18.8
A3	Carbonaceous sediment	29.3	59.6	29.6	10.8	9.9	73.3	26.7	24.5	17.3
A4	Matrix, MM-rich lignite	32.1	52.4	35.5	12.1	11.3	74.6	25.4	23.8	16.1
A5	Matrix lignite	41.3	38.0	33.6	28.4	16.2	54.2	45.8	26.2	15.4
<i>Mavropigi</i>										
M1	Matrix lignite	56.7	21.1	50.4	28.5	17.8	63.9	36.1	22.6	9.8
M2	Matrix lignite	54.5	34.8	44.2	21.0	13.9	67.8	32.2	21.3	9.7
M3	Matrix lignite	62.7	12.9	52.5	34.6	18.5	60.3	39.7	21.2	7.9
M4	Matrix lignite	54.8	24.6	48.8	26.6	15.7	64.7	35.3	20.8	9.4
M5	Matrix lignite	54.9	30.6	47.7	21.6	12.3	68.7	31.1	17.7	8.0

^a $C_{fix} = 100 - (\text{ash} + \text{VM})_{db}$.

from 9.7 to 13.8 MJ/kg on a dry basis, whereas the samples from Mavropigi display higher GCV values ranging between 13 and 18.5 MJ/kg. However, this trend reverses when comparing the dry, ash-free values; the Achlada lignites show values ranging between 23.8 and 27.7 MJ/kg and the Mavropigi lignites between 17.7 and 22.6 MJ/kg, indicating the significant impact of the mineral matter in reducing the Achlada lignite quality.

Mean reflectance of ulminite for both the Achlada and Mavropigi deposits ranges between 0.18 and 0.29% (Table 2), indicating the immature nature of the materials. Using moisture, volatile matter (on a dry, ash-free basis), and gross calorific value (on a moist, ash-free basis) as criteria for rank classification, the samples studied would be classified as lignites (Weichbraunkohle) according to ASTM D388 (1992), or as lignites C according to ECE-UN (1998).

4.3. Ultimate analysis

Ultimate analysis results for the coal samples are shown in Table 3. For the Achlada samples the carbon content ranges between 24.6 and 39.9 wt.% (dry basis), with the low values reflecting the high mineral

Table 3

Results of ultimate analysis from Mavropigi and Achlada deposits (db: on dry basis, daf: on dry, ash-free basis).

Sample	C	H	O ^a	N	S	C	H	O	N	S
	wt.% (db)					wt.% (daf)				
Achlada										
A1	36.8	3.0	16.6	0.6	1.1	63.3	5.2	28.6	1.0	1.9
A2	38.9	2.8	14.9	0.9	1.1	66.4	4.8	25.4	1.5	1.9
A3	24.6	1.9	11.5	0.9	1.5	60.9	4.7	28.5	2.2	3.7
A4	28.6	2.0	13.4	0.8	2.8	60.1	4.2	28.2	1.7	5.9
A5	39.9	2.6	16.2	0.9	2.4	64.4	4.2	26.1	1.5	3.9
Mavropigi										
M1	48.1	3.1	23.8	1.8	2.1	61.0	4.0	30.1	2.3	2.7
M2	38.7	1.8	20.8	1.6	2.2	59.4	2.8	32.0	2.5	3.4
M3	52.5	2.3	29.8	1.4	1.1	60.3	2.7	34.2	1.6	1.3
M4	45.2	1.9	25.3	1.4	1.5	60.0	2.5	33.6	1.9	2.0
M5	40.9	2.0	22.3	1.4	2.7	59.0	2.9	32.2	2.1	3.8

$$^a O = 100 - (\text{ash} + C + H + N + S)_{\text{db}}$$

Table 2

Maceral composition (vol.%, dry, mineral matter free) and random reflectance (Rm%) of lignite samples from Mavropigi and Achlada.

Sample	Achlada					Mavropigi				
	A1 ^a	A2 ^b	A3 ^a	A4 ^a	A5 ^a	M1 ^a	M2 ^a	M3 ^a	M4 ^a	M5 ^a
Rm %	0.18	0.18	0.26	0.28	0.24	0.25	0.20	0.29	0.23	0.23
Maceral	vol.%, dry, mineral matter-free basis									
Textinite	9.4	22.8	1.2	2.4	0.8	4.8	4.8	7.8	4.4	7.0
Ulminite	8.2	51.0	15.6	11.6	20.0	19.2	19.6	55.6	19.2	8.2
Total	17.6	73.8	16.8	14.0	21.4	24.0	24.4	63.4	23.6	29.0
Telohuminites										
Attrinite	73.0	8.0	52.0	49.6	46.0	28.8	35.4	10.6	48.2	30.6
Densinite	1.2	3.0	12.0	12.8	19.4	20.0	7.0	10.6	12.2	10.6
Total	74.2	11.0	64.0	62.4	65.4	48.8	42.4	21.2	60.4	41.2
Detrohuminites										
Porigellinite		1.4		0.8	2.0	0.8	2.8	2.6	0.4	3.6
Levigellinite	1.2	1.2	2.8	3.6	1.0	4.4	0.6	0.8	2.6	1.4
Corpohuminites		7.8	3.2	8.4	2.2	3.6	4.0	2.6	1.0	7.2
Total	1.2	10.4	6.0	12.8	5.2	8.8	7.4	6.0	4.0	12.2
Gelohuminites										
Total Huminites	93.0	95.2	86.8	89.2	92.0	81.6	74.2	90.6	88.0	82.4
Fusinite						1.6	2.2	1.2	0.2	0.4
Semifusinite				0.4		1.0	1.6	0.4	0.2	0.2
Inertodetrinite	1.0		0.4	0.4	0.4	3.4	9.8	2.4	4.0	4.4
Funginite		1.0	1.6	1.2	0.2		0.6	1.2	0.8	1.0
Total Inertinites	1.0	1.0	2.0	2.0	0.6	6.0	14.2	5.2	5.2	6.0
Sporinite		0.2	1.6	0.8	0.8	2.6	2.6	0.8	0.8	1.8
Cutinite		0.2	0.8	0.4	0.2	1.4	1.4	0.6	0.2	2.2
Resinite		2.2	0.4		1.0	0.6	0.2			0.4
Suberinite		0.6	0.4	1.2		0.2				0.2
Alginite	2.4		2.0	0.8	2.4	2.4	0.8	0.8	1.8	2.2
Liptodetrinite	3.6	0.6	6.0	5.6	3.0	5.2	6.6	2.0	4.0	4.8
Total Liptinites	6.0	3.8	11.2	8.8	7.4	12.4	11.6	4.2	6.8	11.6
vol.%, dry, whole sample basis										
Zooclasts										
Clay minerals	30.6	8.0	18.6	15.7	5.0	4.0	5.5	2.0	6.1	7.1
Quartz/Feldspars			1.0	0.6			0.5	0.4		0.5
Gypsum	4.5	4.0	4.8	3.5	5.2	0.5	1.0	0.8	1.0	3.5
Pyrite	1.0	0.5	1.8	1.2	1.8	1.0	2.1	1.2	1.0	1.8
Total minerals	36.1	13.5	26.2	21.0	12.0	5.5	9.1	4.4	8.1	12.9
Tissue	0.2	6.0	0.3	0.3	0.3	0.5	0.6	2.5	0.4	0.7
Preservation Index (TGI)										
Gelification Index (GI)	0.1	2.1	0.6	0.7	1.0	1.2	0.6	3.2	0.6	1.1

^a Matrix lignite.

^b Xylite-rich lignite.

matter (ash) percentage. On a dry, ash-free basis, C ranges between 60 and 66.4 wt.%. The total sulphur concentrations are low in samples A1, A2 and A3, but relatively high (>2 wt.%, db) in samples A4 and A5.

The Mavropigi samples display carbon contents between 38 and 51 wt.% on a dry basis. The C values on a dry, ash-free basis range between 59 and 61 wt.%, slightly lower than the equivalent figures for the Achlada lignite. The S content is similar to that of the Achlada samples, ranging between 1 and 2.7 wt.% on a dry basis.

4.4. Maceral analysis

4.4.1. Achlada lignite

Microscopic examination of the Achlada lignite shows almost identical variations in the overall proportions of maceral groups for most of the samples (Table 2). Huminite is the dominant maceral group (up to 95.2 vol.%). Detrohuminite is the most prevalent huminite subgroup in the majority of the samples, with values up to 74.2 vol.% indicating severe mechanical degradation of the organic matter; attrinite is the main representative maceral of this subgroup. Deviation is observed, however, for sample A3, a xylite-rich lithotype, which has a telohuminites content of 73.8 vol.%. Macerals of the gelohuminites subgroup occur in low to moderate proportions, with corpohuminites being the most representative maceral. The occurrence of this component, particularly in samples A3 and A5, indicates the accumulation of root systems.

Macerals of the inertinite group occur only in minor proportions (up to 2.0 vol.%), suggesting that peat-accumulation was largely unaffected by oxidation processes. Inertodetrinite is the predominant maceral in this group. The proportion of liptinites macerals is also low (<11.2 vol.%) with alginite and liptodetrinite being the most frequently occurring macerals; resinite occurs mainly in the xylite-rich lignite of sample A2.

In general the maceral analysis results show a high degree of fragmentation and low to moderate gelification of the organic matter for the matrix lignite and marly lignite samples; high preservation of the organic matter structure, however, is evident for the xylite-rich A2 sample.

Microscopical semi-quantitative assessment shows that clay minerals are the dominant mineral components, making up to 30 vol.% of the lignite samples. Sulphates (gypsum) make up around 5 vol.% of the Achlada materials, but the visible quartz and feldspar contents are less than 1 vol.%. Pyrite shows values of up to 1.8 vol.%, with framboidal forms being the most frequent. Nevertheless it should be stated that the identification of minerals under the coal-petrographic microscope is not an accurate quantification method and only relative indications are provided.

4.4.2. Mavropigi lignite

In the Mavropigi samples huminite is also the predominant maceral group, with values between 74.2 and 92.4 vol.% (Table 2). Detrohuminite (mainly as attrinite) predominates in samples M1, M2, M4 and M5, with values up to 60.4 vol.%, whereas telohuminite (mostly ulminite) prevails in sample M3. Gelohuminite occurs in moderate abundance (up to 12.2 vol.%), with gelinite and corpohuminite displaying almost similar proportions.

Inertinite is more abundant in the Mavropigi lignites than in the Achlada samples, with total inertinite percentages at Mavropigi ranging between 3.2 and 14.2 vol.%. The inertinite is mainly in the form of inertodetrinite, possibly indicating the occurrence of firing events in or around the palaeomire area (Scott and Glasspool, 2007).

The liptinite content of the Mavropigi lignites is similar to that of the Achlada samples, with low to moderate proportions (up to 12.4 vol.%). Liptodetrinite, alginite and in some cases sporinite are the dominant liptinite macerals in most of the samples studied.

In general the results of maceral analyses for the Mavropigi lignite reveal that the organic matter in most of the samples is significantly fragmented. In addition the relatively high inertinite content suggests that oxidation effects of moderate intensity took place in the palaeomire regime.

The microscopically visible mineral matter has similar features to that of the Achlada samples, with clay minerals dominating in most of the coals studied. The microscopic pyrite content in the Mavropigi samples is higher than in the Achlada materials, and reaches up to 2.6 vol.%. The visible pyrite mainly occurs as framboidal material.

4.5. Geochemical features of ash

The major oxide analyses for the ashes of the Achlada lignites (Table 4) indicate a predominance of aluminosilicates, probably represented mainly by clay minerals. SiO₂ and Al₂O₃ constitute around 80 wt.% of the ashes, whereas CaO makes up less than 8 wt.%. The concentration of Fe₂O₃ is typically 5–6 wt.%, and that of K₂O around 3 wt.%. In general the ashes of the Achlada coals are similar to those of bituminous coal (Raask, 1985; Couch, 1994; Kostakis, 2009), with [CaO + MgO] in this case being approximately equal to [Fe₂O₃]. The SO₃ retained in the ashes varies from 1 to 6 wt.%. The S probably originated from pyrite and from sulphates, as well as from the organic sulphur in the maceral components. As discussed further by Koukoulas et al. (2009), the proportion of SO₃ retained in the ashes is related to the percentage of CaO, suggesting that the availability of Ca provides a controlling factor in fixing the S in the ash in a non-volatile form (e.g. as anhydrite, CaSO₄).

The geochemical features of the Mavropigi ash are somewhat different from those of the Achlada samples. Although SiO₂ (17.2–45 wt.%) and Al₂O₃ (9.2–21.2 wt.%) constitute the main part of the ash

for most of the samples, the concentration of CaO is also significant (13.8–40.3 wt.%). The ash of sample M3 is particularly notable in having low proportions of SiO₂ and Al₂O₃ and a high CaO percentage. The concentration of SO₃ in the Mavropigi ashes is also high, displaying values between 7.5 and 11.5 wt.%. Following on from the discussion above, this is probably related to the higher CaO content. According to the classification of Raask (1985) and Couch (1994) the Mavropigi ashes can be defined as lignite-type ashes since [CaO + MgO] > [Fe₂O₃] (Chudnovsky and Talanker, 2004).

4.6. Mineralogical features of LTA residues

X-ray diffraction data (Table 5) indicate that the LTA of the Achlada samples is dominated by clay minerals, illite and kaolinite (each 35–45 wt.%), with minor proportions (4–8 wt.%) of quartz. Although noted during the microscope study, neither carbonates nor pyrite were detected in the LTAs by XRD analysis.

In addition to the illite and kaolinite indicated by the powder diffractogram data (Table 5), the oriented-aggregates prepared from the LTAs of the Achlada lignites also contain significant proportions of smectite and irregular illite/smectite (Table 6). These components and their significance are discussed more fully by Koukoulas et al. (2009). Smectite and illite/smectite (I/S) are the dominant components, making up 40–55% of the clay fraction, with illite and kaolinite making up around 30% and 20% of the clay fraction respectively.

The remainder of the LTA isolated from the Achlada samples is represented by bassanite (CaSO₄·½H₂O). As indicated from studies of other low-rank coals (e.g. Ward et al., 2001; Kalaitzidis and Christanis, 2002) and discussed more fully by Koukoulas et al. (2009), this mineral was probably formed mainly from organically-associated Ca and S in the coals, released as the macerals were oxidised during the plasma-ashing process.

The LTA of the Mavropigi lignites is dominated by calcium sulphate minerals (Table 5), consisting either of bassanite or a more hydrated gypsum (CaSO₄·2H₂O) component. This is in marked contrast to the LTA of the Achlada samples, where clay minerals are dominant and bassanite occurs only in minor proportions. As discussed by Koukoulas et al. (2010), the gypsum in the Mavropigi LTAs may have been formed from bassanite by absorption of water from the atmosphere after low-temperature ashing but before the XRD analysis. However, as further noted by Koukoulas et al. (2010), small proportions of gypsum are also indicated for some samples by XRD analysis of the raw coal, without any low-temperature ashing process. This suggests that some of the Ca sulphates in the LTA may represent gypsum that was in the coal already, a suggestion further supported by the maceral analyses. Such gypsum may represent either authigenic deposits before sampling took place or crystallization of Ca and SO₄ ions from solution in the pore waters of the lignite

Table 4

Major element oxide concentrations for lignite ash (Rs: slagging index, Rf: fouling index: see definitions in Section 5.2).

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Rs	Rf
	wt.% (dry basis)											
Achlada												Rf_B
A1	53.1	29.1	5.21	1.02	0.15	3.15	2.68	0.08	3.05	1.90	0.19	0.01
A2	51.2	28.3	5.68	1.01	0.19	4.32	2.70	0.03	3.06	2.81	0.21	0.01
A3	53.8	29.9	5.81	0.93	0.13	2.34	3.02	0.07	3.49	1.24	0.26	0.01
A4	47.2	26.5	6.45	0.92	0.25	7.28	3.08	0.06	3.08	5.66	0.74	0.02
A5	51.7	28.6	5.78	1.04	0.26	3.48	2.92	0.03	3.27	2.47	0.45	0.01
Mavropigi												Rf_I
M1	37.4	21.2	6.19	1.14	0.19	19.9	1.99	0.09	1.19	10.1		28.0
M2	45.0	20.8	6.70	1.04	0.17	13.8	3.33	0.11	1.05	7.6		23.8
M3	17.2	9.2	7.64	0.40	0.18	40.3	7.52	0.23	0.59	11.5		55.5
M4	40.1	17.7	6.51	0.94	0.30	21.0	4.53	0.20	1.14	7.5		32.0
M5	38.2	20.6	8.02	0.99	0.28	14.1	4.27	0.44	1.47	11.1		26.4

Table 5

Mineralogical composition (wt.%) for low-temperature ash of lignite samples from Achlada and Mavropigi.

Sample	Achlada					Mavropigi				
Mineral	A1 ^a	A2 ^b	A3 ^a	A4 ^a	A5 ^a	M1 ^a	M2 ^a	M3 ^a	M4 ^a	M5 ^a
Quartz	5.0	4.5	3.7	4.1	7.8	5.9	14.6	4.6	8.5	6.4
Kaolinite	46.8	38.3	47.1	41.5	44.6	25.3	31.6	3.3	23.1	32.6
Illite ^c	40.8	45.4	41.7	37.4	38.0	28.1	26.5		20.4	19.8
Chlorite										5.0
Feldspar (?)								9.3		2.6
Pyrite							0.5			
Bassanite	7.4	11.8	7.5	17.1	9.6	40.6	26.7	4.1	26.0	13.1
Gypsum								53.2	22.1	20.5
Whewellite								25.5		

^a Matrix lignite.

^b Xylite-rich lignite.

^c Also includes expandable clay minerals.

with evaporation during air-drying prior to the raw coal XRD analysis. The remainder, however, and in most cases the majority, probably represents interaction of organically-associated Ca and S during the plasma-ashing process.

In addition to gypsum and/or bassanite, the LTA of one of the Mavropigi samples (sample M3) also contains around 25 wt.% of the calcium oxalate mineral whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$). The more hydrous calcium oxalate mineral weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) is also noted by Koukoulas et al. (2010) from XRD studies of the raw (un-ashed) coal of this coal sample. Although relatively rare, whewellite is also known to occur in other coals (e.g. Bouska, 1981; Goodarzi, 1990; Kalaitzidis and Christanis, 2004). Its occurrence in the LTA of the Mavropigi material probably represents an authigenic accumulation of Ca oxalate in the relevant (telohuminite-rich) lignite bed.

Apart from the bassanite/gypsum and (where present) whewellite, the LTA of the Mavropigi lignites contain a mixture of clay minerals (kaolinite, illite, smectite and in some cases chlorite), along with lesser but still significant proportions of quartz (Table 5). A trace of pyrite and in some cases small proportions of feldspar are also indicated by the XRD data (Table 5). Framboidal nodules of pyrite have been also been encountered during petrographical observations, although only in low concentrations (Koukoulas and Skounakis, 1991).

Oriented-aggregate XRD studies (Table 6) indicate that, in contrast to the Achlada samples, kaolinite is the most abundant component of the clay fraction of the Mavropigi lignites, and that illite and smectite are present in lesser and roughly equal proportions. Although only small proportions are present and the material occurs in conjunction with abundant kaolinite, a relatively strong peak representing a d (001) spacing of 14 Å is noted in the oriented-aggregate X-ray diffractograms. This indicates that the chlorite in the Mavropigi lignite

is an Mg-bearing variety such as clinochlore, rather than an Fe-rich variety such as chamosite, which has been noted as an authigenic product in other coals by Dai and Chou (2007) and Dai et al. (2008). Combined with the occurrence of chlorite also in the associated sedimentary strata (Koukoulas et al., 2010), this suggests that the chlorite in the Mavropigi lignite, where present, is probably of detrital origin.

The comparisons between the mineralogy of the LTA residues and the chemical composition of the laboratory-prepared lignite ashes are discussed in more detail in complementary studies of the two deposits by Koukoulas et al. (2009, 2010). Although there is some variation due to the nature of the materials, and also uncertainty about the chemical composition of some of the clay minerals, the chemical composition of the (high-temperature) ash implied by the LTA mineralogy has been shown in these studies to be consistent with the actual ash composition as determined independently by chemical analysis techniques.

5. Discussion

5.1. Depositional environment

A comprehensive reconstruction of the palaeoenvironment is beyond the scope of this study, and in any event cannot be achieved from the present data due to the broad scale of the sampling program. Nevertheless, a general view of the most evident aspects can be outlined.

Previous studies have shown that the Achlada lignite was formed in a fluvial environment, mainly in the abandoned channels of a meandering river system during flooding periods (Oikonomopoulos et al., 2007). The lithological succession (Fig. 2) shows alternations between high and low hydrodynamic conditions, which resulted in the deposition of sandy and peaty sediments, respectively. Clayey and marly organogenic sediments were also deposited under intermediate hydrodynamic conditions.

The petrographic data from the present study indicate significant fragmentation of the organic matter in the Achlada coals (Tissue Preservation Index, TPI < 1, Table 2) and low to moderate gelification (Gelification Index, GI ≤ 1, Diessel, 1986; 1992 modified after Kalaitzidis et al., 2004) for most of the lignite samples (Fig. 3). The fragmentation of the organic matter is attributed mainly to the herbaceous peat-forming plants, and hence the accumulation mostly of soft tissues, as well as to a hydrodynamic level that favored the mechanical destruction of tissues during short-term transportation. From a TPI vs. GI coal facies diagram (Fig. 3) it is suggested that the palaeomire was one in which mainly herbaceous plants were able to thrive in a reed-marsh environment; only the A2 layer shows evidence of deposition in the forest swamp field. Deposition also took place under moderate to high water-table conditions, which resulted in the accumulation of significant proportions of inorganic material in the form of detrital silicates, mainly illite, smectite, I/S and quartz, within the peat that formed the Achlada coal seams.

The Mavropigi lignite deposit, by contrast, was developed in a lacustrine environment that occupied the broader area of the Ptolemais Basin during the Pliocene (e.g. Anastopoulos and Koukoulas, 1972; Cameron et al., 1984; Georgakopoulos and Valceva, 2000; Papanicolaou et al., 2000; Kalaitzidis et al., 2004). The lithological column (Fig. 2) reveals an alternation of peat-forming periods with extensive flooding events and deposition of marly sediments with abundant shell fragments. The fragmented pattern of the organic matter suggests an origin from herbaceous plant-species for most layers, and only layer M3 shows derivation from mixed herbaceous and arboreal vegetation. The TPI and GI values are similar to those of the Achlada lignite, suggesting formation in a reed-marsh environment under limno-telmatic conditions with moderate water-table levels (Fig. 3).

Table 6

Clay minerals in <2 μm fraction of selected LTAs using oriented-aggregate XRD techniques.

Sample	Kaolinite %	Illite %	Expandable clays %	Nature of expandable clay minerals
Achlada LTA samples				
A1	26	22	52	Smectite + irregular I/S
A2	21	39	40	Smectite + irregular I/S
A3	17	28	55	Smectite + irregular I/S
Mavropigi LTA samples				
M1	50 ^a	21	30	Smectite
M2	68	0	32	Smectite
M4	55	29	16	Smectite
M5	39	36	25	Smectite

^a Includes minor chlorite.

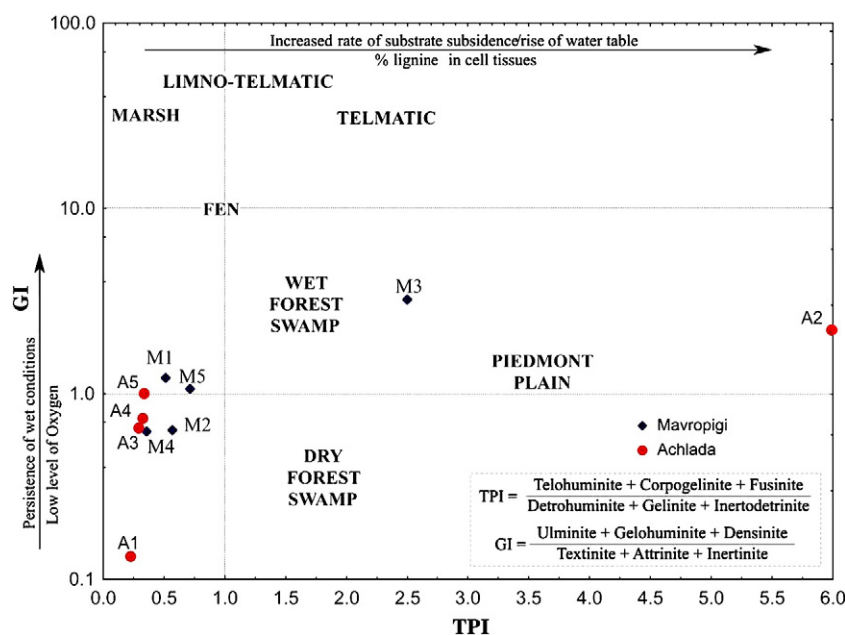


Fig. 3. Coal facies TPI vs. GI diagram (after Diessel, 1986, modified).

Short dry periods caused aerobic exposure of the peat and the formation of inertinite macerals.

The greater proportions of calcium sulphates and oxalates (bassanite/gypsum and whewellite/weddellite) in the LTA, relative to the LTA from the Achlada lignites, are consistent with a lower proportion of detrital input to the paleomire and a greater proportion of Ca associated with the organic matter. The greater abundance of kaolinite, thought to be authigenic, in the clay fraction of the Mavropigi lignites is also consistent with a lower detrital input. Such differences may reflect the wider development of less-contaminated lacustrine environments, compared to the fluvial mires that formed the coals in the Achlada succession.

5.2. Utilization aspects

Since the Achlada and Mavropigi lignites are used by the Greek Public Power Corporation as raw material for its power plants in NW Macedonia, an initial assessment is presented herein of the lignite characteristics in relation to combustion behavior.

The first parameter for efficient utilization is the grindability of the raw coal, since combustion efficiency is inversely proportional to the coal grain-size (Hower, 2008). In general liptinite is the maceral group most resistant to grinding and huminite the least resistant (Trimble and Hower, 2003; Hower, 2008). The predominance of huminite and particularly of attrinite in the samples studied may therefore contribute to a low grinding energy requirement. Although inertinite and liptinite make up more than 10 vol.% of several samples, no severe resistance to grinding would be expected since the fragmented macerals inertodetrinite and liptodetrinite prevail. Deviation might occur for the telohuminites-rich samples M3 and A2, in which the lignin-rich ulminite particles might require more grinding energy.

Regarding the burnout behavior of the studied lignite samples it is expected that their immature nature (low reflectance), along with the predominance of huminite and liptinite relative to inertinite, should lead to increased reactivity (Furimsky et al., 1990; Cloke and Lester, 1994; Choudhury et al., 2008). Prediction of any differences in combustion behavior among the samples, however, is difficult, since in general the petrographic features of the coals are more or less similar, and more detailed studies are required.

To indicate the possible effects of mineral matter in the coals on the behavior of the respective ashes, ash, the slagging index (R_s) and

fouling impact (Benson et al., 1993; Chudnovsky and Talanker, 2004) have been calculated (Table 4). R_s has been calculated only for the Achlada samples, since it is applicable only for bituminous type ashes; for the lignitic type ashes of Mavropigi a fusibility test is required (Chudnovsky and Talanker, 2004), which was beyond the scope of this study. Because the ash chemistry of the Achlada samples is similar to that expected from bituminous coals, the slagging index can be calculated using the equation of Barroso et al. (2007):

$$R_s = \frac{\text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O}(\text{wt.\% ash, db})}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2(\text{wt.\% ash, db})} \quad 1$$

* $S(\text{bulk conc. wt.\% db})$

For the Achlada samples this index ranges between 0.19 and 0.74, indicating low to moderate slagging tendencies. Only sample A4 shows $R_s > 0.6$, which is the level for slagging effects to occur, and hence corrective measures may need to be applied, such as blending different lignite qualities from the mine area.

The fouling behavior for ashes of lignite rank is generally regarded as being related to the sodium content, and hence prediction can be approached from the proportions of CaO, MgO, Fe_2O_3 , and Na_2O in the coal ash (Benson et al., 1993; Chudnovsky and Talanker, 2004). For the bituminous ash types from Achlada the fouling tendency (R_{fB}) is defined according to the formula (Chudnovsky and Talanker, 2004):

$$R_{fB} = \frac{\text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O}(\text{wt.\% ash, db})}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2(\text{wt.\% ash, db})} * \text{Na}_2\text{O}_2$$

According to the results (Table 4) R_{fB} has values between 0.01 and 0.02 and hence it can be predicted that the fouling tendency of the Achlada lignite will be low.

The fouling tendency for lignitic type ashes (R_{fL}), such as the Mavropigi ashes, is defined from the condition that if $R_{fL} = [\text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3] < 20 \text{ wt.\%}$ and $[\text{Na}_2\text{O}] < 1.2 \text{ wt.\%}$ then the coal displays low fouling tendency. In the case of the Mavropigi samples R_{fL} ranges between 23.8 and 53.45 (Table 4), providing evidence for possible fouling impacts.

Because the overall proportion of inorganic matter in the coal is high it is obvious that combustion efficiency cannot be significantly optimized. More detailed studies, including options for removal of mineral matter, should therefore be carried out in order to decrease

the proportion of solid particles giving rise to adverse utilization behavior.

6. Conclusions

This paper has provided an integrated assessment of the petrographical, mineralogical and geochemical features of the Achlada and Mavropigi lignite deposits. The Mavropigi lignite is mainly a matrix lithotype, whereas the Achlada deposit consists both of matrix and xylite-rich lithotypes. Both deposits are thermally immature, with vitrinite reflectance (Rm) of 0.18–0.29% indicating a lignite C rank. The Achlada lignite is characterized by high ash values (>30 wt.%) and low gross calorific value (<13 MJ/kg), whereas the Mavropigi lignite is less enriched in mineral matter, with ash values <30 wt.%. The Mavropigi lignite has gross calorific values of between 13 and 18 MJ/kg, similar to the majority of the lignite deposits in the Ptolemais Basin.

The Achlada lignite was formed in a fluvial environment, mainly in the abandoned channels of a meandering river system during flooding periods. The organic matter was significantly fragmented due to the high level of hydrodynamic activity. Coal facies indices suggest the alternation of reed-marsh and forest swamp environments.

The Mavropigi lignite deposit, by contrast, was developed in a reed-marsh environment under limno-telmatic conditions, with moderate water-table levels, and was affected by short dry periods. It has a lesser proportion of detrital mineral matter and a greater proportion of organically-associated Ca and authigenic Ca sulphate and oxalate components.

Concerning the utilization of these two deposits for power production it is evident that the high proportion of inorganic matter should be taken into consideration in order to optimize the burnout behavior. An initial evaluation suggests that the Achlada lignite seems to have more favorable slagging and fouling properties than the Mavropigi lignite; however, experimental studies are required for more solid conclusions to be reached.

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