

H/C versus O/C atomic ratio characterization of selected coals in Slovenia

Opredelevitev nekaterih premogov na ozemlju Slovenije s H/C proti O/C atomskimi razmerji

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Ključne besede: premogi v Sloveniji, elementna sestava C, H, O, N, S, atomska razmerja H/C – O/C, van-Krevelenov diagram, stopnja karbonizacije ali rang

Abstract

Application of the H/C and O/C atomic ratios plotted into the van Krevelen's diagram is well known approach for chemical characterization of coals, more precisely, of their organic part. Determination of coals by the two atomic ratios closely relies to their petrographic type as well as to their coalification rank. Elemental data, together with the coal quality data of 23 coals from the territory of Slovenia are comprised in this study. Coals vary in age from the Carnian anthracite to the Pliocene ortho-lignites, and were deposited in paralic as well as in intermountain basins of different tectonic settings. The highest H/C and O/C atomic ratios are characteristic for the xylite-rich ortho-lignites from Velenje (Pliocene) and Globoko (Pontian), whereas the lowest for the Orle anthracite (Carnian). The Upper Oligocene "hard brown coals" and younger meta- and ortho-lignites treated in this study are typical humic coals. Relatively high H/C ratios are evident for two sapropelic coals, the Sečovelje para-bituminous and the Raša (Croatia) ortho-bituminous coal, both of the lower Paleogene age. No inertinite coals are known from our country, however, inertinite macerals are recorded in almost all of them.

Izveček

Uporaba H/C in O/C atomskih razmerij, vnesenih v van-Krevelenov diagram, je dobro poznan pristop za kemično opredelitev premogov, bolje rečeno, njihovega organskega dela. Opredelevitev premogov z omenjenima dvema razmerjema je v tesni povezavi z njihovim petrografskim tipom in z njihovo stopnjo pooglenitve ali rangom. V priloženo študijo smo zajeli podatke o elementni sestavi in kakovosti 23-ih premogov z območja Slovenije. Po starosti zajemajo obravnavani premogi razpon od karnijskih do pliocenskih premogov, po stopnji karbonizacije ali rangi pa od antracita do orto-lignitov. Eni so nastali v morsko obalnih (paraličnih), drugi pa v tektonsko različnih medgorskih (intramontanih) okoljih. Najvišja H/C in O/C atomska razmerja so značilna za ksilitni orto-lignit pliocenske starosti iz Velenja in za ksilitni orto-lignit pontijske starosti iz Globokega, najnižji omenjeni razmerji pa ima karnijski antracit z Orel pri Ljubljani. Obravnavani zgornjeoligocenski »trdi rjavi premogi« ter mlajši meta- in orto-ligniti so tipični humusni premogi. Razmeroma visoko H/C atomsko razmerje je značilno za dva »črna« premoga paleogenske starosti, ki imata sapropelski značaj, to je za para-bituminozni premog iz Sečovelj in za orto-bituminozni premog iz Raše v Istri na Hrvaškem. Premogov z znatno povišanimi vsebnostmi inertinitnih maceralnih sestavin pri nas ne poznamo, so pa tovrstni macerali zastopani v manjših količinah v malo da ne vseh naših premogih.

Introduction

Elemental analysis of the carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulphur (S) contents is one of the basic methods for chemical characterization of geological organic matter, including coals, which are petrographically composed of microscopically distinguishable more or less structured plant remains and their amorphous excretions, termed as the coal macerals (e.g. Tissot & Welte, 1978; Stach et al., 1982; Whelan & Thompson-Rizer, 1993; Taylor et al., 1998; Ercegovic, 2002). Both, chemical and maceral composition is primarily dependent on the source coal-forming plant ingredients, and alters considerably with the biogeochemically controlled coalification processes. Coal macerals are divided into three groups, termed as the huminite/vitrinite, liptinite/exinite and inertinite maceral groups. Huminite macerals originate from the cellulose and lignin rich woody tissues of higher plants (trees and bushes, also grasses and mosses) having been flourished in the areas of forest swamps and bush moors. During the process of coalification, they are transformed to less structured and increasingly light-reflecting vitrinite macerals. Liptinite macerals represent highly resistant parts of plants as waxes, resins, sporopollenins, cutins, suberins and algaenans. Inertinite macerals represent suddenly coalified (chared) plant remains and do not alter significantly during coalification.

Coal classifications based on the C, H, O elemental composition, volatile matter content, calorific value and moisture content date back to the 19th century. Among them, the best known is the "Sayler's coal chart" from 1899 and 1931 (Bustin et al., 1983; Thomas, 1992). His classification is applicable for characterization of whole coals (especially for higher-rank coals), with no significant respect to their maceral composition.

Relation between elemental and maceral composition was considerably clarified by van Krevelen (1961) who found out, that the three genetically important maceral groups are characterized by specific H/C versus O/C atomic ratios.

Dark grey liptinite macerals (fluorescing under the blue light irradiation) are relatively enriched in H content, whereas normally to light grey (nonfluorescing) hu-

minite/vitrinite macerals are enriched in O content. The lowest H content is distinctive for the highest reflecting char-coal like inertinites. Due to loss of functional groups (depolymerization of the macromolecular organic matter structure) during the coalification process, initial H and O contents decrease and C content increases. Therefore, in addition to huminite/vitrinite reflectance and specific energy (calorific value), C content of the organic matter is one of the most widely used coalification rank parameters. Differential changes in decreasing H/C and O/C atomic ratios for the three maceral groups are known as the coalification paths. Interpretation of the coal type – whether it is huminitic, inertinitic or liptinitic – can be therefore best ascertained for lower rank coals, because chemical as well as maceral composition of higher rank coals is much more uniform.

In honour to the van Krevelen's pioneering work, a diagram of H/C versus O/C atomic ratios characteristic for the separate maceral groups is now widely known as the "van Krevelen diagram".

The aim of this study is to present elemental C, H, N, O, S composition and H/C versus O/C atomic ratios for a range of coals in Slovenia, and to interpret them in the sense of their geological background and coal genesis. Unfortunately, except for S, elemental data basis for our coals is relatively poor in relation to the kingdom of conventional coal-quality data. Moreover, many coals dealt with in the present paper are not actively mined for tens of years and only relatively old data (before 1965) could be used. Therefore, results of this study serve as limited information. Because H/C versus O/C ratios express not only the petrographic type but also the rank of coalification, they are compared to rank parameters as calorific value, carbon content and vitrinite reflectance.

Selected coals – data collection, analytical methods, and constraints of the study

Locations of the selected coals are presented within the general geological realm of Slovenia in Fig. 1. (adopted after Drovenik, F. et al., 1978; Premru, 1980, 2005; Drovenik, M., 1984; Placer, 1981, 1998 a; Šolar et al., 1998; Poljak, 2000, 2007; Buser & Komac, 2002). Terms for coal rank

in Fig. 1 are cited according to the ECE-UN (1998) classification of in-seam coals (Tab. 1). Rank of coals is defined after data

in Tab. 2 and Tab. 3, and supplemented by the mean random vitrinite reflectance values (Rr %) as cited in Hamrla (1985/86).

Rank classifications			Ref. R _{m-oil}	Vol.M d.a.f. %	Carbon d.a.f. Vitrinite	Bed Moisture %	GCV MJ/kg <i>m.,a.f.</i> <i>(d.a.f.)</i>	Applicability of different rank parametres (simplified after Stach et al., 1982)	
ECE - UN	German	USA							
LOW - RANK	PEAT	Torf		0,2				Carbon (daf)	Calorific value (maf; daf)
				68					
				64	ca 60	ca 75			
	Ortho-LIGNITE	Weichbraunkohle (Soft brown coal)		60					
	15 (28)								
	Meta-LIGNITE			56		ca 35	16,744 (28,7)		
	20 (30)	Matt (Dull)		52					
	Sub-BITUMINOUS COAL	Hartbraunkohle (Hard brown coal)	Sub-Bit	0,4					
	24 (31)		C						
			B	48	ca 71	ca 25	23,023 (30,8)		
MEDIUM - RANK	Para -	Glanz (Brilliant)		0,5				Carbon (daf)	Calorific value (maf; daf)
	0,6		C	0,6	ca 77	ca 8-10	29,302 (33,0)		
		Flamm		0,7					
	Ortho -	Gas-flamm	B	0,8					
	1,0		A	1,0					
	Meta -	Gas		1,2					
				1,4					
	1,4			1,6					
	Per -			1,8					
				2,0					
HIGH - RANK	2,0			2,0				Carbon (daf)	Calorific value (maf; daf)
	Para -	Mager		12					
				8	ca 91		36,309		
	3,0	Anthrazit		3,0					
	Ortho -			4,0					
	4,0								
HIGH - RANK	Meta -	Meta-Anthr.						Carbon (daf)	Calorific value (maf; daf)
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In Tab. 1, traditional German (DIN) and the USA (ASTM) coal rank classifications (Stach et al. 1982) are added to the ECE-UN (1998) classification. The gross calorific value (GCV) boundaries are cited at the *moist, ash-free (maf)* basis and at the *dry, ash-free (daf)* basis. The *maf* to *daf* transformation is made according to the correlation graph by Alpern et al. (1989). In the ECE-UN classification, GCV at the *maf* and *daf* basis respectively is the limiting parameter between the coal-rank classes up to the sub-bituminous – para-bituminous coal boundary, whereas the *Rr* % value is the limiting parameter for the medium- and the high-rank coal classes. Rank parameterization on the basis of carbon content refers to the carbon content of “vitrinite” at the *daf* basis. Applicability of different rank parameters for various coals after Stach et al. (1982) is presented in the most right column.

In the past, in Slovenia, as well as in former Yugoslavia, the term lignite was mostly used in the sense of the USA classification, whereas the terms dull (“matt”) and brilliant (“glanz”) brown coal were used after the German classification. However, to avoid ambiguities, today there is a trend to classify the coals in the wider Balkan region according to the ECE-UN classification as well. In Serbia for example, where as many as 11 coal deposits are in operation at the present (Ercegovac et al., 2005), one outstanding step in this direction was made by a complex argumentation of a new genetic and industrial classification of their brown coals (Ercegovac et al., 2006). The authors studied coals from 19 deposits. On the basis of the ECE-UN (1999, 2000) codification and classification systems, they classified brown coals in Serbia by rank to low-rank C coals or ortho-lignites (with *Rr* % below 0.30), low-rank B coals or meta-lignites (*Rr* % 0.30–0.40) and low-rank A coals or sub-bituminous coals (*Rr* % 0.40–0.55). For other parameters, the reader is referred to the cited paper. Similar work has been carried out also for Greek coals (Papanicolaou et al., 2004).

Analytical data-set for this study is given in Tab. 2, after references *a–p*. Coals of different coal-forming environments and tectonic units are cited according to their increasing geological age – from Pliocene to Triassic (Carnian). Rank classes (abbreviations OL, ML, ... A) are based on the GCV (*daf*) and C (*daf*) values, and for higher rank

coals also on the vitrinite reflectance data from the literature.

Data for coals refer to selected lithotypes (Velenje), samples from coal seams (Globoko, Lendava, Moravci, Sv. Jurij, Kanižarica, Trobni Dol, Sečovlje, Vremški Britof, Zreče and Orle), parts of coal profiles (Trbovlje – Neža and Lopata) and to whole seams in general (Kanižarica, Kočevje, Krmelj, Liboje, Laško, Senovo, Trbovlje–Hrastnik, Zagorje, Pečovnik, Zabukovica, Motnik, and Raša). Number of coal samples and their exact locations are not cited in the reference works *k* and *n*. However, Hamrla (1959), and Germovšek (1963) classified these series of coals and bitumen extracts into the Francis (1961) diagram (conceptually similar to the Seyler's coal chart). Therefore, both coal series are considered as representative in this study.

Both elemental and coal-quality analyses have been carried out at the National Chemical Institute Ljubljana, and the Chemical Laboratory of the Trbovlje–Hrastnik Coal Mine. It should be pointed out that all analyses presented in this study were originally carried out on the “whole coal” samples, (except for bitumens from Sečovlje and Raša).

During more than 50 years, from 1950 onwards, analytical procedures altered in dependence of equipments and standardisation. Up to the 1990s, mainly Yugoslav (JUS) and German (DIN) standards were used, whereas later these were progressively replaced by Slovenian standardisation (SIST) that follows the standards of the International standardisation organisation (ISO). After preparation of coal samples to an air-dried, below 0.2 mm in-size fraction state in accordance to the JUS B.H9.001, JUS B.H9.003 and SIST ISO 5069-1,2 standards, proximate analyses of coals (moisture, ash, combustible matter contents) were carried out according to the next standards, procedures and calculations:

- DIN 51718, ASTM D 3302 and SIST ISO 5068 for total moisture.
- Surface moisture as moisture removed with drying at 40°C to the stable weight state.
- JUS B.H8.310 (volumetric) and JUS B.H8.311 (gravimetric) for determination of hygroscopic moisture (removed at 105°C drying).
- JUS B.H8.312, DIN 51719, and SIST ISO 1171 for ash content after combustion at 815 ± 15°C.

Tab 2. Elemental composition, H/C and O/C atomic ratios, coal quality and coalification rank (by GCV) of the studied coals (after data in references *a-p*). Values in italic are recalculated – approximated (see the text). Abbreviations for rank refer to: OL and ML: ortho- and meta-lignite; SB, PB, OB and MB: sub-, para-, ortho- and meta-bituminous coal, A: anthracite. Other abbreviations: M, A and OM: moisture, ash and organic matter contents; NCV and GCV: net and gross calorific values; MIO, Cr, T: Miocene, Cretaceous, Triassic; PALEOG.: Paleogene (older than Oligocene)

Age	Environment	Tect. unit	COAL seam / deposit / lithotype	Rank Reference N. of samples	Elemental composition						Atomic ratios		Coal quality					Rank	
					C	H	O	N	O+N	S org	H/C	O/C	S tot	M	A	OM	NCV	NCV	GCV
					mass %								mass %					MJ/kg	MJ/kg
					daf basis								d b.	ar basis				daf	daf
PLIOCENE	Lacustr. - intermont.	Karavanke / S Alps	Velenje – X	a 1	57,80	6,30	33,90	0,40	34,30		1,299	0,440	1,61	10,30	6,50	83,20			
			Velenje - XD-fD	a 2	65,00	4,60	26,20	2,20	28,40		0,843	0,303	1,85	20,35	7,40	72,25			
			Velenje - GfD, fDG	a 3	67,00	4,70	23,90	2,10	26,00		0,836	0,268	2,06	21,47	9,30	69,23			
			Velenje - MfD, fDM	a 2	63,60	4,60	28,20	1,90	30,10		0,862	0,333	1,31	14,50	24,90	60,60			
			Velenje - X	b 5										17,02	4,83	78,15	17,475	22,36	24,05
			Velenje - XD-fD	b 11										15,19	8,16	76,65	18,432	24,05	25,69
			Velenje - XD-fD	b 8										15,76	6,33	77,91	19,107	24,52	26,14
			Velenje - GfD-fDG	a 20										15,13	6,12	78,75	19,590	24,88	26,42
PONTIAN	Paralic - deltaic	Pannonian basin	Globoko - seam 2.3	c 5	63,78	5,68	28,65	1,19	29,84	0,70	1,060	0,338	1,33	52,01	6,72	41,27	9,166	22,21	26,66
			Globoko - seam 2.2	c 5	63,17	5,64	29,54	1,16	30,69	0,48	1,064	0,352	1,40	44,82	10,27	44,91	10,228	22,77	26,60
			Globoko - seam 2.3	d 24										45	11	44	9,9	22,50	26,35
			Globoko - seam 2.2	d 18										46	12	42	9,7	23,10	27,13
			Globoko - seam 2.1	d 9										43	17	40	8,9	22,25	26,23
			Lendava - seam 1.0	e 1	66,72	5,82	23,89	1,20	25,09	2,37	1,039	0,269	2,98	32,94	11,38	55,68	14,168	25,45	28,25
			Lendava - s.1.0 (upp. p)	e 1	66,97	5,86	23,65	1,22	24,87	2,31	1,042	0,265	2,98	37,26	10,34	52,40	13,218	25,23	28,34
			Lendava - s.1.0 (low.p.)	e 1	66,02	5,70	24,69	1,16	25,85	2,43	1,029	0,281	2,93	35,08	15,10	49,82	12,443	24,98	28,03
			Moravci Mt 6/82 - 781 m	f 1										21,70	15,36	62,43	17,500	28,03	30,13
			Moravci Mt 6/82 - 783m	g 1							0,970	0,300							
MIO-PLIOC. ?	Lac. - intermont.	Dinarides	Moravci Mt 7/93 - 929m	h 1	65,53	5,41	24,35	1,26	25,62	3,44	0,984	0,279	3,98	20,14	9,48	70,38	17,846	25,36	27,30
			Sv. Jurij TER 1/03 -148m	i 1	67,65	5,85	24,99	0,39	25,38	1,12	1,030	0,277	1,88	9,61	8,48	81,91	21,801	26,62	28,23
			Kanižarica – seam 1	OL-OL j 6						2,78			2,17	23,40	32,65	43,95	10,050	22,86	25,41
			Kanižarica – seam 2	j 13						3,05			2,44	22,43	33,10	44,47	10,500	23,53	26,05
			Kanižarica – seam 3	j 23						2,47			2,42	24,50	25,07	50,43	12,200	24,14	26,59
			Kanižarica – seam 4	j 29						2,93			3,05	26,70	19,90	53,40	13,033	24,37	26,86
			Kanižarica	OL-ML k ?	65,25	5,15	25,70	1,35	27,05	2,58	0,940	0,296	3,79	27,00	19,61	53,39	13,067	24,47	26,91
			Kočevoje	OL-ML k ?	65,35	4,90	25,55	1,25	26,80	3,03	0,893	0,294	4,33	26,50	11,74	61,76	15,314	24,80	26,98
			Kočevoje	OL-ML k1 12	65,18	5,97	24,54	0,96	25,50	1,53	1,091	0,283							

Age	Environment	Tect. unit	COAL	Rank	Reference	N. of samples	Elemental composition						Atomic ratios		Coal quality					Rank	
							C	H	O	N	O+N	S org	H/C	O/C	S tot	M	A	OM	NCV	NCV	GCV
							mass %								mass %					MJ/kg	MJ/kg
							daf basis								d b.	ar basis				daf	daf
MIO			Krmelj	OL-ML	k	?	65,85	5,35	24,75	1,45	26,20	2,61	0,968	0,282	2,82	32,00	16,34	51,66	12,236	23,69	26,45
Upper OLIGOCENE	Paralic – coastal plain	Pann. basin – within S Alps and Dinarides (Sava folds)	Trbovlje - Neža - unit IV	OL-ML	I	4	66,89	5,52	24,69	1,86	26,55	1,03	0,983	0,277	2,38	15,70	36,94	47,36	11,734	24,78	26,86
			Trbovlje - Neža - unit III			6	66,85	5,52	24,97	1,88	26,85	0,83	0,984	0,280	1,58	20,19	7,36	72,45	18,909	26,10	28,05
			Trbovlje - Neža - unit II			11	66,56	5,50	25,16	1,89	27,05	0,89	0,985	0,284	2,26	21,27	16,05	62,68	15,917	25,39	27,49
			Trb. - Neža – u. I (upp.p)			10	66,73	5,46	24,94	1,88	26,82	0,99	0,975	0,281	2,34	19,14	25,75	55,11	14,682	26,64	28,75
			Trb. - Neža – u. I (low.p)			10	66,50	5,52	25,05	1,89	26,94	1,05	0,989	0,283	2,30	19,67	34,38	45,95	11,649	25,35	27,68
			Trb. - Lopata – unit E			8	66,89	5,49	24,82	1,87	26,69	0,92	0,978	0,279	1,83	15,75	24,06	60,19	15,081	25,06	26,95
			Trb. - Lopata – unit D			18	66,85	5,50	24,68	1,86	26,54	1,10	0,980	0,277	3,86	16,56	27,97	55,47	13,785	24,85	26,85
			Trb. - Lopata – unit C			6	66,79	5,50	24,86	1,87	26,73	1,02	0,981	0,279	3,34	19,35	10,25	70,40	18,354	26,07	28,01
			Trb. - Lopata – unit B			12	67,07	5,55	24,60	1,85	26,45	0,93	0,986	0,275	2,56	21,00	7,19	71,81	18,887	26,30	28,29
			Trb. - Lopata – unit A			6	66,73	5,51	24,67	1,86	26,53	1,25	0,984	0,278	6,43	19,09	12,97	67,94	17,546	25,83	27,78
	Pann. basin – within S Alps and Dinarides (Sava folds)	Pann. basin – within S Alps and Dinarides (Sava folds)	Liboje (Li)	OL-ML	k	?	67,85	5,45	21,40	1,50	22,90	3,77	0,957	0,237	3,35	20,00	22,23	57,77	14,756	25,54	27,64
			Laško (La)			?	71,65	5,45	21,15	1,40	22,55	0,37	0,906	0,222	0,85	22,50	9,34	68,16	17,477	25,64	27,70
			Senovo (Sen)			?	69,50	5,50	19,80	1,60	21,40	3,59	0,943	0,214	3,78	19,00	16,31	64,69	16,654	25,74	27,73
			Trb. - Hrastnik (T-H)			?	69,55	5,35	19,80	1,65	21,45	3,59	0,917	0,214	3,68	22,00	15,52	62,48	16,202	25,93	28,03
			Zagorje (Zag)	ML-SB	k	?	70,80	5,80	20,65	1,30	21,95	1,39	0,976	0,219	1,82	23,00	12,42	64,58	16,794	26,01	28,21
			Pečovnik (Peč)			?	71,95	5,55	20,00	1,25	21,25	1,25	0,919	0,209	1,52	18,00	11,34	70,66	18,929	26,79	28,68
			Zabukovica (Zab)			?	71,30	5,40	21,00	1,35	22,35	0,93	0,902	0,221	1,20	16,50	10,36	73,14	19,890	27,19	28,98
			Motnik (Mo)			?	73,60	5,10	16,50	1,10	17,60		0,826	0,168	4,41	11,50	2,66	85,84	24,199	28,19	29,68
			Trobni Dol (T. Dol)	SB	m	1	69,73	5,24	20,61	1,32	21,93	3,12	0,896	0,222	3,16	19,60	10,22	70,18	19,603	27,93	29,82
PALEOG.	Lagoonal	Adria f. land	Sečovelje (Seč)	PB	n	6	71,27	5,97	12,10	0,76	12,86	9,90	0,999	0,127							32,6
			Raša	OB	n	?	77,69	5,75	4,14	2,02	6,15	10,40	0,882	0,040							34,3
			Asphalt bitumen - Raša				83,10	8,70	0,48	0,12	0,60	7,60	1,247	0,004							
			Extract from coal - Sečovelje		n	?	67,60	6,62	13,12	0,66	13,78	11,90	1,167	0,146							
			Bitumen from sapropel. limest.				66,10	6,80	12,16	1,44	13,60	13,50	1,226	0,138							
K-Tc	Par	Din	Vremski Britof (VrB)	MB	n	6	82,25	4,52	2,71	1,11	3,82	9,40	0,656	0,025							35,5
PALEOG	Lac. - fluv	Pann.b / E Alps	Zreče - Radana seam	OB	o	4	80,60	5,25					0,776	0,035							32
			Zreče - Osredok seam			2	84,60	4,20					0,592	0,035							32,5
			Zreče - Rugelj seam			4	80,20	5,45					0,810	0,035							34
			Zreče - Stranice seam			4	82,30	5,60					0,811	0,035							32,6
			Zreče - Pucka seam			3	79,80	5,25					0,784	0,035							31,2
Cr	Lag																				
T	?	Din	Orle	A	p	1	94,27	1,17	1,90	0,00	1,90		0,148	0,015	2,37	1,96	10,98	87,06	29,022	33,34	33,66

References to Table 2: a) Hočevár, 1998 (In: Markič et al., 1998; tab. 7, 8) – b) Markič et al., 1999 (tab. 3) – c) Geol. Surv. Slo – Markič (personal archive) – d) Marin et al., 1988 (In: Markič & Rokavec, 2002) – e) Geol. Surv. Slo – Markič (personal archive) – f) Jelen, 1985/86 – g) Škerlj, 1983 – h) Kralj Peter et al. 1993 a, 1993 b – i) Markič 2003 (pril. 1) – j) Markič 1995 (tab. 12, 13, 14) – k) Jencič, 1951 (In: Germovšek, 1963; tab. 1) – k1) Babšek, 1956 (In: Jelenc et al., 1956) – l) Uhan, 1991 (pril. 2, 7) – m) Grad et al., 1996 (tab. 1); with correcture – n) Hamrla, 1959 (tab. 11, 12) and 1987 (tab.1) – o) Hamrla, 1985/86 (tab.1) and 1987 (tab. 1) – p) Češmiga, 1959 (p. 244-245)

- Combustible or organic matter is an auxiliary datum gained by subtracting the sum of moisture plus ash from 100 %.

Elemental analysis of organic matter of coals was carried out according to the following standards:

Sulphur:

- JUS B.H.8.313 and SIST ISO 157 for the three forms of sulphur – the sulphate, the pyritic (or marcasitic), and organic sulphur. Procedure for sulphate sulphur was extraction with diluted hydrochloric acid, and determination of sulphur in the extract, either gravimetrically, volumetrically, or with instrumental methods. Pyritic sulphur was determined indirectly from iron content obtained by solution in nitrogen acid. Organic sulphur was determined as a difference between the total sulphur content and the sulphate plus pyritic sulphur.
- JUS B.H.8.315 and SIST ISO 334 for determination of total sulphur with the Eschka method (dissolution in oxygen atmosphere until the total sulphur passes into the sulphate form and then gravimetric or volumetric determination).
- JUS B.H.8.316 and SIST ISO 351 for determination (titrimetric or instrumental) of total sulphur with the method of high-temperature (1350°C) combustion in the oxygen flow.

Carbon and hydrogen:

- JUS B.H.8.319, DIN 51721, and SIST ISO 609 for high-temperature (HT) combustion
- SIST ISO 10693 for determination of carbonate content
- JUS B.H.8.311, DIN 51718, and SIST ISO 5068 for moisture content

Organic carbon content was calculated as the difference between the total and the carbonate carbon. Total carbon and hydrogen of coal samples were gravimetrically or instrumentally determined by HT combustion (1350°C) in the oxygen flow. Gravimetric determination was based on total oxidation of carbon into carbon dioxide and of hydrogen to water. Carbonate carbon was determined by dissolution with hydrochloric acid

and measurement of the produced carbon dioxide volume.

Nitrogen:

- JUS B.H.8.320 and SIST ISO 333 were used for nitrogen determination by heating in concentrated sulphuric acid in presence of catalysts. The formed ammonia sulphate was distilled and the ammonia formed was determined by titrating.

Oxygen:

- Oxygen content was calculated as the difference between the total combustible (organic) matter and the sum of carbon, oxygen, hydrogen and nitrogen.

Still acceptable accuracy of analytical results within a laboratory should not surpass the following values: 0.05 % for sulphur contents, 0.12 % for hydrogen, 0.25 % for carbon, and 0.05 % for nitrogen contents.

Gross calorific value (GCV) of coals was determined in calorimetric bomb according to the JUS B.H.8.318, DIN 51900, and SIST ISO 1928 standards. In coal quality assessments, mostly the net calorific values (NCV) were taken into consideration. Also in the original references to Tab. 2, only the NCV values could be found. Therefore, in this study, recalculation from the NCV to the GCV as cited in Formula 1 should be done.

The C, H, N, O, S elemental composition in Tab. 2 is expressed in mass % at the *daf* basis of the “whole coal” samples, and recalculated to the H/C and O/C atomic ratios. O and N contents were not analysed separately for the Trbovlje–Neža, the Trbovlje–Lopata and the Trobni Dol coals, but were analysed as the (O + N) contents. Average O portions of 93 % in relation to the (O + N) contents referring to the Trbovlje–Hrastnik and the Zagorje coals (reference *k*) are taken into account in these cases.

Elemental composition is supplemented by the coal-quality data including moisture content (M), ash content (A), combustible (organic) matter content (OM), net calorific value (NCV) and sulphur (Sorg. and Stot.) content – all at the *as-received* (*ar*) basis. Stot. is recalculated also to the *dry* basis (*db*). However, complete elemental and parallel coal-quality analyses have not been carried out in all cases. The only coal-quality

data of a given coal (without corresponding elemental data) serves only as approximate information to its elemental composition based on different than coal-quality set of samples. For example, the average NCV value of 17.475 MJ/kg for the five Velenje-X (pure xylite) samples serves as an approximate information to the elemental composition of the single Velenje-X sample (which is not one of the previous five).

In the most-right four columns in Tab. 2, the NCV at the *ar* basis is recalculated to the NCV at the *daf* and at the *maf* basis and to the GCV at the *daf* and the *maf* basis, respectively. The NCV of coals is mostly used as a technological parameter in combustion processes (energy efficiency), whereas GCV is used as a rank parameter. In spite of that the GCV at the *daf* basis is the worst parameter to utilize for establishing coal rank boundaries (Alpern et al., 1989), it is used in this study, because original bed moisture and/or moisture holding capacity values (required for the *maf* calorific value evaluation) have not been uniformly defined in the case of our samples.

Somewhat different, more or less complicated and rank dependant expressions are known for the GCV – NCV recalculations (Thomas, 1992; ISO standards 1170, 1928). In Slovenia, the GCV (*daf*) was routinely recalculated from the NCV (*ar*) according to the following formula (Žuža – pers. comm., 1996):

$$\begin{aligned} \text{GCV}_{\text{daf}} (\text{ccal/kg}) = & \\ = \frac{[\text{NCV}_{\text{ar}} (\text{ccal/kg}) + \text{M}_{\text{ar}} (\%) \times 6] \times 100}{\text{OM}_{\text{ar}} (\%)} + & \quad (1) \\ + \text{H}_{\text{daf}} (\%) \times 54 \text{ccal/kg} \end{aligned}$$

where M = moisture content, OM = combustible organic matter content and H = hydrogen content.

Coal-rank and coal-quality data in Tab. 3 are presented in this paper as additional information. Coal-quality data (RCMWRA, 2002) refer to whole reserves of coal in separate deposits. The GCV (*daf*) is recalculated according to Formula 1, taking into account an average H content of 5.4 %. Rank classes (based on GCV) and grade (based on ash (A) content at the *dry*

Age	COAL (whole deposit)	Coal rank			Coal quality							
		Class	GCV	Rr %	M	A	OM	NCV	S-tot		A	Grade
		(by GCV)	MJ/kg		mass %			MJ/kg	mass %		mass %	(by ash)
			daf basis		ar basis				ar basis	d basis	d basis	
PLIOCENE	Velenje field	Ortho - lignites	24,57	0,24	35,70	15,80	48,50	10,45	1,38	2,15	24,57	low
	Šoštanj field		25,31		34,20	23,30	42,50	9,40	1,40	2,13	35,41	very low
PONTIAN	Lendava		26,12	0,28	26,75	16,90	56,35	13,31	1,79	2,44	23,07	low
	Globoko		26,12	0,23	45,00	11,00	44,00	9,80	0,88	1,60	20,00	
PLIOCENE	Ilir. Bistrica		26,15		57,40	12,00	30,60	6,20	0,40	0,94	28,17	very low
MID MIOCENE	Krmelj		26,43	0,25	28,75	25,45	45,80	10,83	1,38	1,94	35,72	
PONTIAN	Kanižarica		26,56	0,32	26,00	23,00	51,00	12,30	1,95	2,64	31,08	
OLIGOCENE	Trbovlje		26,75	0,32	21,15	27,90	50,95	12,47	2,41	3,06	35,38	
	Zagorje		26,87	0,32	19,20	24,70	56,10	13,90	1,01	1,25	30,57	
	Ojstro		27,21		20,40	21,90	57,70	14,48	2,90	3,64	27,51	low
	Hrastnik		27,54	0,32	20,70	21,15	58,15	14,78	2,38	3,00	26,67	medium
	Dol	Meta-lignites	28,14		18,40	13,00	68,60	18,00	1,00	1,23	15,93	
MIO-PLIOC.	Kočevje		28,47		31,30	12,35	56,35	14,63	3,11	4,53	17,98	low
OLIGOCENE	Senovo		28,48	0,34	18,80	19,40	61,80	16,36	2,73	3,36	23,89	
	Laško		29,52	0,32	16,50	23,45	60,05	16,57	0,62	0,74	28,08	
PONTIAN	NE Slovenia		29,98		21,70	15,36	62,94	17,50	1,43	1,83	19,62	medium
OLIGOCENE	Liboje	Subbitum.	30,77		24,40	26,80	48,80	13,80	1,65	2,18	35,45	very low
PALEOGENE	Sečovelje	Para-bitum.	31,63	0,53	5,35	13,40	81,25	24,47	10,70	11,30	14,16	medium
OLIGOCENE	Zabukovica	?	33,56	0,41	17,20	28,90	53,90	17,00	1,16	1,40	34,90	very low

Tab. 3. Coal-quality (after RCMWRA, 2002) and coalification rank data for whole coal reserves in separate coal deposits.

basis) are termed after the ECE-UN (1998) classification. Rr % values are cited after Hamrla (1985/86). Coals are ranked according to their increasing GCV.

Geology, typology, coalification-rank, and elemental composition of the selected coals

Orle

The Orle anthracite (Rr: 4.5 % – Hamrla (1985/86); GCV (*daf*): 33.7 MJ/kg) represents the oldest coal treated in this study. It occurs in three lenticular beds, two up to 0.5 m and one up to 4 m but mostly 1 m thick, within 15 m thick sequence of bituminous mudstones and limestones of the Carnian age (the Rabelj beds) (Gostiša et al., 1984). Carnian biomicritic carbonates are interpreted as the lagoonal sediments, with C-org. contents between 0.14 and 2.51 %, and kerogen consisting mainly of terrestrial plant remains (Ogorelec et al., 1996). Their high maturity rank is ascertained by Rr values of 2.2–3.2 % (Ogorelec et al., 1996) and 3.0–4.0 % respectively (Rainer et al., 2002).

Characteristics of the Orle anthracite in Tab. 2 are cited after Češmiga (1959). Very low H/C and O/C ratios are clearly consistent with its high coalification rank. S (*db*) content of ca 2.4 % is consistent with the lagoonal biomicritic (alkaline) character of the coal-bearing strata.

Vremski Britof, Sečovlje, and Raša

The Vremski Britof, the Sečovlje and the Raša coals (the later in the territory of Croatia) have been studied in detail by Hamrla (1959). They are known as the extremely sulphur-rich coals (S-tot-*daf* up to 12 % !) lying within dark-coloured layers of lagoonal limestone, frequently rich in sapropelic organic matter. Coal-bearing freshwater limestone layers are interbedded within light-coloured brackish and marine limestones. All the three deposits comprise numerous coal beds (e.g. ca 40 in Raša), from some centimetres to 1 m, extremely to 2 m thick. Coal-bed thicknesses decrease upwards to younger strata.

The Vremski Britof coal layers that are developed in five coal-bearing horizons (each with several thin coal beds) belong to the Liburnian formation of the uppermost Cretaceous (Maastrichtian) to Paleocene age (Hamrla, 1959; Drobne, 1979; Hötzel &

Pavlovec, 1979; Jurkovšek et al., 1996). In a wider area, dark-coloured carbonates of this formation are characterized by 0.08–0.43 % of C-org content, with an exception of 0.74 % C-org at the Vremski Britof locality. Kerogen is composed of equal parts of terrestrial and amorphous matter (Ogorelec et al., 1996).

The Sečovlje and the Raša coals are developed within the Paleogene limestone layers above the Cretaceous rudist-rich limestone. They are known as the “karstic coals” (Hamrla, 1959). In Sečovlje, the lowermost (and the thickest) coal seam lies almost directly on the karstified Cretaceous limestone. The situation is similar in Raša. Lower Eocene i.e. Cuisian (or transitional Ilerdian to Cuisian) age of the Sečovlje (and correspondingly of the Raša) coal-bearing strata is ascertained by Drobne (1979) and assumed by Hamrla (1985/86, 1987).

Maturity rank of the Liburnian and Paleogene carbonates ranges between 0.55 and 1.5 % Rr (Rainer et al., 2002).

The highest coalification rank is ascertained for the Vremski Britof coal (Rr: 1.0–1.125 %) (Hamrla, 1959, 1985/86), i.e. meta-bituminous coal by the UCE-UN (1998) classification. Vitrinite reflectance of the Raša coal is 0.64 % (ortho-bituminous coal) and that of the Sečovlje coal 0.5–0.525 % (para-bituminous coal). The GCV (*daf*) is also the highest for the Vremski Britof coal (35.5 MJ/kg) and somewhat lower for the other two coals, 32.6 and 34.3 MJ/kg respectively.

The CHONS (*daf*) elemental data in Tab. 2 are adopted from Hamrla (1959; tab. 11). They are based on six samples from Sečovlje, six samples from Vremski Britof and “numerous published data after Dermelj (1955)” (Hamrla (1959; p.237) for Raša. Number of samples of the “extract from coal” and of the bitumens is not precisely known. Based on petrography and relatively high H/C ratio in respect to their coalification rank, the Sečovlje and the Raša coals are clearly sapropelic coals. As pointed out by Hamrla (1959), they are rich in bituminite (or “secondary resinite” in Stach et al., 1982; p.259). Considerable admixture of cutinite is supposed in the case of the Sečovlje coal. Sapropelic character of both coals slightly decreases upwards to younger coal seams (Hamrla, 1959). Petrographic type of the high-rank Vremski Britof coal can not be clearly ascertained from the CHO

data. However, it is humic according to its maceral composition (Hamrla, 1959).

To our opinion, relatively high calorific value of the Sečovelje and of the Raša coal is at least partly due to their sapropelic (hydrogen-rich) character. Namely, in combustion, the hydrogen-carbon combination releases more heat than the oxygen-carbon combination (Osborne 1988; p.24). Correspondingly, liptinite macerals are known as having somewhat higher specific calorific values than the other two maceral groups (Bustin et al., 1983; tab. 29 – after Kroger et al., 1957).

Zreče

Coals of the Zreče district in NE Slovenia, close NE of the Labot fault, are temporarily comparable to the Vremški Britof coals, but were deposited in much more contrasted tecto-sedimentary environments, from lagoonal within prevailing carbonate sedimentation to lacustrine within prevailing fluvial sedimentation. They have also been studied most thoroughly by Hamrla (1987), especially in the sense of their stratigraphic significance.

The Zreče ortho-bituminous coal seams are lenticular in shape, from 0.1 to 2 m thick. The lower-most Pucka seam, interpreted as the lagoonal coal, is deposited within the Upper Cretaceous (Maastrichtian) mudstone and marlstone layers, which transit upwards to the rudist-rich reef limestone (the Gosau formation). The Stranice seam is deposited within a platy dark limestone that forms the limnic base of the Paleogene (pre-Oligocene) strata. The younger three coal seams are also of the Paleogene (pre-Oligocene) age, but were deposited within periodic limnic environments in the frame of the prevailing fluvial environment characterized by medium to very coarse clastics.

According to petrographic composition, all the five coals are humic coals. The Rr value of the Upper Cretaceous Pucka seam is 0.795 %, and that of the four Paleogene coals from 0.74 to 0.785 % (Hamrla, 1985/86, 1987). Their GCV (*daf*) varies between 31.2 and 34.0 MJ/kg. Similar rank level for all the five coals (termed by Hamrla (1987) as the high-volatile bituminous rank) is mainly considered as the consequence of the Oligocene volcanic activity (the Karavanke and the Pohorje tonalites; see Fig. 1) and not so much of their burial history.

H/C atomic ratios for the five Upper Cretaceous and Paleogene coals in Tab. 2 re-

fer to the Hamrla's (1987) data. Because O/C ratios are not cited in the mentioned work this ratio is uniformly approximated to 0.035 in Tab. 2 from the rank-neighbouring (by C *daf* and Rr) Raša and the Vremški Britof coals.

It should be mentioned here, that one sub-bituminous coal layer (Rr: 0.41 %) of the Middle Miocene (Helvetian) age and even one ortho-lignite seam of the Plio-Quaternary age (Rr: 0.22 %) occur above the previously described pre-Neogene coals. Both seams are very thin (0.1–0.5 m), and are not included in Tab. 2 (no elemental data).

Upper Oligocene coals (from Trbnj Dol to Trbovlje in Tab. 1)

Upper Oligocene coals (plural is used due to different localities) in central Slovenia occur within the Pseudo-Socka beds (*in sensu* Jelen et al., 1992; Grad et al., 1996; Aničić et al. 2004; – formerly Socka beds) deposited in the W-E trending Tertiary synclines of the Sava folds (Petrascheck, 1926/29; Pleničar & Nosan, 1958, Kuščer, 1967; Buser, 1978, 1979; Cimerman, 1979; Premru, 1983 a,b; Placer, 1998 b). Deposition of Tertiary sediments from Oligocene onwards took place in the realm of the Pannonian basin. Coal genesis is best ascertained for the Zagorje-Trbovlje-Hrastnik coal (Kuščer, 1967; Uhan, 1991, Bruch, 1998; Hafner, 2000; Bechtel et al., 2004), and can be generalized to other coals as well. Coal deposits from Motnik to Pečovnik (Fig. 1) occur in the Motnik syncline, those from Zagorje to Trobni Dol in the Laško syncline and the Senovo coal deposit in the Senovo syncline.

Tectonic structure of the Oligocene coal deposits is moderately to strongly tectonically deformed, also with overthrust strata.

It is typical that only one regionally more or less synchronous coal-prevailing bedset (*in sensu* Reineck & Singh, 1980; fig. 153), at different sites from some metres to 25 m thick, occurs in all deposits. In the coal-prevailing bedsets, coal is interlayered by thinner than coal-beds inorganic partings, consisting mainly of claystones, marls and tuffs. Where the partings are only cm to dm thick, a term “coal seam” is used instead of a bedset. Tuff interlayers, especially characteristic for coals from Zagorje to Trobni Dol (Fig. 1), originate from the well known Upper Oligocene to Lower Miocene volcan-

ism. Its main centre was the Smrekovec region (Kralj Polona, 1996). Some smaller volcanic centres existed as well, one of them in the Trobni Dol district (Hamrla, 1985/86; Grad et al., 1996, Kralj Polona, 1998). Sequentially and regionally variable composition of volcanoclastics is andesitic to rhyolitic (Kralj Polona, 1996, 1998). Absolute age of the tuff interlayers in the locality of the Trbovlje – Neža profile has been ascertained to 25 ± 1 Ma (Odin et al., 1994). As a within-peat sediment, tuff material was presumably important as a nutrient supplier for vegetation growth. Also important were carbonate-rich partings (Hafner, 2000), giving rise to an alkaline character of the peat-water geochemistry.

Peat formation took place within freshwater eutrophic topogenous mires with luxuriant and in-species diversified vegetation. Resulting coals are predominantly of the humic type, most often with upwards decreasing mineral-matter contents and upward increasing degree of gelification. Peat accumulation ended due to drowning and establishment of a freshwater lake. In areas of relatively minor drowning, sapropelite was formed above the humic peat. In other areas, humic coal is sharply overlain by marl. Freshwater marl transits upwards to the brackish variety (with fishes), and later-on into marine clay of the Kiscell type.

In the Trbovlje area (Neža profile in Tab. 2), geochemical segmentation of the coal seam into four units by Uhan (1991) is confirmed by floristic (Jelen; In: Bechtel et al., 2004) and maceral (Markić; In: Bechtel et al., 2004) assemblages. *Taxodiaceae-Cupressaceae-Palmae* (TCP) flora is characteristic for the lower part of the coal seam, whereas *Myricaceae-Polypodiaceae* (MP) and later-on *Fagaceae* (F) flora is characteristic for its upper part. Freshwater diatoms (Horvat; In: Jelen et al., 1988/89), sponge spicules and *Botryococcus* algae are found in the upper part as well. In summary, Sachsenhofer (In: Bechtel et al., 2004) interpreted the Trbovlje coal seam to be formed within the following depositional environments from the bottom to the top: wet forest swamp (TCP flora and high tissue preservation petrographic index), bush moor (MP flora), reed moor close to alkaline lake (dwarf plants and high gelification index) and lake (characterized by *Botryococcus* algae and sponge spicules). In the Trbovlje-

Lopata profile (Tab. 2), coal is divided into even five units.

In spite of their freshwater character, the Upper Oligocene coals are relatively sulphur-rich, with S-tot (*db*) contents between ca 1 % (Laško and Zabukovica) and 4.5 % (Motnik). Such sulphur contents indicate alkaline peat-forming environments that can be explained by the prevailing carbonate composition of the basement and the hinterland areas, as well as by carbonate-rich partings.

According to data in Tab. 2, GCV (*d.a.f*) of the Upper Oligocene coals varies between ca 26.9 MJ/kg (Trbovlje-Neža and Lopata) and 29.75 ± 0.07 MJ/kg (Motnik and Trobni Dol). After data in Tab 3, this variability ranges even between 26.7 MJ/kg (Trbovlje) and 33.6 MJ/kg (Zabukovica). Vitrinite reflectance (*Rr*) is the highest for the Trobni Dol coal (0.60 %) and coals from Motnik (0.48 %) eastwards to Pečovnik ("Štore": 0.41 %), whereas it varies between 0.30 and 0.34 % for the rest of coals (Hamrla, 1985/86). In regard to the GCV (*daf*) data from both tables, coals from Trbovlje Laško, Senovo, Hrastnik and Zagorje are ortho- to meta-lignites according to the ECE-UN (1998) classification. More ambiguous is the classification for the Liboje coal, falling into classes between ortho-lignite and sub-bituminous coal, and for the Pečovnik, Zabukovica, Motnik and the Trobni Dol coals, falling into classes from meta-lignites to para-bituminous coals. It is more clearly to designate these coals as the "Hartbraunkohlen" (prevailingly "Glanz") according to the German classification.

Somewhat different conclusions can be attained from the C (*daf*) contents. They vary between 66.5 and 69.5 % for the Trbovlje, Liboje and the Senovo coals, therefore indicating their meta-lignite to sub-bituminous coal rank. C (*daf*) contents for the rest of coals exceed 70 % (with a slight exception of the Trobni Dol coal), and can be classified as sub-bituminous coals, the Motnik coal even as para-bituminous coal.

The highest vitrinite reflectance of the Trobni Dol coal is interpreted by thermal influence due to volcanism in the vicinity (Hamrla, 1985/86), which was rhyolitic in composition, with deposition of volcanoclastics in a marine environment (Kralj Polona, 1998). The volcanic activity was somewhat younger than the initial coal formation. An older explanation was given by Petra-

scheck 1926/29 (Grad et al. 1996) who pointed out an influence of marine environment after the peat formation solely. In the case of Motnik, an increased coal-rank may be explained by the large southward overthrust of the Savinja Alps (Mesozoic carbonates) over Oligocene and Miocene sediments as interpreted by Premru (1983 a, 1983 b)

Elemental CHONS (*daf*) data in Tab. 2 are taken from Germovšek (1963), Uhan (1991) and Grad et al. (1996). The lowest H/C and O/C ratios are characteristic for the Motnik coal and are consistent with its relatively high rank, whereas only low H/C ratio is consistent with the relatively high rank of the Trobni Dol coal. The highest O/C ratio is ascertained for the lowest rank Trbovlje-Neža and Lopata coals. In their uppermost part (characterized by algae, spicules of sponges and diatoms) an increased H/C ratio is not detected.

Krmelj

In the Krmelj depression, which is only 4 km long, 1 km wide, and surrounded by the Mesozoic carbonates, three up to 7 m thick lenticular coal seams are deposited within Middle Miocene (Tortonian) freshwater clayey sediments with sandy and gravely intercalations (Češmiga, 1959; Pleničar & Premru, 1970; Pleničar et al., 1975;). Coal seams are composed of low-grade coal and shaly coal partings (coal/shale bedsets). They lie at some localities very close to the Mesozoic carbonates. Freshwater coal-bearing sequence is up to 120 m thick. It is covered by marine marls, limestones and calcarenite.

Sedimentary fill in the Krmelj depression is often compared to that in the Senovo area. It is supposed that both areas were a unified basin during the Miocene or even Oligo-Miocene time (Pleničar & Premru, 1970), with shifting areas of peat formation. Namely, only one coal seam of the Upper Oligocene age occurs in the Senovo region and no coal is known from the Miocene strata. The Senovo coal is comparable to the already described Trbovlje-Hrastnik and related coals. In Krmelj, Oligocene sediments were not deposited, or have been eroded.

Low vitrinite reflectance (R_r : 0.25 %) (Hamrla, 1985/86), and low calorific value (GCV *daf*: 26.45 MJ/kg) (Germovšek, 1963; RCMWRA, 2002) classify the Krmelj coal as the ortho-lignite. Sulphur content of nearly 3 % (*db*) indicates an alkaline environment

of the peat formation due to carbonate geological setting of the hinterland.

Kočevje and Kanižarica

The Kočevje and the Kanižarica coal basins are typical freshwater intermontane basins in the territory of External Dinarides, both of relatively small dimensions (1.5 and 9 km²) with four to six main coal seams within lacustrine clayey and marly sediments intercalated by fluvial sands. Coal-bearing sedimentary fill of the Kočevje basin was formed in the period from Middle Miocene to Pliocene and Villafranchian (Dozet, 1983), whereas that of the Kanižarica basin during the Pontian stage (uppermost Miocene, formerly also lower Pliocene) (Bukovac et al., 1983 a, b). In both basins, the preserved thicknesses of Neogene sediments amount to 200–300 m. Thicknesses of coal seams in the Kočevje area vary from 1 to 22 m (Dozet, 1983). To our opinion, such a variability can be explained as a consequence of very differentiated thicknesses of original peat, its differential compaction due to local floristic differences (e.g. tree-dense areas contrasted by dwarf-plants areas), and as a consequence of frequent non-coaly and mineral-rich coal partings. The Kanižarica coal is somewhat more uniform, occurring in four main seams, up to 6 m thick (Markič, 1995).

The Kočevje strata are moderately deformed as a syncline, whereas in Kanižarica, they are horizontal in the centre of the basin but very tilted along the periphery (dips to 70°) due to very young gravitational tectonic activity.

Petrography of the Kočevje coal has been studied by Hamrla (In: Jelenc et al., 1956) and of the Kanižarica coal by Žepič & Markič (1992). Coals of both deposits are macroscopically very heterogeneous, from dark brownish-black, also brilliant (fine detrital gelified and vitrite-rich varieties), to brown xylite-rich varieties. Also frequent are mineral-rich varieties. Resinous xylite is attributed mostly to conifers, whereas brilliant vitrite bands to foliage plants (Hamrla; In: Jelenc et al., 1956). They are composed of typical low-rank macerals, mainly of the huminite group. Abundant is resinite-rich textinite.

Available chemical and vitrinite reflectance data classify humic coals from the both deposits as ortho- to meta-lignites, with characteristically upwards (to younger coal seams) decreasing rank. C (*daf*) con-

tents of vitrite-rich concentrates (fraction $< 1.4 \text{ g/cm}^3$) were analysed for the lower four Kočevje seams (Babšek; In: Jelenc et al., 1956). They decrease upwards from 69.2 to 64.5 % (meta-lignite rank) and are comparable to the average C (*daf*) content of the Kočevje coals (65.35 %) as well as to the average C (*daf*) content of the Kanižarica coals (65.25 %) as reported by Germovšek (1963) (Tab. 2). Meta-lignite rank of the Kočevje coals is confirmed by the GCV (*daf*) of 28.5 MJ/kg as cited in RCMWRA, 2002) (Tab. 3). However, somewhat lower GCV (*daf*) for these coals is cited in Germovšek (1963), i.e. ca 27 MJ/kg (Tab. 2), therefore an ortho-lignite rank. In Kanižarica, GCV (*daf*) of coals decreases upwards from ca 27 MJ/kg to 25.5 MJ/kg (Tab. 2), therefore indicating the ortho-lignite rank. The only vitrinite reflectance information exists for the lowermost coal in Kanižarica (Rr: 0.32 %; Hamrla, 1985/86) - i.e. ortho- to meta-lignite rank transition.

Significant coal-rank decrease toward younger coals in total sedimentary sequences of Kanižarica and Kočevje, which are only ca 250 m thick, can be attributed to different peat forming floral assemblages that were differently affected by humification-vitrinitization processes (*in sensu* Diessel, 1992), and to presumably variable heat flows due to post peat/coal formation.

Due to their position in the intermontane basins within Cretaceous carbonates, coals from the both deposits are sulphur-rich, with S-tot (*db*) contents of about 4 %. They are also known as the coals of a considerably increased radioactivity.

Coals of NE Slovenia (Lendava, Moravci and Sv. Jurij)

The best explored coal deposit in the territory of NE Slovenia (Pannonian basin) is the Lendava one (Marin et al., 1989a). In the wider area, along moderate slopes of the Ormož-Selnica anticline, several coal seams at different localities have been exploited in the past (Pleničar, 1954; Takšić, 1967; Mioč & Marković, 1998 a,b). Also known are coals in deep boreholes across the whole territory of NE Slovenia (Marin et al., 1992). All these coals are typically paralic, of the Pontian age (according to very extensive paleontological investigations of the Ostracoda microfauna by Živadina Škerlj between 1980 and 1990; numerous internal reports at the Geol. Surv of Slovenia).

Coal-bearing strata geometry is very simple, characterized by horizontal to moderately tilted stratification.

The Lendava coal-bearing sedimentary sequence consists of alternating layers of deltaic marls and sands intercalated by thin coal beds. The later are grouped into three coal-bearing freshwater units, each several tens of meters thick, and several tens of meters apart. Non-coal-bearing sedimentary sequences are brackish. Only three coal seams are 1 to 2 m thick. The lowermost and the uppermost coal seam are vertically ca 100 m apart.

Due to gelification and presumably similar original floristic assemblages, the Lendava coals are petrographically homogeneous - i.e. banded to massive, and brownish-black to black in colour. Maceral composition is humic, with few liptinitic and inertinitic components (Markič, 1983). An average GCV (*daf*) of all the three seams is 26.1 MJ/kg (as summarized after RCMWRA, 2002) (Tab. 3). Vitrinite reflectance is in the range of 0.25–0.28 % Rr (Hamrla, 1985/86; Jelen, 1985/86). Both values classify the Lendava coal as the ortho-lignite. However, GCV (*daf*) of the three samples in Tab. 2 is higher than 28 MJ/kg, therefore indicating the meta-lignite rank. The meta-lignite rank is also attributed to the Sv. Jurij and the Moravci coals (Tab. 2) as well as to the coals of NE Slovenia in general (Tab. 3), all lying in greater depths than the Lendava coals.

S-tot (*db*) contents of the Lendava and the NE Slovenia coals range mostly from 1.8 to 2.4 % (recalculated from the RCMWRA, 2002 data in Tab. 3) but are significantly higher in the case of samples in Tab. 2 (3–4 %).

In addition to the elemental CHO data for coals in Tab. 2, the reader is referred to Jelen (1985/86), who regionally studied organic parameters of the NE Slovenia Tertiary sediments. According to him, H/C atomic ratios of kerogen of the the Pontian clay, organic clay and marl (well 3 – Moravci) range between 1.10 and 1.19 and the O/C ratios between 0.25 and 0.30. The former are slightly higher in comparison to coals.

It should be pointed out that the whole territory of NE Slovenia represents an area of relatively high heat flow density, greater than 100 mW/m² (Rajver & Ravnik, 2002). By the same authors, one of the highest temperature/depth gradients is ascertained for

the Lendava district, i.e. 3.5–4° C/100 m up to the depth of 2000 m. It is presumed, that the geothermal pattern was similar also in the Pontian period and enhanced the coalification/maturation transformations of the organic matter.

Globoko

The Globoko coal deposit is of the same age and of the same type as the Lendava one, i.e. Pontian and paralic, in the realm of the western margin of the Pannonian basin. Also characteristic is alternation of freshwater coal-bearing and brackish water non coal-bearing sedimentary units. But, coal in Globoko is a typical ortho-lignite. It is low gelified and xylite-rich. Up to twenty lignite beds, from some centimetres to 2 m thick, are grouped into three lignite-bearing (freshwater) units (Marin et al., 1989b; Markič & Rokavec, 2002). The lower and the middle unit are 10 to 20 m thick, whereas the upper one up to 65 m. Brackish sediments in between are of the similar thicknesses. In comparison to Lendava, the Globoko strata are more deformed (dips: 0–25° toward S), also reversely faulted due to S–N stresses characteristic for the genesis of the Sava folds. Lower rank of the Globoko coals in comparison to the Lendava and the NE Slovenia coals is generally explained by the lower heat flow density in the case of the Globoko area, being in an order of 60 mW/m² (Rajver & Ravnik, 2002).

The most important lignite seam is the uppermost one ("seam 2.3") in the middle lignite-bearing unit. It is 2.2 m thick. Underlying two seams ("seams 2.2 and 2.1") are mostly only 1 m thick. Coal seams of other two units reach greater than 1 m thicknesses only locally.

The Globoko lignites are petrographically uniform. This indicates that peat forming vegetation did not change considerably by time and also not spatially. Depth related rank differences are not supposed. Lignites differ mostly only in their mineral-matter content, which generally decreases toward upper seams. In this context, elemental composition of the two seams in Tab. 2 is assumed to be representative enough for the Globoko lignites in general.

The ortho-lignite rank of the Globoko lignites is characterized by the GCV (*daf*) of ca 26–27 MJ/kg (Tab. 2 and 3) and by the *Rr* value of 0.23 % (Hamrla, 1985/86). S-tot (*db*) content varies from 1 to 2 %.

Slightly less alkaline environment is supposed in comparison to the Lendava and the NE Slovenia coals. This can be explained by fluvial influence, ascertained by sandy bodies (inflows) between lignite seams as well as directly above them in the case of the uppermost lignites of the middle and of the upper lignite-bearing unit.

Velenje

The Velenje basin is a typical pull-apart intermontane lacustrine basin of the Pliocene to Quaternary age. It was formed by a polyphase dextral strike-slip tectonical activity related to the Periadriatic lineament movement. It is filled by more than 1000 m thick sequence of fluvial to lacustrine sediments, with an up to 100 m (extremely to 160 m) thick ortho-lignite seam approximately in the middle (Brezigar 1985/86; Brezigar et al. 1987; Vrabec, 1999). Basement and the hinterland of the basin is built up of the Mesozoic carbonates to the north and of the Oligocene andesitic tuffs to the south.

Vegetation growth and peat accumulation was developed in a topogenous, eutrophic, and Ca-rich (alkaline) lacustrine depositional environment. Fluvial influence was more or less important at the initial stage of the peat formation and along the basin periphery. The whole lignite seam is separated into the following vegetation environments from the bottom to the top: wet forest swamp – dry forest swamp – bush moor – wet forest swamp – fen (Markič & Sachsenhofer, 1997). Mineral matter content decreases upwards, whereas gelification increases upwards. According to palynological data of Šercelj (1968, 1985/86) and Bruch (in Hemleben et al., 2000), *Taxodium*, *Sequoia*, *Osmunda* and *Tsuga* floristic species were the most important contributors to the forest and bush vegetation. In addition, biomarker investigations have been carried out by Bechtel et al. (2003), and stable isotope studies by Pezdič et al. (1998), Bechtel et al. (2003), and Kanduč et al. (2005).

Typical humic ortho-lignite character of the Velenje lignite is reflected by its petrographic appearance and rank parameters. It consists of xylitic fragments within fine detrital matrix, and variable quantities of fuzite and mineral impurities. Ratios between pure xylite and fine detrital matrix, which is gelified to different degrees, are

classified into ten classes (Markič et al., 2001). Microscopically, it consists of 85–95 % of the huminite macerals. Liptinite (<10 %) and inertinite (< 5 %) components are enriched in the lower ash-rich part of the seam (Markič & Sachsenhofer, 1997). The GCV (*d.a.f*) of the Velenje lignite as a whole (the Velenje and the Šoštanj field) is reported to be ca 25 MJ/kg (RCMWRA, 2002) (Tab. 3). Its vitrinite reflectance *R_r* is estimated by Hamrla (1985/86) to 0.24 %. S-tot (*db*) content through the seam varies mostly from 2 to 3 % (Markič & Sachsenhofer, 1997).

Elemental composition in Tab. 2 refers to typical lithotype varieties, namely to pure xylite (X), mixture of xylitic fragments and fine detrital matrix (XD-fD), gelified and strongly gelified fine detrital matrix (GfD, fdG), and to mineral (calcite)-rich fine detrital matrix (MfD, fDM). Due to lack of calorific value data for these samples, calorific values are added for similar lithotype varieties from different samples. The later vary in GCV (*d.a.f*) from ca 24 MJ/kg (X) to 26.5 MJ/kg (GfD–fdG). Based on numerous samples it can be clearly concluded that the effect of coalification is higher in the case of gelified fine detrital matrix than in the case of woody xylite. Among others, this conclusion agrees with the Saturated hydrocarbons / Aromatic hydrocarbons versus gelification

diagram after Bechtel et al. (2003; Fig. 5) showing decreasing Sat.HC / Arom.HC ratio toward gelified macerals.

Discussion and Conclusions

Atomic H/C versus O/C ratios of the selected coals after data in Tab. 2 are graphically presented in Fig. 2 and Fig. 3. In Fig. 2, the liptinite, cutinite, huminite – vitrinite and inertinite lines (coalification paths) after van Krevelen are plotted together with H/C and O/C atomic ratios. For a better insight, names of coals are cited in Fig. 3.

The GCV (*daf*) variability of the coals, comprising all data from Tab. 2, is plotted in Fig. 4. In Fig. 5 are plotted only those GCV data that are paired with the CHONS data. An exception is made for the Velenje lignite because no paired data exist for it. For additional information, the GCV (*daf*) ranking of the Slovenian coals on the basis of data referring to the whole reserves (RCMWRA, 2002) as cited in Tab. 3 is plotted in Fig. 6. Discrepancies in ranking of coals – if ranks of the same coals in Tab. 2 and Tab. 3 are compared – are due to different nature of data acquisition and due to heterogeneity of coals, which are mostly low-rank and of low to very low grade (ash (*db*))

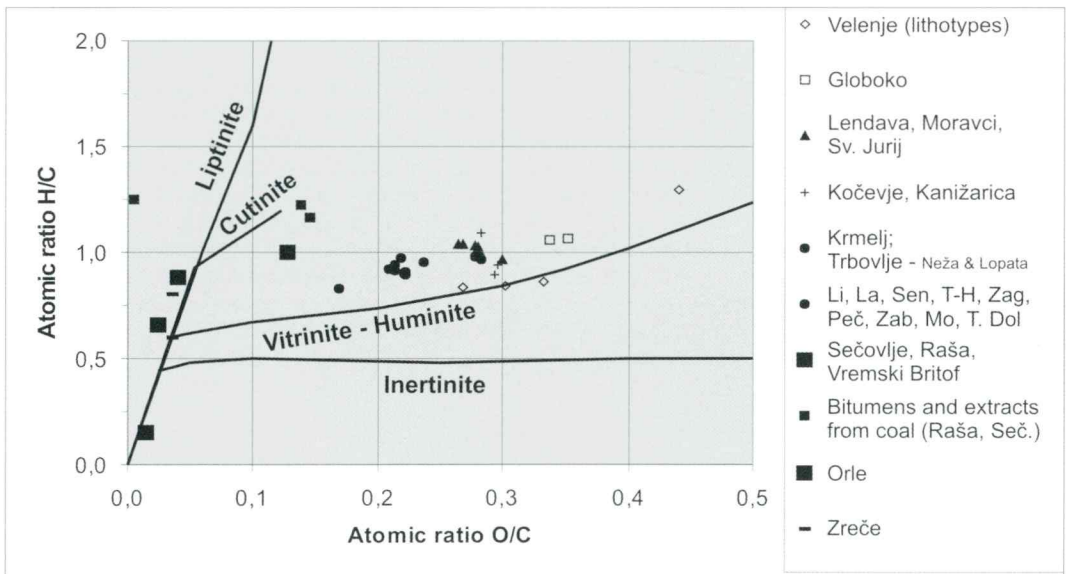


Fig. 2. H/C versus (O/C atomic ratios for the selected coals; shown are coalification paths for liptinite (and cutinite), huminite-vitrinite and inertinite as published by Bustin et al. (1983) after Van Krevelen (1961; In: 1981). For abbreviations in the legend see Fig.3.

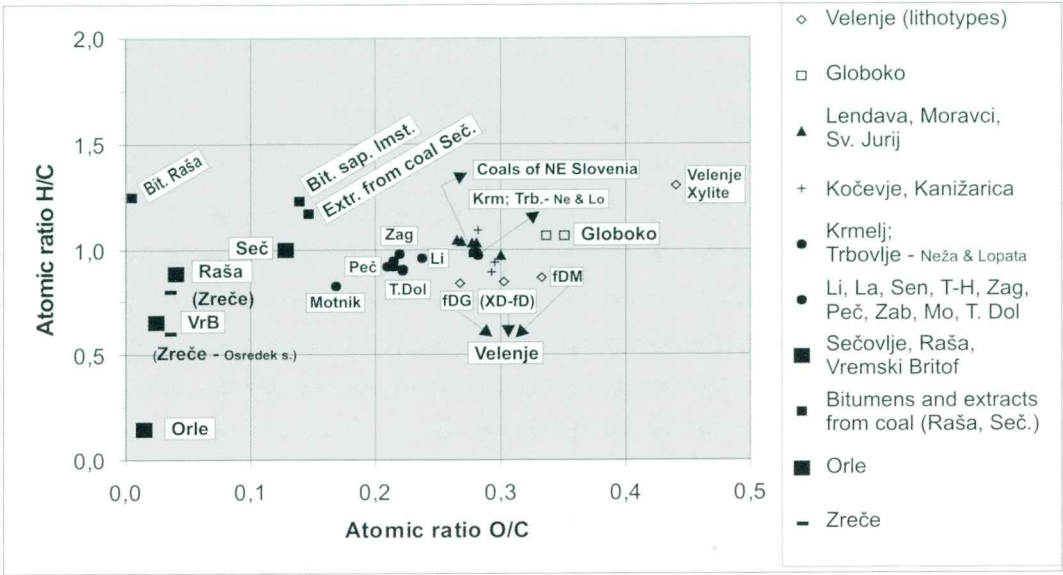


Fig. 3. The same H/C versus (O/C atomic ratios as in Fig. 2 – cited are localities. Where not fully written, abbreviated names for coals are the following: Li – Liboje; La – Laško; Sen – Senovo; T-H – Trbovlje–Hrastnik; Zag – Zagorje; Peč – Pečovnik; Zab – Zabukovica; Mo – Motnik; T. Dol – Trobni Dol.; Seč – Sečovlje.

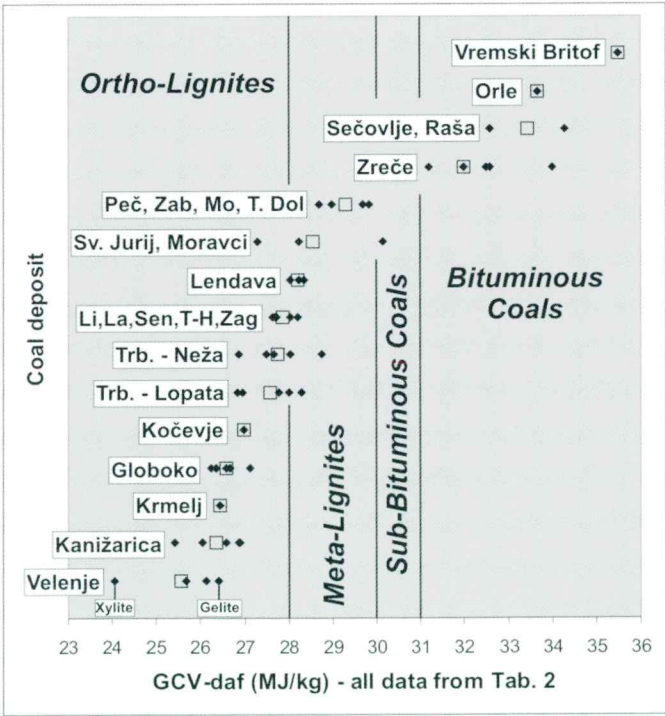


Fig. 4. Ranking of coals by the Gross calorific values (GCV) at the dry, ash-free basis (*daf*); empty squares are averages; included are all the GCV data from Tab. 2. For abbreviations see Fig. 3.

contents mostly above 20 %). Correlation between the rank parameters GCV (*daf*) and the carbon content C (*daf*) is given in

Fig. 7. Relatively poor correlation between the two parameters ($r^2 = 0.76$) is attributed to the fact, that C (*daf*) content refers to the

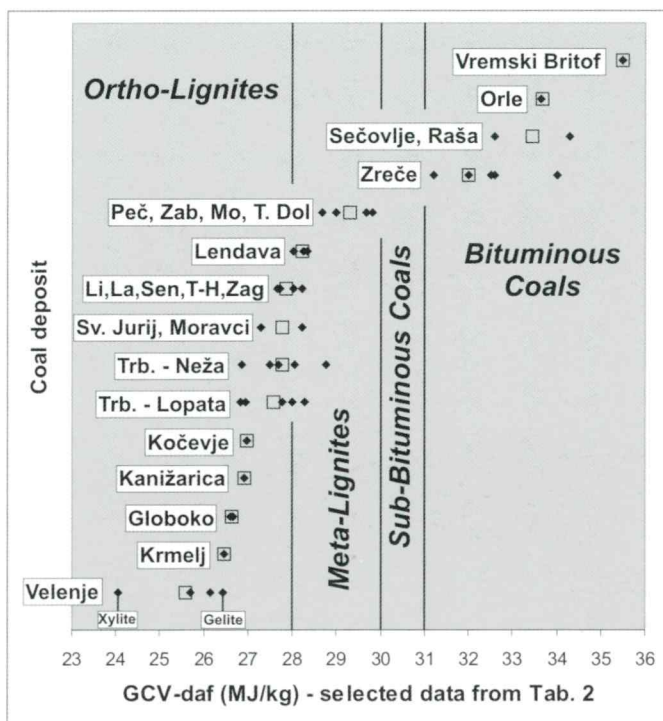


Fig. 5.
Ranking of coals by the Gross calorific values (GCV) at the dry, ash-free basis (*daf*); empty squares are averages; included are only those GCV data from Tab. 2 that are paired with the elemental CHONS data.
An exception is made for Velenje. For abbreviations see Fig. 3.

“whole coal” analytics – and not to pure organic matter or “vitrinite”. Decreasing O/C and H/C atomic ratios with increasing rank (by GCV) are shown in Fig. 8 and Fig. 9 respectively.

Majority of the selected coals belongs to the humic coal type (Fig. 2 and 3). Only the Sečovlje and the Raša coals are clearly sapropelic coals. Inertinitic macerals are well known from all the selected coals, but in so low contents that they do not shift a bulk CHO chemical composition toward the inertinite line in the van Krevelen diagram (Fig. 2).

The lowest-rank coals, namely xylite from Velenje and xylite-rich ortho-lignite from Globoko are characterized by the highest H/C and O/C ratios (Fig. 2 and 3). H/C and O/C ratios for the gelified fine detrital (GfD and fDG) and xylo-detrital (XD-fD) lithotype varieties of the Velenje lignite fit well to the huminite-vitrinite line (Fig. 2). The lowest O/C ratio of the strongly gelified fine detrital (fDG) lignite from Velenje is consistent with the relatively highest degree of coalification of this lithotype (as observed by microscopy). Namely, as thoroughly discussed by Diessel (1992), fine detrital humic organic matter is earlier

and more easily affected by the biochemical coalification processes than the higher resistant woody (xylitic) fragments. Highly gelified components of low-rank coals known as eu-ulminite and densinite, which are characterized by relatively low H/C and O/C ratios, are often treated as to be “pre-coalified” (e.g. Naeth et al., 2004).

Interesting is difference in H/C ratio between the petrographically comparable Globoko xylite-rich lignite and the Velenje xylo-detrital (XD-fD) lignite. Relatively higher H/C ratio of the Globoko lignite can be explained by more anaerobic conditions (and higher content of hydrogen-rich liptinitic/exinitic components), consistent with its paralic peat-forming environment, whereas the Velenje peat accumulated in an intermountain environment, which was more aerobic due to fluvial influence.

An increased H/C ratio in comparison to the van Krevelen’s huminite-vitrinite line (Fig. 2) is more or less characteristic for all the Pontian, Mio-Pliocene and the Upper Oligocene humic coals (Tab. 2). Among them, the highest H/C ratios are evident for the Pontian paralic meta-lignites of NE Slovenia (Lendava, Moravci and Sv. Jurij), and are comparable to the H/C ratio of the Globoko

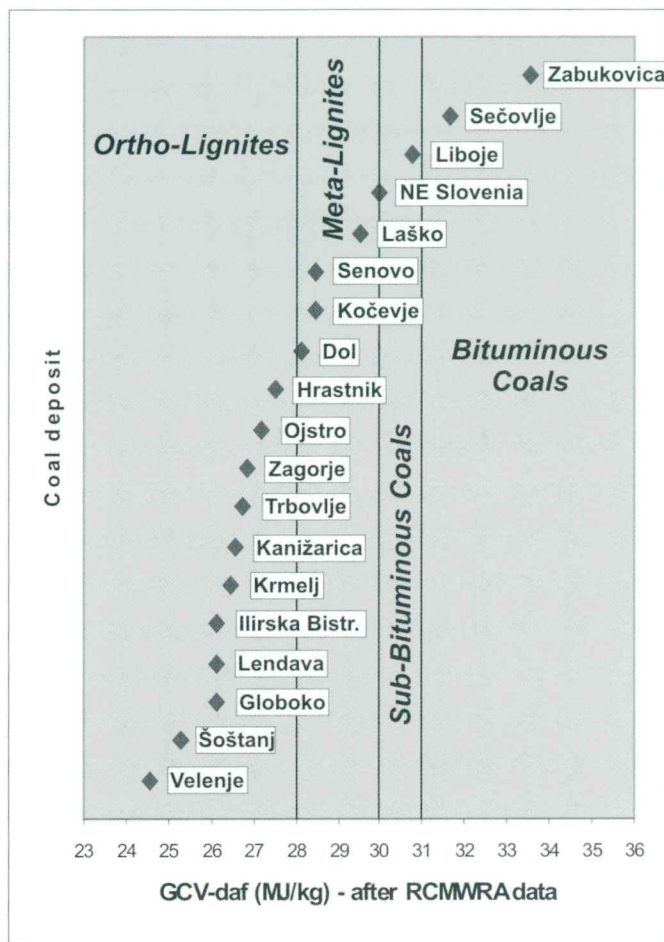


Fig. 6.
Ranking of coals by the GCV (*daf*)
on the basis of data from RCMWRA
(2002) referring to the whole coal
reserves in various deposits.

ortho-lignite of the same age and the same (paralic) environment. Difference in rank between the NE Slovenia and the Globoko coals is expressed by considerably lower O/C ratio in the case of the NE Slovenia coals. Taking into account a thermal influence as a considerable factor of the enhanced coalification of the NE Slovenia meta-lignites it can be concluded, that thermally influenced depolymerization during the coalification process affected more severely the O-C than the H-C molecular bonding. From this statement it becomes more logic, why the O/C versus GCV correlation ($r^2 = 0.85$) is better than the H/C versus GCV correlation ($r^2 = 0.54$) (Fig. 8 and 9).

The Upper Oligocene humic coals, in general best designated as "hard brown coals", are characterized by clearly lower O/C ratios in comparison to the younger coals of the ortho- and meta-lignite rank.

The lowest O/C ratio is characteristic for the relatively high-rank Motnik coal, and the highest O/C ratios are evident for the relatively low-rank Krmelj and Trbovlje-Neža and Lopata coals. Similarly, H/C ratios decrease by increasing rank as well. Correspondingly to rank, they are somewhat lower than the H/C ratios of the NE Slovenia and Globoko lignites. Normal decrease in H/C and O/C ratios by increasing rank from the Globoko and the NE Slovenia coals of the Pontian age toward the Upper Oligocene coals of the Sava folds is interpreted by the fact, that all these coals origin from similar peat forming environments, i.e. paralic, eutrophic, topogenous mires along the Pannonian basin margins – nevertheless of two types – the deltaic one (thin coal beds in NE Slovenia and Globoko) and the coastal plain one (Upper Oligocene thick coals); (according to terminology in Bustin

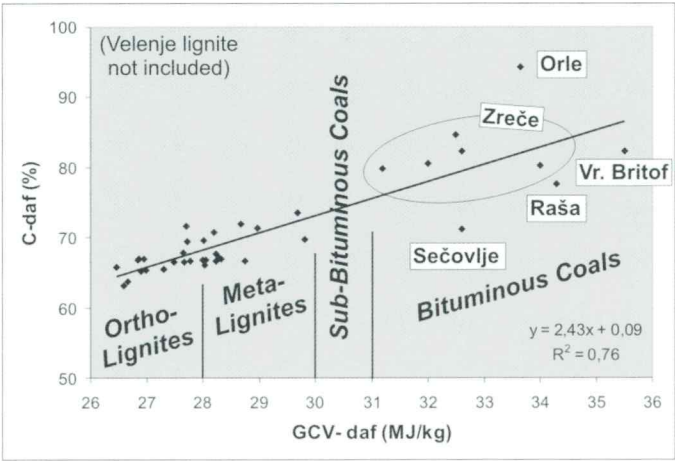


Fig. 7.
Correlation between the GCV (*daf*) and C (*daf*) content – after data in Tab. 2.

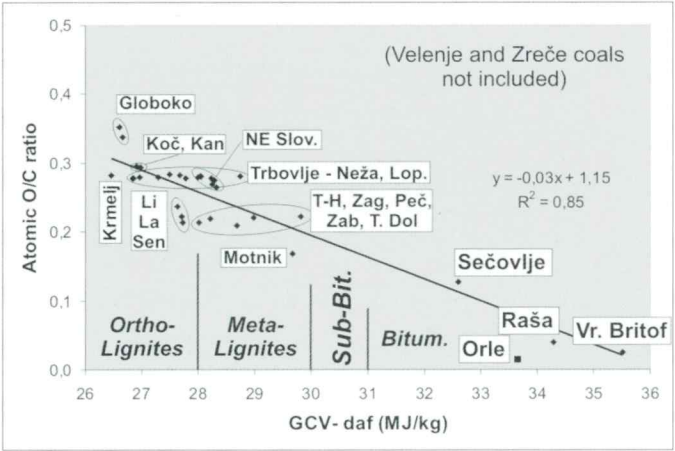


Fig. 8.
Correlation between the GCV (*daf*) and atomic O/C ratio – after data in Tab. 2. For abbreviations see Fig. 3, and, Koč – Kočevje; Kan – Kanižarica.

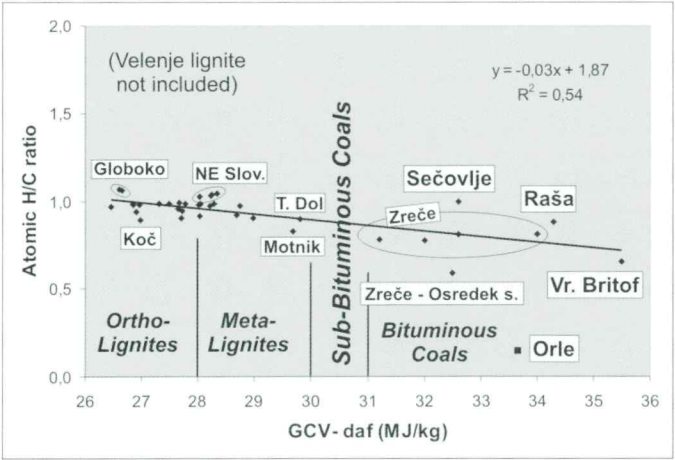


Fig. 9.
Correlation between the GCV (*daf*) and atomic H/C ratio – after data in Tab. 2.

et al., 1983). Somewhat higher H/C ratio of the paralic Upper Oligocene hard brown coals in relation to the intermontane limnic Velenje lignite (prevalingly composed of the XD-fD lithotype variety) is explained by higher anaerobiosis in the case of the former coals. More aerobic conditions in the case of the Velenje lignite, due to fluvial influence, water table changes, and forest fires, are reflected in relatively frequent occurrences of inertinitic components (fuzinite, textinite B and semidegradofusinite).

H/C ratios of the Sečovlje para-bituminous (Rr: 0.51 %) and of the Raša ortho-bituminous coals (Rr: 0.64 %), deposited within Paleogene limestones, are similar as for the majority of the lower rank Upper Oligocene coals, but their O/C ratio is considerably lower (Fig. 2 and 3). Relatively high H/C ratio in respect to their rank classifies both coals as the clearly sapropelic coals. Considerable admixture of cutinite is supposed for the Sečovlje coal. Sapropelic character of the Sečovlje and of the Raša coals (both very rich in S content) is consistent with their anaerobic lagoonal depositional environment, rich in dissolved sulphate and sapropelic organic matter. In Fig. 2 and 3, H/C and O/C ratios for the "asphalt bitumen", "extract from coal" and "bitumen from sapropelic limestone" are given for an additional comparison.

The Vremški Britof coal (Rr: 1.1 %; also S rich,) of the Uppermost Cretaceous to Paleocene age is classified as the meta-bituminous coal. By Hamrla (1959), it is micro-petrographically characterized as the humic coal of the lagoonal environment.

By far the lowest H/C and O/C ratio is ascertained for the Orle anthracite of the Carnian age, being characterized by the C (daf) content of 94 % Rr value of 4.5 % and the GCV (daf) of 33.66 MJ/kg.

The study revealed, in spite of the constraints referring to a relatively poor database, that CHONS characterization provides a good tool for coal determination in relation to both, petrographic type and coalification rank. It is very recommended that this type of analytics would be applied more frequently in the future.

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