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# Petrological and geochemical characterization of Ge-bearing coals from the eastern Rhodopes, Bulgaria

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**ABSTRACT:** The coals from Pchelarovo and Vulce Pole are perhydrogenated coals showing high sulphur content (3.2 - 6.2 wt%) and significant Ga and Ge contents (0 - 480 ppm) in organic matter (OM). The coals from Medenbuk could be perhydrogenated coals modified by weathering processes. They show low sulphur content (1.5 wt%), high homogeneous Ge contents in OM (~2500 ppm) and an unusual enrichment in Ge (up to 0.8 wt%) and V (2.8 wt%) in weathered zones of framboidal pyrite. Sulphur isotopic study of pyrite and organic sulphur provides evidence of bacterial reduction of dominantly seawater sulphates. However taking account the geological context of the three basins, the introduction of volcanic fluids in the basins of Pchelarovo and Vulce Pole during their formation cannot be excluded.

**KEYWORDS:** coal geochemistry, germanium, sulphur isotopes, eastern Rhodopes, Bulgaria

## 1 INTRODUCTION

Coal is the main energy resource in Bulgaria and is the subject of numerous investigations on metal contents on the primary resource and on ashes after combustion in power stations. Coals from Pchelarovo, Vulce Pole and Medenbuk were previously studied for their Ge content (Eskenazy, 1996). Investigations on sulfur content and distribution, and on relationships between organic matter and metals are good indicators of the geological deposition. This abstract presents preliminary petrological and geochemical data of coals from the three coal deposits, in the aim to understand their conditions of deposition.

## 2 GEOLOGICAL SETTING

The Pchelarovo, Vulce Pole and Medenbuk coal deposits are located in the Eastern Rhodopes, resulting from the continental Macedonian - Rhodope - North-Aegean magmatic arc (Harkovska et al., 1998), formed after the Late Cretaceous-Palaeocene collision of the Serbo-macedonian and Rhodopes Massifs with the Pelagonian microplate. Coal-bearing sediments were deposited within intra-orogenic ex-

tensional basins during the final stage of continental collision in the Paleogene.

### 2.1 Pchelarovo

The Pchelarovo coal deposit is located about 20 km north of Kardzhali. Coal-sediments belong to the Pchelarovo depression quite close to the southeast of the Borovitsa volcanic area. The basement of the basin is composed of immature conglomerates and sandstones, reworking the metamorphic basement (Central Rhodopean dome and metamorphosed Palaeozoic basement). The basin is infilled by Paleogene sediments composed of pyroclastic and volcanic rocks of upper Eocene and Oligocene ages. The petrology of the sandstones intercalated with coal layers at Pchelarovo shows a high proportion of devitrified hyaloclastic components in the sediments, indicating that coal deposition is contemporaneous with explosive volcanism whose volcanic centers were close to the northeastern border of the Borovitsa caldera. An intercalated marl-calcareous layer with microfossils indicates a marine transgression. A previous study of advanced argillic alteration (AAA) in Bulgaria has shown that volcanic rocks of the area are strongly hydrothermally altered (Kunov, 1999). Complementary isotopic (S, O, H) data on alunite indicate that AAA is of magmatic-hydrothermal

origin with an important participation of external seawater-derived fluids (Lerouge et al., 2006). Coals occur as 5cm-thick vitrinite layers rich in pyrite (samples 6 to 9), or as thin seams (11-12). The sample 7 is characterized by small perpendicular fractures infilled by pyrite.

## 2.2 Vulce Pole

The coal samples were collected close to the Vulce Pole village in a tectonic depression 25 km long in east-west direction and 3-4 to 10 km wide, filled by Oligocene sediments. Coals occur as 10 to 50 cm-thick seams (samples 29 and 31). The basement of the basin consists essentially of gneisses and amphibolites. Coal-bearing sediments of the basin are dominantly conglomerates and sandstones with intercalated volcanic tuffs and rare limestone at the bottom of the series, and clay layers at the top. The petrology of conglomerates and sandstones indicates immature sediments with a dominant contribution from the reworked basement (gneiss, granite) and an important component of devitrified volcanic clasts, suggesting that coal deposition is contemporaneous with explosive volcanic episode. Matrix of the elements is not abundant; carbonates are absent or rare, nodules of pyrite infill partially the porosity of some layers of sandstone and conglomerates suggesting sedimentation rather in a continental domain with late circulation of H<sub>2</sub>S-bearing fluids. The volcanic centre close to the basin is the Madjarovo complex (120 km<sup>2</sup>) in the south, dated by the <sup>40</sup>Ar/<sup>39</sup>Ar method on biotite and sanidine at around 32-33 Ma (Singer and Marchev, 2002). It induced intense magmatic-hydrothermal activity, marked by minor barren advanced argillic alteration and a well-developed epithermal adularia-sericite alteration associated with a base-metal-Au-Ag mineralization (Singer and Marchev, 2002).

## 2.3 Medenbuk

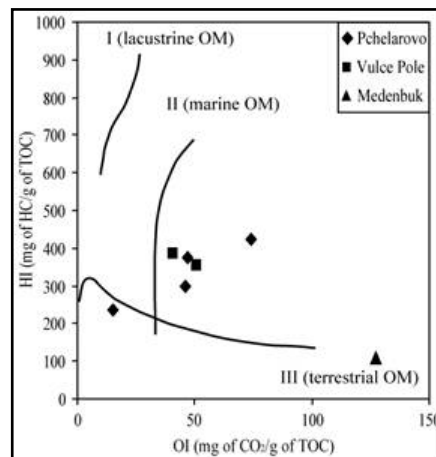
The coal sample (58) was collected from an outcrop of Paleogene sediments, located 20 km from Medenbuk. The basement of the basin is dominantly represented by gneisses and amphibolites of Proterozoic age. The coal-bearing sediments are close to the border and the basement of the basin; they are immature sandstones reworking exclusively components from the basement, consisting of gneisses, bioclast-rich carbonates but also mafic rocks marked by presence of epidote, amphibole and clinopyroxene. The matrix is abundant and represented by

micritic carbonates, strongly suggesting deposition under relatively deep marine conditions. The coal was present as small lenses, then partly reworked in a fracture. Nodules of pyrite are observed in sandstones directly above coal lenses.

## 3 RESULTS

### 3.1 Coal characterization

HI, OI, Tmax, S1 and S2 were analysed by Rock-Eval® RE6 pyrolysis according to standard methods. Vitrinite reflectance measurements were performed using a Leica DMR XP microscope under reflected light, following ICCP procedures.



**Figure 1: Location of Bulgarian coal samples in Van Krevelen's HI-OI diagram.**

The coals from Pchelarovo are composed of dominantly collotelinite with minor humotelinite and semifusinite, whereas the coals from Vulce Pole and Medenbuk are composed of dominantly humotelinite with some collotelinite.

The vitrinite from the three basins shows high carbon contents (79-86 wt%), consistent with a bituminous high to medium volatile coal rank. However the vitrinite reflectance and Tmax values are low, rather indicating a sub-bituminous rank (Table 1). The coals from Vulce Pole and Pchelarovo are characterized by a bright green-yellow fluorescence and by abnormally high HI values and relatively low OI. These characteristics are typical of perhydrogenated coals (Jimenez et al., 1998).

The sample 9 from Pchelarovo has OI and HI values characteristic of humic coals (Fig. 1). The coal from Medenbuk is very different with

a low fluorescence intensity high OI and low HI values. These characteristics may be interpreted by two ways. First, the sample is an immature humic coal. Second, it could be a perhydrogenous coal comparable to that from Vulce Pole and Pchelarovo, which could have been altered through hydrothermal processes or weathering. The presence of secondary gypsum and iron oxi-hydroxides in the coal lenses and the low fluorescence are in favor of the second assumption.

N°	C %	S %	S2 (mg HC / g rock)	Tmax (°C)	Ro (%)	Mean Ro (%)
Pchelarovo						
6	84	4.5	75.75	419	0.41	0.46
9	80	6.2	30.61	415	0.47	
11	80	3.8	90.46	413	0.45	
12	86	3.2	93.46	414	0.49	
Vulce Pole						
29	83	4.3	141.33	370	0.27	0.30
31	84	4.3	163.88	374	0.33	
Medenbuk						
58	79	1.5	32.01	404	0.32	

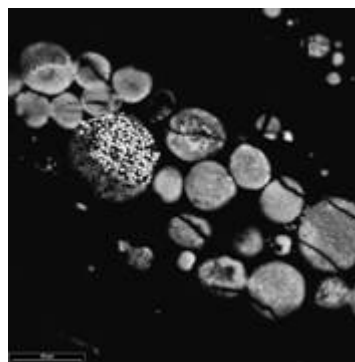
**Table 1: Rock-Eval pyrolysis, vitrinite reflectance, and C-S data measured by EPMA with a 10 kV acceleration voltage and a current beam of 20 nA.**

### 3.2 S, Ga, Ge and V distribution

Organic matter from the three coal deposits was analyzed for C, S, Fe and metal contents, using a Camebax SX50 electron microprobe.

S contents are high whereas Fe contents are low, showing that sulphur can be attributed to organic matter. Organic sulphur contents show that Medenbuk (1.5 wt%) is a medium-sulphur coal and Pchelarovo (3.2 – 6.2 wt%) and Vulce Pole (4.3 wt%) are high-sulphur coals. They may be compared with coals overlain by a marine roof in which most of the sulphur is derived from seawater sulfate (Chou, 1990).

Ge and Ga contents were measured in vitrinite of the three ore deposits, with a 20 kV acceleration voltage and a current beam of 20nA. The ranges of Ga content in the three ore deposits are quite similar: 0-260 ppm at Pchelarovo and Vulce Pole, and 0-330 ppm at Medenbuk. The ranges of Ge content at Vulce Pole and Pchelarovo are similar (0-480 ppm). On the other hand, Ge contents in OM from Medenbuk are high ( $2418 \pm 1033$  ppm,  $n = 12$ ) and associated with significant V contents (0-1100 ppm). Unusually high Ge and V contents (respectively up to 0.8 and 2.8 wt%) were measured in iron oxides (Fig. 2) resulting of the alteration of primary framboidal pyrites.



**Figure 2: Backscattered electron image of partially oxidized framboidal pyrites showing high Ge and V contents.**

### 3.3 Sulphur isotopes

Sulphur isotope analysis of pyrite, organic matter and secondary gypsum was performed using a CFIRMS system coupled with Flash EA and gas bench. Results are given in Table 2.

N°	observations	$\delta^{34}\text{S}$ (‰ CDT)
Pchelarovo		
6	vitrinite	+10.0
7	Secant pyrite in coal	+2.9
8	Sub// pyrite in coal	+3.5
9	Sub// pyrite in coal	+4.1
	vitrinite	+6.3
12	vitrinite	+9.6
Vulce Pole		
31	vitrinite	+2.2
34	patches of pyrite in sandstone	+5.6
36	patches of pyrite in sandstone	+10.2
38	patches of pyrite in sandstone	+6.5
Medenbuk		
58	vitrinite	-12.1
58	Secondary gypsum in coal	-28.5
59	nodule of pyrite in sandstone	-30.2; -30.5

**Table 2: Sulphur isotopic data on organic matter and sulphides from the three coal deposits.**

#### 3.3.1 Pchelarovo

Organic sulphur and syn-sedimentary pyrite have a relatively narrow range of  $\delta^{34}\text{S}$ . Independent of the geological context, these values may be interpreted by two ways: 1) bacterial reduction of marine sulphates in a relatively closed system, and 2) input of magmatic-hydrothermal fluids in the basin during its formation. Taking into account the contemporaneous volcanic activity of the basin ( $\delta^{34}\text{S}_{\text{fluid}} \sim 0-3$  ‰, Lerouge et al., 2006) and the presence of marine sediments at Pchelarovo, the sulphur origin could be related to both circulation of volcanic-magmatic and seawater-derived fluids during the deposition of the sediments, with the

basin evolving as a relatively closed system. The  $\delta^{34}\text{S}$  of secant sulphides crosscutting the stratification is around +3 ‰ and is not significantly different from the  $\delta^{34}\text{S}$  of the syn-sedimentary sulphides, suggesting either a partial remobilization of the syn-sedimentary sulphides, or a persistence of circulation of the same type of fluids during sedimentation and diagenesis.

### 3.3.2 *Vulce pole*

The  $\delta^{34}\text{S}$  of the pyrite infilling the porosity of sandstones varies between +5.6 and +10.2 ‰ (CDT), whereas  $\delta^{34}\text{S}$  organic matter is close to +2.2 ‰. Values are heterogeneous and higher than the  $\delta^{34}\text{S}$  of the magmatic fluids associated with the Madjarovo volcanic activity. The data cannot exclude the participation of magmatic fluids in the basin, but they preferentially indicate bacterial reduction of sulphates present in the fluids of the basin. The positive and heterogeneous values could result from evolution of sulphate-reducing bacteria in isolated microenvironments.

### 3.3.3 *Medenbuk*

The  $\delta^{34}\text{S}$  of syn-sedimentary pyrite in coal can be deduced from the secondary gypsum produced by weathering of pyrite. The  $\delta^{34}\text{S}$  value of gypsum is -28.5 ‰; that is quite close to the  $\delta^{34}\text{S}$  of the pyrite infilling the porosity of sandstone. The  $\delta^{34}\text{S}$  of vitrinite is slightly higher than  $\delta^{34}\text{S}$  of pyrite, as usual at Pchelarovo and most of coal deposits. This homogeneity of the  $\delta^{34}\text{S}$  and the highly negative values are consistent with sedimentary sulphides resulting from the bacterial reduction of marine-derived sulphates in an open system for sulphates, and also in good agreement with petrological features of the studied samples.

## 4 DISCUSSION

The three coal basins were deposited during the late intra-orogenic extensional phase of the continental collision in the Paleogene. Coals are rich in sulphur incorporated in organic matter and sulphides, and in metals. Coal from Medenbuk shows particularly high Ge content. Sulphur isotopes in organic matter and pyrite are used to interpret fluid origins. The  $\delta^{34}\text{S}$  values of organic sulphur and pyrite range from -30 to +10 ‰ (CDT), consistent with sulphate bacterial reduction. However the complexity of

the isotopic data requires to take into account the geological context. The three coal basins are different:

1) Depositional environment: The Medenbuk and Pchelarovo basins contain marine sediments just above coal seams. A part of sulphur (in organic matter and sulphides) results from the bacterial reduction of seawater-derived sulphates, in an open system at Medenbuk and in a closed system at Pchelarovo.

2) Contemporaneous volcanism: Pchelarovo and Vulce pole are close to volcanic centres, Medenbuk is far from any volcanism. Positive  $\delta^{34}\text{S}$  values may be partly attributed to volcanic fluids involved in the basin at Pchelarovo and Vulce Pole.

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