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SEDIMENTOLOGY

BLACK SHALES FACIES FROM AUDIA FORMATION (THE EASTERN CARPATHIANS), A SHALE GAS POTENTIAL

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The anoxic formations from the external flysch zone of the Eastern Carpathians, with high organic matter content, present great interest for their natural gas potential.

Our study on the Audia Nappe, Audia Formation, and Black Shale Member from Covasna Valley comprises - a field reconstruction of the stratigraphic record, mineralogical analyses of black slates, and shales or silty-shales by semi-quantitative X-ray diffracti a geochemical analysis of the organic-matter content of the black-shale leveles (total organic carbon (TOC), Rock-Eval pyrolysis data (RE), and a sequential loss on ignition (LOI) to estimate the organic and carbonate content.

Black shales petrotype is recognized throughout the entire succession, and represents an intra-basinal deposit, many times in couple with siliceous rocks (cherty or flint lamina or beds). The total organic carbon (TOC) is reported to average 1.28, and is generally highest in the slate, and black shale beds; Vitrinite reflectance (Ro) reflects a greater thermal maturity of the source rock, which in turn influences the expected hydrocarbons generated; Kerogen II (mainly marine algae) under normal-marine salinity and dysaerobic conditions is sub-mature to mature, and within the oil window.

In this way, the black shales can be considered a good potential mature oil- and gas-prone source rock.

Key words: Eastern Carpathians, Audia Formation, Black shales, Shale gas, Organic matter.

INTRODUCTION

The increasing understanding of the geological formations rich in natural gas has led to a reconsideration of the rocks that generate hydrocarbons and their re-classification as source rocks of a play. Due to this new perspective the bituminous formations from the Eastern Carpathians should be reevaluated using a new approach.

The anoxic formations, with high organic matter content, present great interest for their natural gas potential. These formations are found in the external flysch zone of the Eastern Carpathians, K1 in age (Audia Nappe, Tarcau Nappe, Audia Formation (AF) also known as Black Shales Formation), Oligocene (Tarcau Nappe and Vrancea-Lower Menilites, Bituminous Marls, Dysodilic Shales), Inferior Miocene (Kliwa Formation-Cornu Formation) [2, 3, 5, 13, 20, 22] (Fig. 1).

The black shales from Audia nappe, Covasna Valley, are part of the same geological context.

Location: Geological Setting

Audia Formation or black shale series is part of the Moldavide, Audia nappe, Tarcau nappe and, even Vrancea nappe (in which it has as an equivalent the Sărata Formation - Amadori M.L. *et al.*[1]) and it extends from Buzau Valley to the northern part of Romania (Fig.2). The thickness of

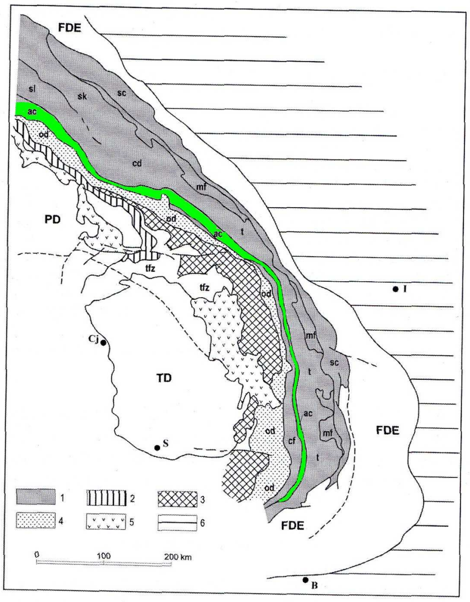


Fig. 1. Location of the Audia Nappe of the Eastern Carpathians (Săndulescu, 1990).

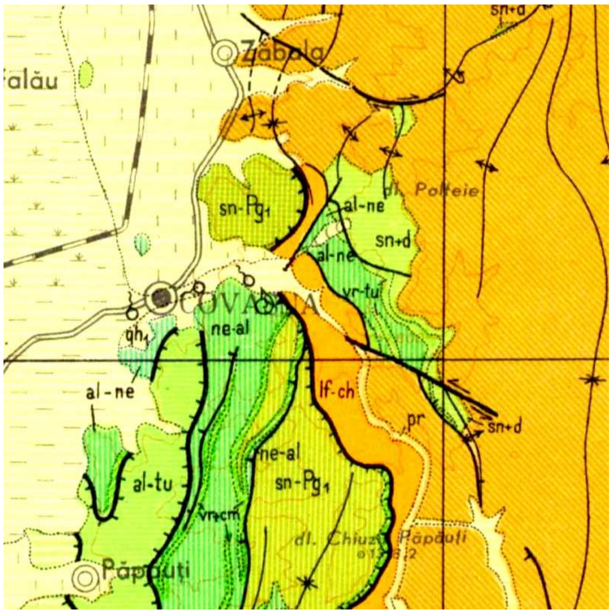


Fig. 2. Location of study area; Audia Nappe zone of the Eastern Carpathians.

AF is variable (110–300 m). AF age is considered by most workers to be Lower Cretaceous (140-93 Ma) and is devided into 3 members (LM=with siderite, MM=with lidiene, UM= with Qz-sandstones). The median member, the one containing black shales and lidiene, might be of interest for its natural gas potential.

This formation is well exposed (outcrops) in Covasna Valley (zona Caşin, pârâul Dela-Câmpulung Moldovenesc, valea Zagonul Mare, bazinul văii Bistriţa şi valea Moldovei) (Fig. 3).

Previous researches

The first mention of the black shales area was Ughlig (1903), and then in 1908 S. Athanasiu has separated the *Audia strata*, subsequent workers have described, dated and placed this formation in tectonic units: Băncilă (1955) [4], Filipescu-(1955), Ionesi (1971), Săndulescu (1984). Grigorescu (1972)[10], Ionesi (1971)[11], Grasu (1988)[7], Ştefănescu *et al.* (2006)[22], Amadori *et al.*, (2012)[1] have provided vast amounts of information about the mineralogy, petrography, paleontology, stratigraphy and organic matter content of the AF (Fig.3).

The deposit thickness has variable values from one place to another (100–300 m), and their lithology is dominated by siliciclastic sequences, with sandstones, silty and shales, slate terms or marls, associated in couples, predominantly periodical.

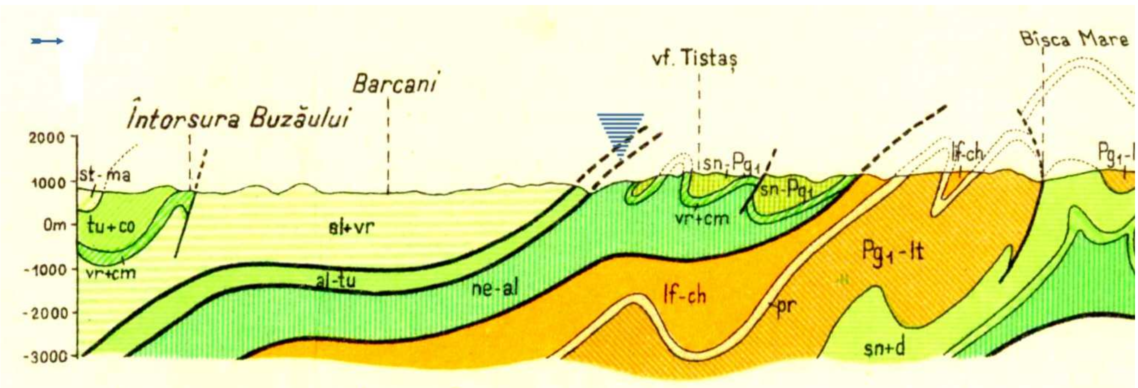


Fig.3. Cross section of the Eastern Carpathian Chain, with Cretaceous, and Paleogene Formations, by IGR Map.

METHODS

Our study on the Audia Nappe, Audia Formation, and Black Shale Member from Covasna Valley (Plate 1) comprises:

– a field reconstruction of the stratigraphic record, and sampling (4 microsequences and 10 samples) for mineralogical, petrographic, and geochemical analyses;

– mineralogical analyses of black slates, and shales or silty-shales by semi-quantitative X-ray diffraction (XRD); using a PANalytical machine (Cu anode, λ = 1.4060 Å) and the HighScore computer program with ICDD PDF 2 database at the Mineralogy Dept, Bucharest University, analist Alexandra □eclăman)

– a geochemical analysis of the organic-matter content of the black-shale leveles (total organic carbon (TOC), Rock-Eval pyrolysis data (RE), qualitative evaluation of the organic richness in a petroleum potential versus total organic-matter (PP/TOC) diagram, and qualitative evaluation of the origin and thermal maturity of the organic matter in a hydrogen index versus maximum temperature (HI/Tmax) diagram;

– a sequential loss on ignition (LOI) to estimate the organic and carbonate content of shales and marls based on sequential heating of the samples in a muffle furnace at 105 °C, 550 °C, and 900 ^{o}C.

The detailed knowledge of the Lower Cretaceous – Audia clastic sequences required the deployment of sequence analysis, namely the layer-by-layer mapping of the entire profile, identification of depositional facies by decoding the limits between the layers and sequences, their grain size analysis.

ANALYTICAL DATA – RESULTS AND DISCUSSION

The Cretaceous sequence of Audia Nappe is made up of heterogeneous, mainly fine-grained, siliciclastic and carbonatic lithofacies (sandy marls, immature and super-mature arenites, including pelagic intervals composed predominantly of black shales, black slate, bituminous marls, and siliceous deposits (silexites and cherty beds). Whole sequence represent a part of the Cycle I with pelagic and/or hemipelagic deposits [1].

Microfacies and facies associations

The researched sequence is open on a 100 m thickness.

Elevated on 1:20 scale, it could outline 4 microsequences (facies associations) (Fig.4) well delimited and distinctive through their beds particularities (thickness, expansion...), through the facies association type, grainsize and petrographic contents. Specific sedimentary structures, internal or superficial, act as depositional markers in the beds position control.

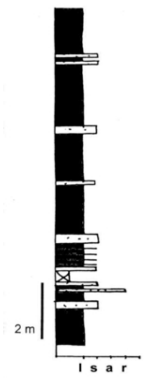


Fig. 4. Log from Covasna Valley.

Grouping the facies in the geometry of the examined suite allows distinctive, compatible and defining associations for environments and positions (compared to the potential source). These associations can be called mesosequences. They alternate from base to the top and indicate transitions from the pelagic, basinal facies to slope facies.

Black shales petrotype is recognized throughout the entire succession, and represents an intra-basinal deposit (which show anoxic conditions in the basin), many times in couple with siliceous rocks (cherty or flint lamina or beds).

Black shales description

Black shales beds, layer or lamina (1–2 to 10 mm in thickness) are black, grey, green or red in color, and grain size for lutite-siltylutite-silty. Petrotypes are shales, silty-shales or slate. Sedimentary structures are: horizontal lamina, continuous or discontinues, with repetitive couples (black-grey; black-red; red-green).

Mineralogical composition by X-ray analysis is (Table 1, and Fig. 5–6):

Chemical composition, by Grasu 1988), [7]:

Whole rock chemical analyses done by Grasu (1988) [7] for the median member –black shales with lidiene and for the superior one, quartz-glauconite sandstone, indicate temporal variations of Si, Al, Fe and K oxides (Table 2). In the black shales member this variations are periodical and represent the crossing from an anoxic environment to an oxygen rich one.

Table 1

Mineralogical composition of Black shale samples from Covasna Valley

	RA15 - %	**RA16 - %**
Quartz (Q)	33	34
Albite (Ab)	6	
Illite (il)	41	26
Clinoclore (Cl)	12	
Dolomite (Do)	1	
Ankerite (Ak)	1	
Zeophilite	1	
Calcit (Ca)	5	31
Carlinite		8
Ulvospinel		1

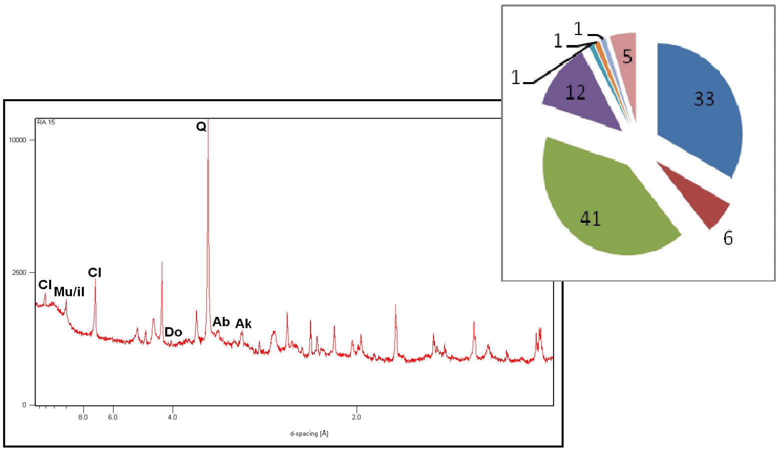


Fig. 5. RA15 diffractogram sample (black shale from Covasna Valley- Audia Nappe).
Only the peaks of the minerals of interest were marked.

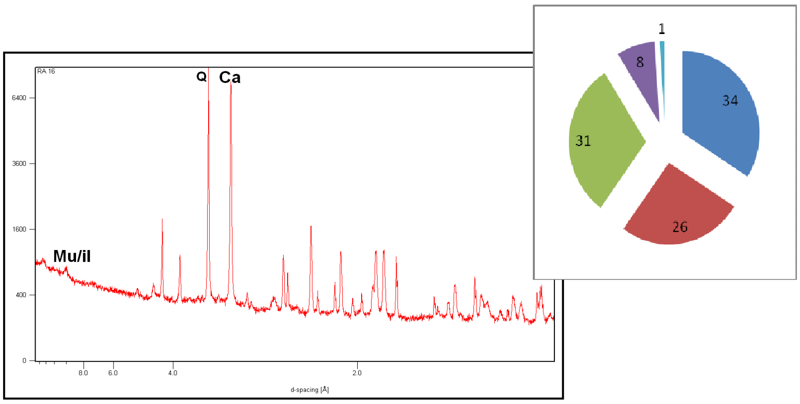


Fig. 6. Diffractogram of RA16 sample (black shale from Covasna Valley- Audia Nappe).
Only the peaks of the minerals of interest were marked.

Table 2

Chemical composition of AF (Grasu, 1984)

Black shales, and silicolite from AF. Moldova and Bistri a Valley (Papiu *et. al.* – 1975)							
(%)	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O
Black shales	54.82 89.00	0.08 – 19.90	0.29 – 4.69	0.27 – 2.66	0.57 – 7.99	0.30 – 2.46	0.32 – 3.65

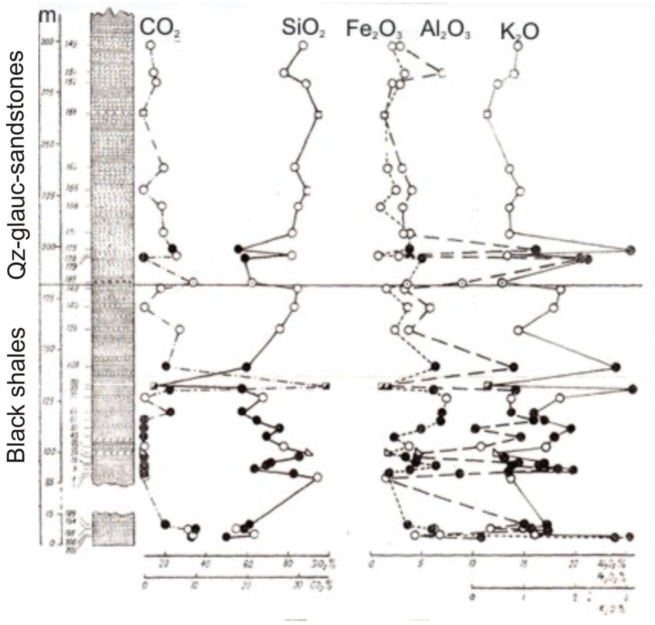


Fig. 7. SiO_2, Fe_2O_3, Al_2O_3, K_2O variance with CO_2 in the Audia formation (after Grasu,1988).

Organic Carbon Content and Thermal Maturity

For to have a termogas black shales potential (AF) we did more analysis types: organic matter (OM), total organic carbon (%TOC), vitrinite reflectance (%Ro), kerogen type and, from that, mature temperature (of not) in burrial sediments time.

The results of these are in Tables 3–5, and Figures 8–9.

The total organic carbon (TOC) content by weight percent in the Black Shale is reported to average 1.28%. The organic content is generally highest in the slate, and black shale beds. In the Fig.8 we can see a comparison with TOC from Sinaia Formation (Lower Cretaceous, too), and Tarcău Fm (Eocene).

Table 3

OM, $CaCO_3$, LOI, and TOC data for samples from Covasna Valley.

Samples	**OM[%]**	**CaCO3%**	**LOI tot%**	**TOC[%]**
RA14	2.93	3.05	4,27	0,76
RA15	5.18	5.89	7,77	1,35
RA16	2.00	57.02	27,07	0,52

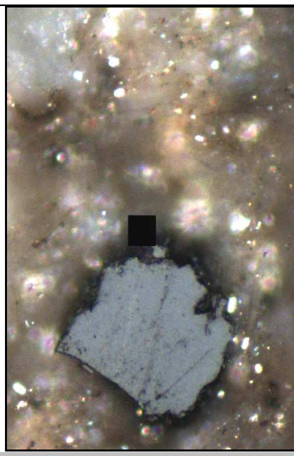
Table 4

Rock-Eval analysis data for Covasna Valley samples

Sample	**TOC (wt.%)**	**S1(mg/g)**	**S2(m/g)**	**S3(mg/g)**	**HI**	**OI**	**PI**	**Tmax °C**
International standard:	2-4 =good	1.5	3.07		65-70			>420 = matur
CO01-1-1	1.31	0.07	0.71	0.25	54	19	0.09	457
CO01-1-2	1.23	0.05	0.71	0.23	58	19	0.07	455
For comparation, A-SărataFm from Vrancea Nappe (Amadori *et al.*, 2012):								
119	1.63		4.87		298		0.16	439
118	1.34		3.68		274		0.1	440
117	1.71		6.74		394		0.39	440
116	0.81		1.59		196		0.09	438

Table 5

Vitrinit Reflectance (Ro%), and Kerogen data, Covasna Valley samples

Vitrinit Reflectance(Ro%)		Internat.standard > 1,1	
Min Value	1.04	**Kerogen**	
Max Value	1.34	K2 - H>C	
Mean Value	**1.19**	K1=Ro, 1.14-1.21%. K2=Ro, 0.98-0.89%	
# of Measurements	23		
Strd Deviation	0.09	Kerogen type IV fragments	
The mean Ro,ran of the primary kerogen is 1.19% based on 23 measurements. Organic matter is thermally mature and in the oil generation zone.			

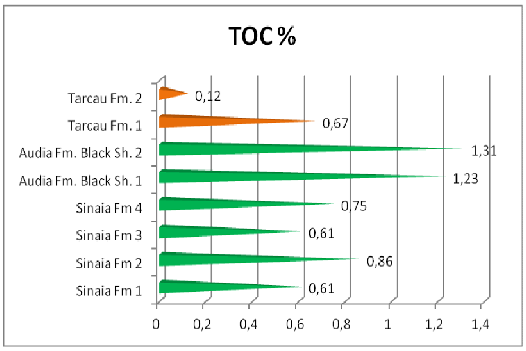


Fig. 8. TOC diagrame with data from AF, compare with Tarcău Fm, and Sinaia Fm.

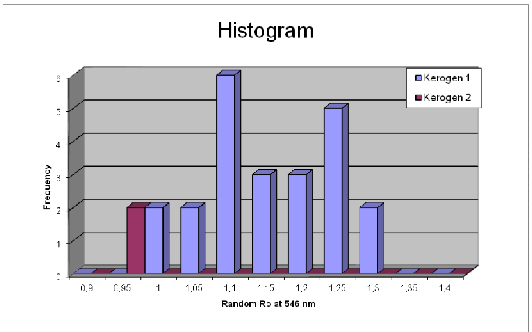


Fig. 9. Kerogen frequency from Covasna Valley sample-CO011.

Vitrinite reflectance (Ro) is the measure most commonly cited to assess the thermal maturity of the Black Shale. An increasing value of Ro reflects a greater thermal maturity of the source rock, which in turn influences the expected hydrocarbons generated (Table 5).

The sample contains moderate amounts of primary kerogen type III (gas-prone). Two types of kerogen are identified; a lower-reflecting type 2 and a higher-reflecting type 1. The latter is more abundant. Kerogen is mature and within the oil window. The matrix is argillaceous and contains pyrite. Kerogen type IV fragments are also present.

CONCLUSIONS

The Audia formation and the median member with black shales and lidiene could be interpreted as having originated in a deep-water slope-to-basin setting (Fig. 10).

The lithofacies suggest that the sea floor was below storm wave base and the oxygen-minimum zone. Oceanic circulation was restricted and the water column stratified, accounting for the dysaerobic to anaerobic conditions of deposition. Marine upwelling contributed to blooms of planktonic radiolarians and the production of phosphate grains.

Probably, LOG record, facies succession (couples, and microsequences) considered, deposition began during a second-order highstand of sea level, and superimposed on this overall fall were numerous third-order fluctuations (parase-quences) of relative sea level.

The sediment burial, and diagenesis permitted an evolution of organic matter to dry-gas window because:

– the shale source rock formed from type II kerogen (mainly marine algae) under normal-marine salinity and dysaerobic conditions;

– The total organic carbon (TOC) is reported to average 1.28, and is generally highest in the slate, and black shale beds;

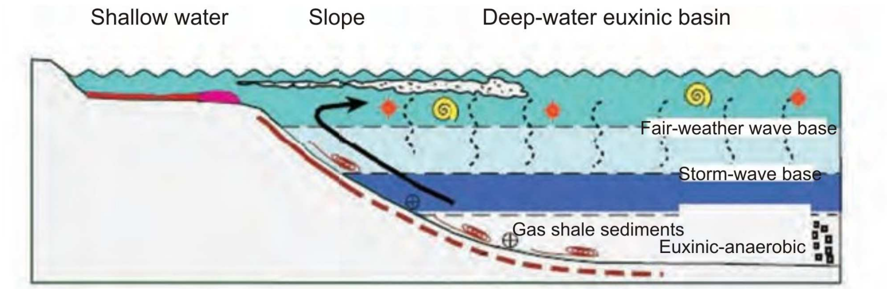


Fig. 10. Depositional model for Black shales from Audia Formation.

– Vitrinite reflectance (Ro) reflects a greater thermal maturity of the source rock, which in turn influences the expected hydrocarbons generated;

– Kerogen II is sub-mature to mature, and within the oil window.

In this way, the black shales can be considered a good potential mature oil- and gas-prone source rock.

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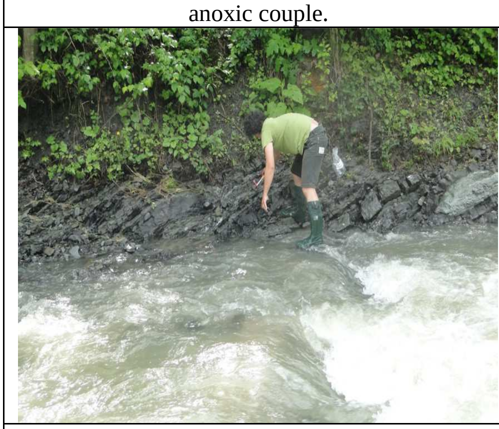
Plate 1

1. Black shales outcrop in Covasna Valley: oxic-anoxic couple.

2. Black shales outcrop in Covasna Valley – detail.



3. Black shales outcrop in Covasna Valley: a mesosequence with paralel stratification.

4. Black shales outcrop in Covasna Valley: exfolietion, and joints.

5. Black shale sample (RA15) from Covasna Valley.

6. Black shale sample (RA16) from Covasna Valley.