JETS OF TWO PROVENANCES FROM NORTHERN BULGARIA

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Introduction

It is commonly believed that jet originates from driftwood that was subjected to bituminization under anoxic conditions in marine environments. The process of bituminization can occur either *in-situ*, due to expulsion of bituminous substances from resinous materials within the jet; or *ex-situ*, due to impregnation of the driftwood with bitumen from the surrounding rocks. Bacterial fingerprints are also commonly found, because of microbial degradation of the driftwood during drifting, or within the sediments.

In Bulgaria jet occurs mostly in the central northern parts of the country within rocks of Jurassic and Cretaceous age. Jet's petrographic, physical (microhardness, vitrinite reflectance, R_o) and chemical (ultimate analysis, functional groups) characteristics are extensively studied. However, up to present very limited data on the biomarker composition exist. Therefore, the main purpose of the present study is to provide information for the soluble organic matter (SOM) composition making assumptions for the parent material and depositional environment.

The present study is based on four samples, collected from the jet appearances of Cretaceous age (Aptian) near Nikolaevo village, Pleven district (samples 1, 2 and 3), Moesian platform, and from Lessidren location (sample 4), Fore-Balkan, Early Jurassic age (Lias).

SOM was prepared by accelerated extraction by DCM for 1 hour at 75^{o}C and 50 bars in a Dionex ASE 200 instrument. Asphaltenes were precipitated and fractional compositions were determined by MPLC using Köhmen-Willsch instrument. The saturated and aromatic hydrocarbons were GC-MS studied by Thermo-Fisher Ultra ion trap instrument, equipped with a 25-m DB-1 fused silica column, 70^o-300^{o}C, 4^{o}C/min and 15 min isothermal period. Internal standards were applied, i.e. deuterated nC$_{24}$ (for saturated HC) and binaphthyl (for aromatic HC).

Results

Characteristics of jet samples and their EOM fractional compositions are given in Table 1.

Table 1*Refraction index, ultimate analyses, Rock Eval data, yields and fractional compositions of SOMs.*

Jet	R_o	Ash^d	V^{daf}	Rock Eval data			Soluble organic matter (SOM)				
		%		T_{max}	HI	TOC	Yield	wt.%			
							%	Sat.HC	Ar.HC	NSO	Asph.
1	0.23	1.3	58.8	402	248.8	64.74	0.53	6.4	3.01	54.80	35.78
2	0.21	1.8	55.9	401	215.5	64.81	0.50	6.98	1.90	42.86	48.26
3	0.28	4.5	53.0	405	185.0	60.18	0.46	9.49	2.43	44.67	43.41
4	0.34	2.6	52.8	419	245.6	72.24	0.38	7.88	5.67	65.52	20.94

^{d} – dry basis; ^{daf} – dry ash free basis;

Jets characteristics, i.e. R_o, 0.21-0.34%, volatiles, 52.8-58.8% and TOCs, 60-70%, cover the ranges for immature coals. Samples are characterised by very low ash yields, 1.3-4.5%. Rock Eval data reveal enhanced HI, ~ 200 mg/g TOC, low T_{max}, ~ 400ºC (samples 1-3) and a bit higher value, 419ºC, for sample 4. According to preliminary data sample 4 is more mature.
SOM are characterised by high portions of NSO compounds and asphaltenes (> 80%), while hydrocarbons are ~10%, as typically found in immature samples. Aliphatic hydrocarbons are more abundant then aromatics, 1.5-4.0 folds higher, consistent with high HI values. The *n*-alkanes distributions are strongly dominated by short-chain members, with expressed maxima at $n C_{17}$ and $n C_{18}$, and CPI in the range 1-2. These signatures argue for OM of possible microbial origin.
Relatively narrow range for Pr/Ph ratio was calculated, 0.42-0.65, indicating anaerobic conditions during deposition. Cross-plots in Pr/$n C_{17}$*vs.*Ph/$n C_{18}$ argue for marine Type II kerogen, deposited in anoxic environment (Fig.1a).The Rock Eval data correlations in T_{max}*vs.*HI diagram confirm this assignment. Cross-plots of Pr/Ph *vs.* C_{29}/C_{27} regular steranes diagram denote possible mixed origin of the organic matter, i.e. from bacteria and from land plants (Fig.1b).
Diterpenoid biomarkers are similar in all samples – minor pimarane, and major 16α(H)-phyllocladane. Samples 1, 2, 3 lack any triterpenoid biomarkers, while sample 4 contains also compounds of lupane and ursane skeletons, as well as their A-ring degradation products. Based on the biomarker assemblages, for Nikolaevo locality jets most probably originate from gymnosperm vegetation. For Lessidren jet, however, either angiosperm origin, or most probably *ex-situ* bituminization can be suggested.
By *m/z* 231 tracking appreciable amount of triaromatic steranes has been determined, which could be explained by an enhanced microbial activity. Values for hopanes isomerisation are a bit dispersed, but all are lower than equilibrium of ~0.6. The ratio of 20S/(20S+20R)-isomers of αααC_{29}steranes is in the range 0.22-0.27. The cross-plots of homohopane index H_{31}αβ S/(S+R) *vs.* C_{29} regular sterane S/(S+R) (Fig.1c) depict jets immature to early mature stage, a point well correlated with R_o data.

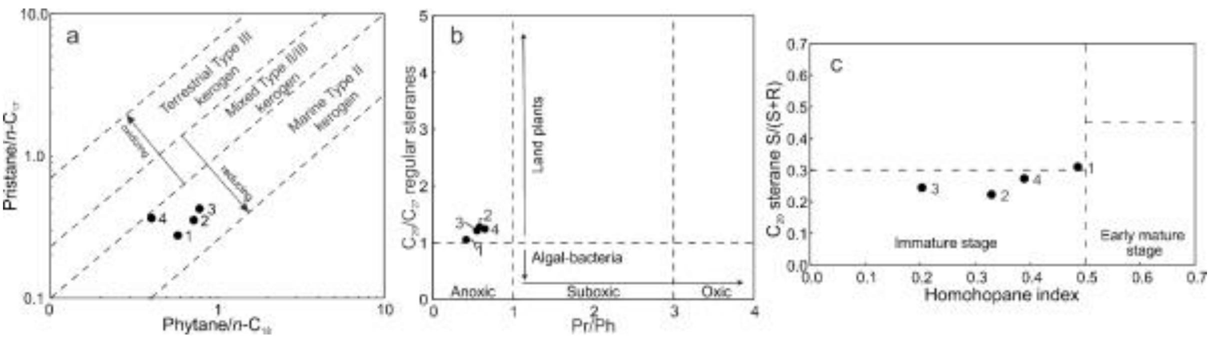

Figure1. *Correlations of biomarkers (a - Cross-plot of Ph/nC_{18}vs.Pr/nC_{17}; b - Cross-plot of Pr/Phvs.C_{29}/C_{27} regular steranes); c – Cross-plot of Homohopane index vs. C_{29} sterane S/(S+R)*

Conclusions

Results from bulk analyses and from information at molecular level have revealed that jets of two provenances from Northern Bulgaria have been structured from gymnospermous wood deposited in anoxic environment. Thus, it can be assumed that jetification has proceeded in marine environment with overlying shale layers. However, some differences in the jets characteristics and transformations were depicted, i.e. R_o, T_{max}, *ex-situ* bituminization, etc.