



ABSTRACT BOOK OF 37th TSOP ANNUAL MEETING



Sofia, Bulgaria

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OF 37th TSOP ANNUAL MEETING
Sofia 12-14 Sept. 2021

EDITORS:

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ISBN 978-954-92584-0-0

Peat-forming depositional environments within the Oligocene Bobov dol Basin, SW Bulgaria

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Keywords: Bulgaria, Oligocene subbituminous coal, organic petrology, biomarkers

Organic petrological and geochemical analyses were conducted on sixteen coal and carbonaceous shale samples from seams Ia, I and IIa from the Oligocene Bobov dol Basin, Bulgaria. The latter represents a N-NW to S-SE elongated graben structure, about 25 – 30 km long and 8 – 10 km wide. Its formation is related to the post-orogenic extensional development of the Late Alpine orogen on the territory of Bulgaria and is further complicated by compressional events during the Savian tectonic phase (Early Miocene). The graben infill comprises 1.0 – 1.5 km thick Oligocene to Early Miocene siliciclastic sediments, overlying various denudated pre-Paleogene basement rocks (Vatsev, 2014). Recent revision of the basin's lithostratigraphic scheme include 6 formal units, covering the time span from Rupelian to Late Egerian-Ottungian (Vatsev, 2015, 2014). The coal-bearing Bobovdol Fm. is up to 100 m thick and covers significant parts of the northern half of the graben. It is composed of a complex cyclic alternation of fluvial-deltaic and lacustrine siliciclastic sediments and coals. The base of the individual cycles is typically represented by fine- to coarse-grained sandstones (12 – 40 m thick), followed upwards by carbonaceous shale and/or coal beds (0.7 – 5.0 m thick) and laminated sandy- to silty (\pm calcareous/bituminous) claystones, and argillaceous sand- and siltstones (8 – 30 m thick) (Vatsev, 2015). Up to 14 coal beds are present, but only 6 (numbered I to VI from base to top) of them were considered economically significant and were subjected to underground and open-pit mining since the beginning of 20th century (Kamenov, 1959). Locally, seam Ia located below the first widespread coal seam (I) was also mined despite its high ash yields. The spatial distribution of the coal seams reveal a shift of the peat formation during the deposition of Bobovdol Fm. from NW (seams I to III) towards SE (seams IV – VI) (Kamenov, 1959). The coals are predominantly humic (Valčeva, 1985; Zdravkov and Kortenski, 2004), but several 2 – 3 cm thick sapropelic interbeds were also detected within the IVth coal seam (Konstantinova, 1956). Average organic carbon contents of 75.5 % (dry ash-free; daf) and calorific value of 31.38 MJ/kg (daf), as well as volatile matter in the range of 45.3 – 49.1 % (daf) and vitrinite reflectance between 0.40 and 0.43 % classify the coals as subbituminous C rank (Valčeva, 1985).

The studied coal seams are predominantly composed of huminite (75 – 95 vol.%), accompanied by subordinate contents of liptinite (3 – 14 vol. %) and inertinite (0 – 13 vol. %) macerals. Highly gelified ulminite (avg. 30.6 vol. %) and rare textinite (avg. 2.3 vol.%) with resinite/exsudatinitic cell infillings (Fig. 1e), argue for predominant gymnosperm origin of the organic matter. The plant remains are embedded in attrinitic (avg. 24.1 vol. %; in samples with higher mineral contents; Fig. 1f) or densinitic (avg. 20.6 vol. %; Fig. 1a) groundmass, often displaying reddish internal reflections. Stratified leaf-derived tissues are present in all studied samples, but are especially abundant (up to 27 vol. %) within the lower parts of seams Ia and I. Because of them, cutinite (avg. 1.0

vol. %) and fluorinite (avg. 0.7 vol. %; Fig. 1c, d), together with resinite (avg. 1.8 vol. %), are the most common liptinite macerals. Most of the samples contain also abundant liptodetrinite (avg. 2.3 vol. %), almost exclusively represented by scattered highly fluorescing liptinite particles, with fluorescent color strongly resembling that of

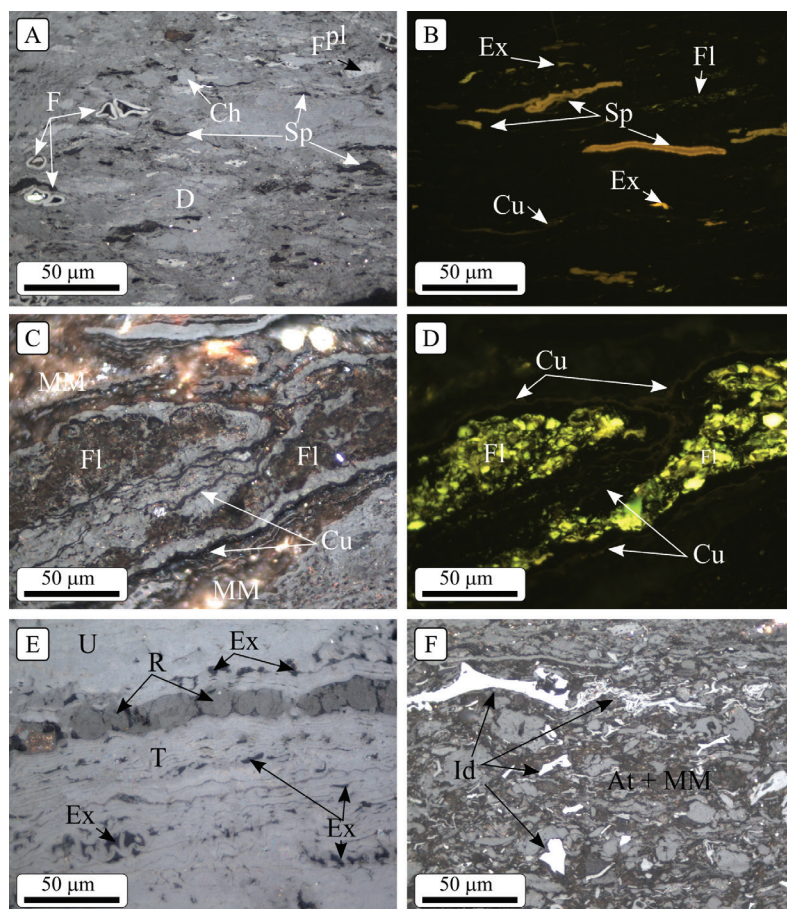


Figure 1. Representative photomicrographs of Bobov dol coal: A) Densinitic (D) groundmass with scattered corpohuminite (Ch), microsporinite (Sp), fungal sclerotia (F) and plectenhymae (F^{pl}); B) Typical liptinite composition: microsporinite (Sp), cutinite (Cu), fluorinite (Fl), and exsudatinite (Ex); C) Leaf tissues in association with cutinite (Cu) and fluorinite (Fl) within mud-rich (MM) groundmass; D) Same as C) – fluorescent light; E) Association of textinite (T) with resinite (R) and exsudatinite (Ex) cell inclusions, and ulminite (U); F) Mud-rich attrinitic (At+MM) groundmass with abundant inertodetrinite (Id) particles; Micrographs A, C, E, F taken under incident light, whereas B and D taken under blue excitation light.

fluorinite. This observation suggests that at least part of the groundmass might have originated from the decomposition of plant leaves. Microsporinite (Fig. 1a, b), suberinite, alginite, and exsudatinite (Fig. 1b, e) were also detected, but occur in subordinate amounts (<1 vol. % each). Inertinite macerals (avg. 2.3 vol. %) are sporadically detected and are mostly represented by funginite (Fig. 1a) and inertodetrinite (Fig. 1f). The inertinite content (inertodetrinite+ semifusinite) is more pronounced (up to 14 vol. %) only in one sample at the base of seam I.

Bulk organic geochemical results support the presence of gas-prone (HI < 200 mg HC/g TOC) Type III organic matter with good to very good hydrocarbon generation potential (Rock Eval: S₁+S₂ = 13 – 130 mg HC/g coal). Low random huminite reflectance (R₀ = 0.40 – 0.54%), T_{max} values (394 – 425 °C) and molecular ratios (i.e. avg. CPI = 3.9; avg. 22S/(22S+22R) C₃₁ hopanes = 0.1; and avg. 20S/(20S+20R) αααC₂₉ steranes = 0.3) argue for immature organic matter. Abundant cedrane-type sesquiterpenoids (up to 4086 μg/g TOC; avg. 1043 μg/g TOC) and phyllocladane- and pimarane-type diterpenoids (up to 4586 μg/g TOC; avg. 1138 μg/g TOC; Fig. 2) are consistent with significant organic matter contribution from Cupressaceae family. Minor concentrations of lupane- and oleanane-type triterpenoids (avg. 6.9 μg/g TOC) argue for a subordinate role of angiosperm vegetation to peat formation. The presence of C₃₀-dammar-13(17)-enes (R+S) in several samples of seams I and IIa, however, indicate that ferns might have been locally present within the mire. Low concentrations of steranes (avg. 3.1 μg/g TOC) with strong predominance of the C₂₉ compounds (R+S; avg. 66 %) is consistent with the predominant terrestrial organic source and do not support significant algal/phytoplankton contribution (C₂₇ steranes – avg. 12.8 %). The presence and local abundance (up to 37 μg/g TOC) of diasteranes and diasterenes, on the other hand, support peat formation in clay-rich sedimentary environment. Limited bacterial activity is evidenced by the presence of minor amounts of hopanes (avg. 6.1 μg/g TOC), hop-17(21)-enes (avg. 0.9 μg/g

