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Oil-prone mudstones from Shavar Formation, SE Bulgaria

Нефтогенериращи глинести скали от Шаварската свита, ЮИ България

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The Maastrichtian to Paleocene (Ypresian) Shavar Formation belongs to the lower part of the Krumovgrad Group from the East Rhodope Mountain (Goranov, Atanasov, 1992). It was deposited in several half graben basins formed along the periphery of the Kesebir metamorphic dome due to movements along a large regional low-angle detachment fault (Bonev, 1996). Shavar Fm is dominanted by coarse terrigenous rocks, composed exclusively of sand- to boulder-size gneiss, schist, amphibolite and marble grains from the underlying high-grade metamorphic core (Goranov, Atanasov, 1992; Marchev et al., 2004). In its type section, the formation is up to 350 m thick and is dominated by talus deposits of poorly sorted matrix-supported breccia and conglomerates, irregularly alternating with sandstones and calcareous mudstones/marlstones and at least two olistostrome units (Goranov, Atanasov, 1992). The presence of coaly layers and dispersed organic matter within the Shavar Formation was noted back in the early 1980s (Goranov, Atanasov, 1992), but up to now no attempts to characterize the organic matter were carried out. During the recent drilling in the area, however, the surprising discovery of pronounced crude oil odor within the mudstone intervals of Shavar Fm was detected. The lithological and organic geochemical characteristics of one mudstone interval were recently reported (Zdravkov et al., 2019). In this short overview, we present a summary of our most important findings.

The studied mudstone interval is ~35 m thick and forms the base of a 10 m thick alluvial/fluvial package at the base of a thick olistostrome unit (Fig. 1a). Macroscopically the interval is composed of unclearly laminated to massive dark grey to black silty- to sandy calcareous mudstones (carbonate content between 12 and 23 wt%) with scattered gravel- to pebble sized clasts. The rock is composed of mineral-bituminous groundmass, encompassing significant amounts of medium- to coarse silt-sized siliciclastic (mostly quartz and mica) grains and diagenetic components (mostly calcite, but also rare dolomite crystals). No significant differences in the amounts of siliciclastic grains exist between the individual lamellas, thus implying no seasonal imprint on the sedimentation. Nevertheless, the silt-size of the siliciclastic grains and the fine stratification of mica argue for deposition in low-energy environment. The matrix is composed of chlorite and kaolinite, intermixed with illite and/or mixed-layered illite/smectite. Abundant pyrite (up to 5–10 vol%) in the form of euhedral crystals or framboidal aggregates typically scattered within the groundmass is also present. Because of the absence of vein pyrite, nor any insights of hydrothermal alteration, pyrite can tentatively be considered to originate from the activity of sulfate reducing bacteria. The organic matter is represented almost exclusively by bituminite in the form of well stratified streaks and small lenses within the mineral matrix. Terrestrial organic matter is scarce. The week fluorescence of the groundmass is due to the presence of multiple micrometer-sized oil droplets or streaks.

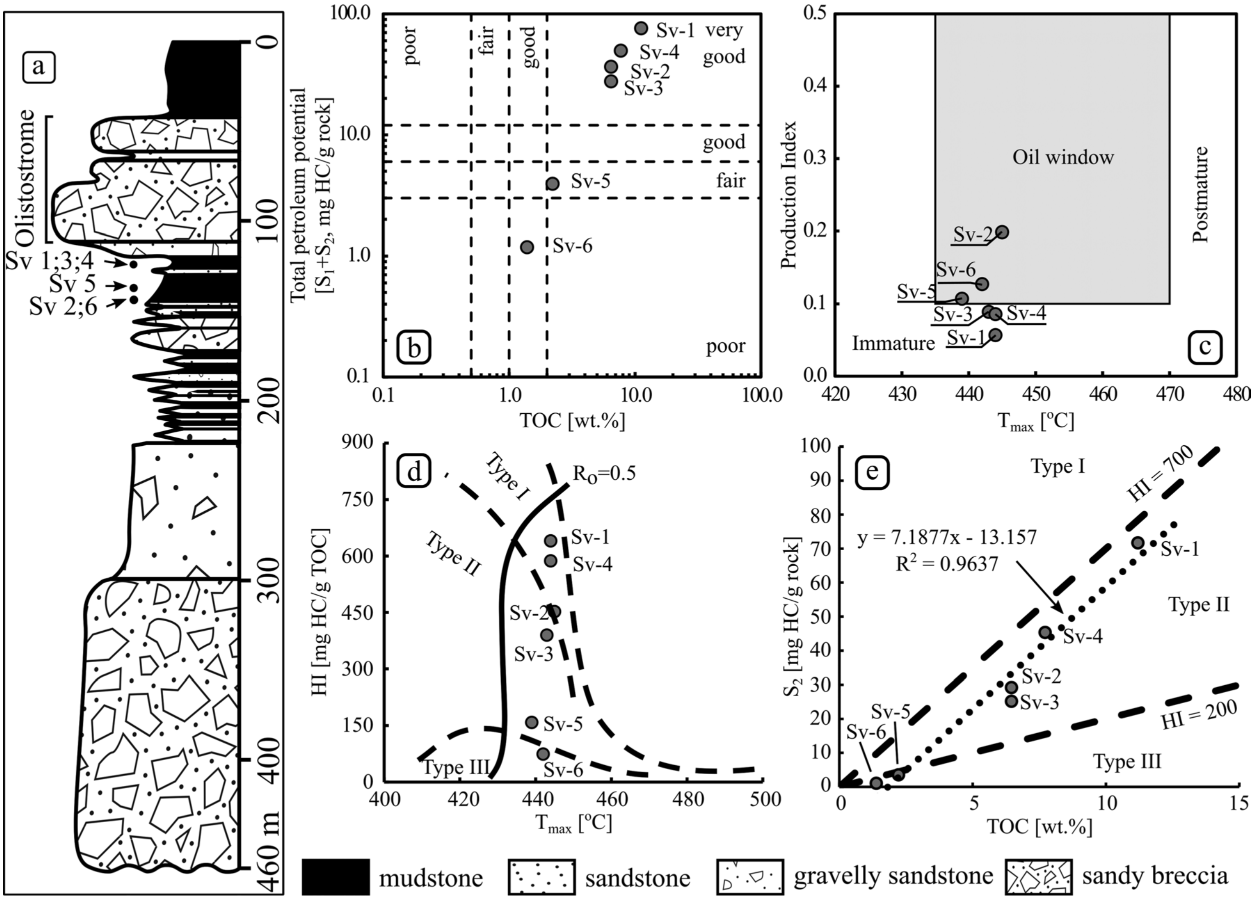

Fig. 1. Simplified lithology profile of drill hole DH-1: *a*, Cross plots of: *b*, S_1+S_2 vs. TOC; *c*, PI vs. Tmax; *d*, HI vs. Tmax (after Sykes, Snowdon, 2002); *e*, S_2 vs. TOC (after Langford, Blanc-Valleron, 1990).

Organic carbon (TOC) contents vary significantly from 1.4 wt% in sample Sv-6 from the lower part of the studied mudstone interval up to 11.2 wt% in its upper part (sample Sv-1). Based on these values the rocks can be classified as good to excellent source rocks (Peters, Cassa, 1994). However, since the hydrocarbon generative capacity of a rock depends also on the origin of the organic matter, we also utilized the total petroleum potential (S_1+S_2, mg HC/g rock) in order to evaluate the source rock characteristics of the mudstone. The plot of the total petroleum potential versus TOC (Fig. 1b) indicates very good hydrocarbon generative potential of the rocks. Exception exists only for samples Sv-5 and Sv-6 from the lower part of the studied interval. For these samples, however, slightly increased production index (PI) values were calculated (Fig. 1c), thus arguing for a bit more enhanced oil formation.

The HI values range from 74 up to 640 mg HC/g TOC. The cross plot of HI versus T_{max} (Fig. 1d) suggests variations in the organic matter (OM) type between the individual samples. Thus, Type I OM can be suggested for samples Sv-1, Sv-2 and Sv-4, Type II OM for samples Sv-3 and Sv-5, and Type III OM for Sv-6. However, this is in contrast with the petrographic data, which clearly indicates almost complete lack of neither vitrinite, nor terrestrially derived liptinite. Furthermore, a good correlation exists between HI and TOC (R^2 = 0.9376) thus arguing for dilution of the OM by the mineral matrix is the most probable reason for the lower HI values of samples Sv-5 and Sv-6. Therefore, Type I organic matter can be assumed for the entire mudstone interval. A plot of S_2 versus TOC (Fig. 1e) further supports this hypothesis. The slope of the regression line indicates true average HI value of about 720 mg HC/g TOC, which is consistent with Type I OM. Significant matrix effect ($TOC_{(inert)}$ = 1.83 wt%) is also evident from this plot. Because of the matrix effect, considerable fraction (about 31%) of the TOC is expected to be retained within the rock matrix.

T_{max} values in the range 439–445 °C indicate early mature organic matter (Peters, Cassa, 1994) and suggest onset of oil generation. In order to determine the degree of maturation of the organic matter a cross-plot of PI versus T_{max} (Fig. 1b) was used. The plot clearly indicates that the studied mudstones are at the onset of the oil window and are characterized by initial petroleum formation. Based on this observation, it can be speculated that the organic matter was subjected to temperatures not higher than about 100 °C. This temperature assessment is consistently lower than the presumed temperatures of ore formation from the base of the Shavar Fm. (~200–250 °C; Marchev et al., 2004; Márton et al., 2010), and therefore precludes direct influence of hydrothermal fluids on organic matter maturation. Considering the observed T_{max} values it can further be suggested that the mudstones contain indigenous hydrocarbons, since petroleum contamination is typically manifested by anomalously low pyrolysis temperatures (i.e. $T_{max} < 400$ °C; Espitalié, Bordenave, 1993).

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