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Hydrocarbon composition of bitumens of Upper Jurassic deposits of Kashpir oil shale-bearing basin (Russia)

Nadezhda S. BURDELNAYA, Dmitry A. BOUSHNEV and Sergey V. LYUROV

Institute of Geology of Komi SC RAS, 54 Pervomayskaya str., Syktyvkar, 167982 Komi, Russia;
e-mail: burdelnaya@geo.komisc.ru, boushnev@geo.komisc.ru, lyurov@geo.komisc.ru

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Kashpir oil shale deposit, located in the Volga region, is left one of two, previously developed, most important (after Baltic kukersites in Leningrad region and Estonia) oil shales resources in Russia. The organic carbon content (C_{org}) ranges >40%. Besides these oil shales are characterized by increased content of organic sulphur which has a high concentration due to specific sedimentation environment of organic matter (OM) in sediments (Riboulleau *et al.* 2000).

The samples under study were taken from a section near the city of Syzran, in the vicinity of old shale mine 5. In the section of shale rocks the interbedding of oil shales, argillaceous oil shales, kerogen clays and carbonate grey, dark grey and brown clays is observed. All the rocks are saturated by fine-disperse OM of different concentration. Altogether 4 oil shales members are observed with the thickness from 0.08 to 0.3 m. All the rocks are littered by shell detritus. In argillaceous rocks there are many deformed shells and bivalve prints, also ammonites and belemnites are found. In OM-rich rocks macrofauna is found considerably rarer. Among ammonites the representatives of *Zaraiskites, Dorsoplanites* and numerous bivalves *Buchia* are determined. The visible thickness of the layer is 2.8 m.

C_{org} content changes from 0.85 to 37.34% in the studied section. According to gas chromatography data the distribution of normal and isoprenoid alkanes changes upward the section. The OM content is sharply dominated by acyclic isoprenoid hydrocarbons. Pristan/phytan ratio <1 in all the samples which testifies to reducing environment predominance during sedimentation both with low and high C_{org}. Odd carbon number (C_{15}-C_{19}) of n-alkanes is <1 (except sample KS-1/7), and mid-chain (C_{21}-C_{25}) C high (C_{27}-C_{31}) n-alkanes ranges considerably >1, and for medium range CPI in oil shales are the highest (except sample KS-1/7). In OM of clays the hump in the range of high-molecular-weight hydrocarbons, characteristic for steranes, is absent. In the samples KS-1/2, KS-1/4, KS-1/10 normal hydrocarbons C_{16}, C_{18} dominate, in other fractions the content of these compounds is not so expressed against the background of other n-alkanes. This fact could be connected with the change of redox environment during sedimentation, but Pr/Ph ratio in these samples insignificantly differs from these values of other samples. It can be suggested that isoprenoid components of initial OM were exposed to the least reworking by bacteria during OM formation of the stated above deposits.

Practically in all the samples, except KS-1/7 and KS-1/10, low n-alkanes C_{13}-C_{19} dominate. The increased concentrations of C_{15}-C_{17} n-alkanes resulted from the participation of phytoplankton in the OM formation of the studied sediments. C_{27}, C_{29}, C_{31} normal hydrocarbons peaks, which are prevalent in high plant waxes, expressed to a lesser extent relative to the given compounds identified in the OM from oil shales of the Sysola shale-bearing region (Boushnev & Lyurov 2002), which resulted from the low input of terrigenous component to the composition of OM. A certain medium variant of n-alkane distribution presented by higher algae – characteristic C_{21}, C_{23}, C_{25} homologues predominance is fixed for all the samples.

Desulphurization of oil shale bitumen polar fractions, done on Raney nickel, resulted in the equal content of hydrocarbon components in all three studied fractions. In desulphurization products the n-alkanes (C_{14}-C_{31}) are present. The distribution of normal and isoprenoid alkanes is slightly different from the hydrocarbon content of desulphurization products of bitumen polar fractions from the Sysola shale-bearing region which was obtained earlier. If the desulphurization products of Sysola bitumens are dominated by phytane on the background of n- and iso-alkanes, in the desulphurization products of Kashpir bitumens just minor change of isoprenoid/n-alkane ratio at the transition from free to desulphurized fractions is stated. Concerning the Sysola deposits a sharp isoprenoid predominance is observed relating to n-alkanes (3-4 times), basically due to increasing concentration of phytane. Considerable changes are observed in low n-alkanes where in the process of desulphurization even n-alkanes C_{16} and C_{18} concentration sharply increases. The content of the given compounds also slightly prevails over odd low structures in the content of free hydrocarbon fraction which testifies to the active contribution of initial biostructures C_{16}, C_{18} to the content of Kashpir deposit OM.

Thus, hydrocarbon content of bitumens of deposits with increased C_{org} is sharply different from the content of normal and isoprenoid hydrocarbons of organic carbon-poor deposits by great concentrations of isoprenoid hydrocarbons, by isolating two n-alkanes predominance areas, by the increased contribution of low hydrocarbons (C_{14}-C_{18}), supported by the content of desulphurization products of bitumen polar fractions.

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Up-to-date discoveries and perspectives for hydrocarbon exploration in the Upper Jurassic formations of the Polish Carpathian foreland

Piotr GLINIAK

Polish Oil and Gas Company, ul. Lubicz 25, PL-31503 Kraków, Poland; e-mail: glip@geonafta.krakow.pl

Key-words: hydrocarbon accumulations, traps, reservoir, seal, prospective effect.

A number of hydrocarbon accumulations with recoverable reserves ca. 6.5 million tons of oil equivalent, e.g. Grobla, Pławowice, Łąkta, Tarnów-Jurassic, Dąbrowa Tarnowska, Smęgorzów, Gruszów, Partynia-Podborze, Korzeniow, traped within the epicontinental Upper Jurassic formations have been discovered so far in the Polish Carpathian foreland and the Carpathian basement (Fig 1). The traps are of combined structural and stratigraphic type. Reservoir rock types are found to vary between matrix-dominated porous rocks to dual-porosity and dual-permeability rocks and from porous fractured to entirely fractured rocks. The types of reservoir rocks could ultimately be linked to sediment type, diagenetic processes, and position in the basin. Location of hydrocarbon accumulation is strictly connected with fault systems developed within the Mesozoic formations. The traps are sealed by Miocene claystones-mudstones and/or Upper Cretaceous marls.

Results of recently carried out analysis of the petroleum system, especially identification of sufficient source rocks combined with effective geochemical and thermodynamic conditions for hydrocarbon generation and migration, indicate that there are still perspectives for further oil and gas discoveries within the Mesozoic formations, especially the Upper Jurassic ones. Using modern techniques of geophysical and geological data acquisition, integration and interpretation, like e.g. modeling of seismic images by artificial neural networks, is crucial for further successful exploration. It enables us for identification and classification of different genetically hydrocarbon traps. Interpretation of 2D and 3D seismic images

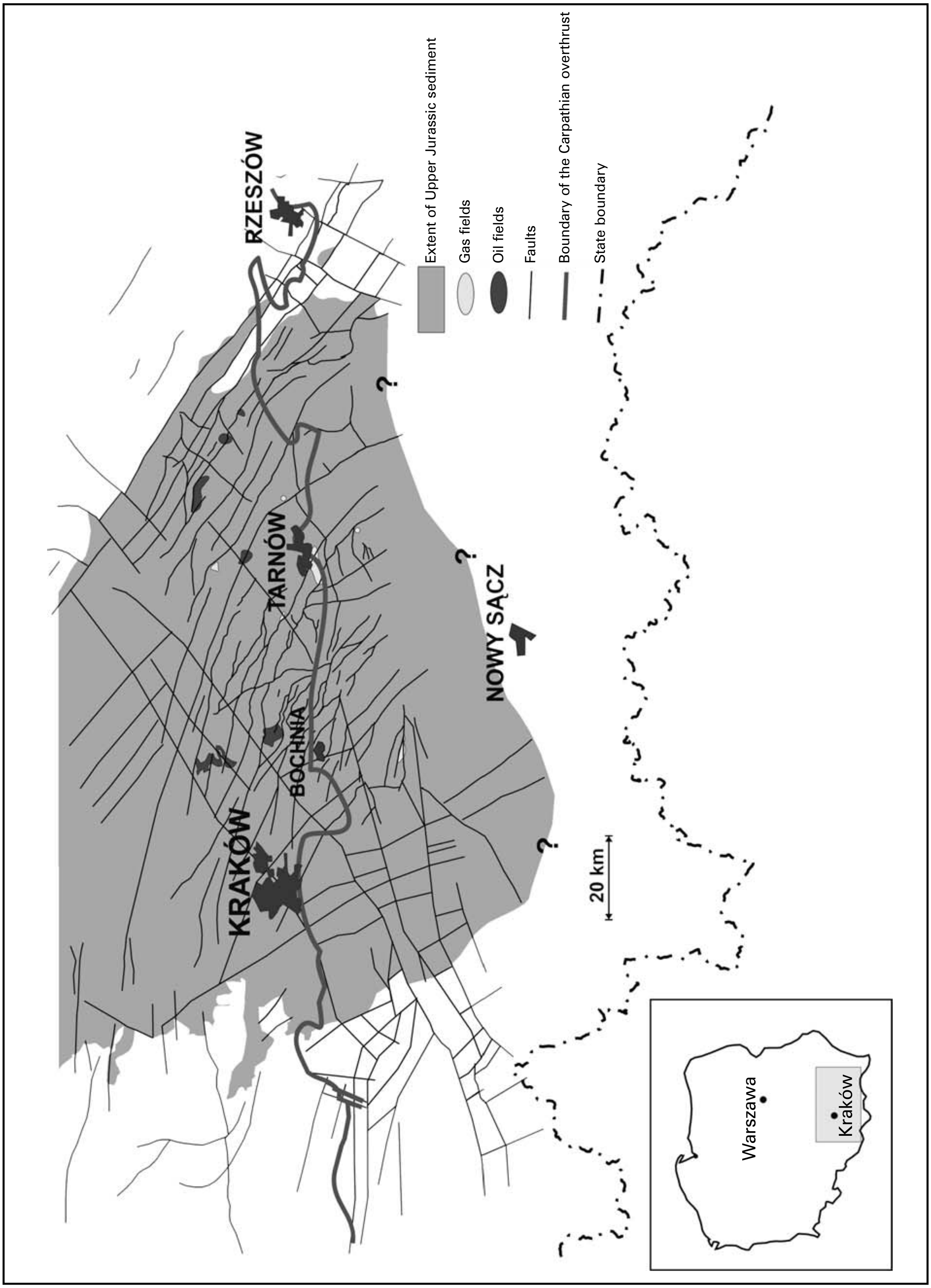

Fig. 1. Extent of Upper Jurassic sediment of the Polish Carpathian foreland and Carpathians basement.

is carried out using several additional procedures connected with PAL and RAVE applications of the Landmark Inc. software package. Also, additional analysis of seismic data based on differentiation of frequency image for particular objects like Fourier & Karhunen-Loeve transformations and spectral decomposition is used.

Recently, a detailed facies and stratigraphic analysis of the Mesozoic formations of the Carpathian foreland resulted in defining some new possibilities of finding hydrocarbon fields within traps of a combined stratigraphic and tectonic type. Existing fields were used as case stories for identification of criteria for finding new prospective traps. Taking into account regional tectono-stratigraphic model of evolution of the Late Jurassic-Cretaceous sedimentary basin gives a perspective for further successful exploration in the areas formerly regarded as non-prospective.

Prediction of source rocks: Jurassic case study

Jan GOLONKA[1], Michał KROBICKI[1], Tadeusz SŁOMKA[1], Anna WAŚKOWSKA-OLIWA[1], Wolfgang KIESSLING[2], Natalia J. BOCHAROVA[3], Mary EDRICH[4], David FORD[4], Robert PAUKEN[4] and Jim WILDHARBER[4]

[1]Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Al. Mickiewicza 30, PL-30059 Kraków, Poland; e-mail: krobicki@geol.agh.edu.pl, jan_golonka@yahoo.com
[2]Museum of Natural History, Berlin, Germany
[3]Russian Academy of Science, Moscow, Russia
[4]Mobil Exploration and Producing Center, Dallas, Texas, USA

Key-words: Jurassic, source rocks, hydrocarbons, Tethys, Carpathians.

The Late Jurassic source rock studies included thirty six hydrocarbon provinces worldwide. Regions were evaluated to obtain the Source Rocks Prediction Value (SRPV). The effectiveness of three major processes (biologic productivity, depositional preservation, and non-dilution) responsible for organic richness of the rocks was evaluated. The value between 1 and 5 (5 being most effective) was assigned by at least five experts to each region. The results were combined to obtain an average value. The three values, one for each of the major processes, were multiplied together to produce a SRPV, range 1-125. To calibrate the method SRPV's were assessed of the five independent areas and plotted against the measured Source Potential Index (SPI) values. The SPI is a measure of cumulative petroleum potential defined as the maximum quantity of hydrocarbons (in metric tons) that can be generated within a column of source rock under 1 m^2 of surface area (Demaison & Huizinga 1991). Average SPI measurements have been published for the Late Jurassic marine source rock sequences found in the mentioned above 5 independent Late Jurassic tectono-depositional provinces. The calibration allowed to rank all thirty six provinces and obtain the modeled SPI value for each province.

The Northern Tethyan Carpathian Basin was ranked ninth. The authors are evaluating now the actual possibility to find new Jurassic/Early Cretaceous source. The high organic productivity in these basins was presumable caused by upwelling (Golonka & Krobicki 2001), as well as restricted conditions in the narrow rift basins. According to Picha *et al.* (2005) the Upper Jurassic organic-rich Mikulov marls representing world-class source rock were found in the wells in southeastern Czech Republic and northeastern Austria. These 1400 m thick organic-rich rocks with TOC value 0.2-10% sourced oils in the Vienna Basin and Carpathian subthrust. The similar source rocks perhaps exist in the deeper subthrust areas in Polish, Slovakian and Ukrainian Carpathians.

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Hydrocarbon generating potential and their migration *versus* the diagenetic changes in Upper Jurassic and Lower Cretaceous sediments in the Polish Lowlands

Krystyna WOŁKOWICZ, Małgorzata POŁOŃSKA and Izabella GROTEK

Polish Geological Institute, 4 Rakowiecka st., PL-00975 Warsaw;
e-mail: Krystyna.Wolkowicz@pgi.gov.pl, Malgorzata.Polonska@pgi.gov.pl, Izabella.Grotek@pgi.gov.pl

Key-words: hydrocarbon generating potential, diagenesis, Upper Jurassic, Lower Cretaceous, Polish Lowlands.

The material studied came from selected boreholes, mainly in the Mid-Polish Trough: Korabiewice PIG 1, Magnuszew IG 1, Narol PIG 1, Narol PIG 2, Oświno IG 1, Poddębice PIG 2, Strzelno IG 1 and Tomaszów Lubelski IG 1. In the Upper Jurassic section, marine carbonates predominate (e.g. Radlicz 1997). At the Jurassic/Cretaceous boundary, the basin shallowed substantially, and carbonate-sulphate deposits formed. During the subsequent stage of Lower Cretaceous sedimentation, carbonate and siliciclastic rocks were deposited (e.g. Marek 1997).

The sediments underwent diagenetic processes influencing their reservoir properties. In the Upper Jurassic carbonate rocks, dissolution of many constituents, especially bioclasts, led to formation of numerous pores. Also heavy dolomitization enhanced their secondary porosity. Chemical compaction produced stylolite sutures, acting as possible migration ways for fluids. The reservoir properties were negatively affected by mechanical compaction and cementation, due to denser packing of grains and filling the pores with calcite and anhydrite. Diagenetic processes led to formation of rocks with various levels of porosity or very poorly permeable (<0.1mD).

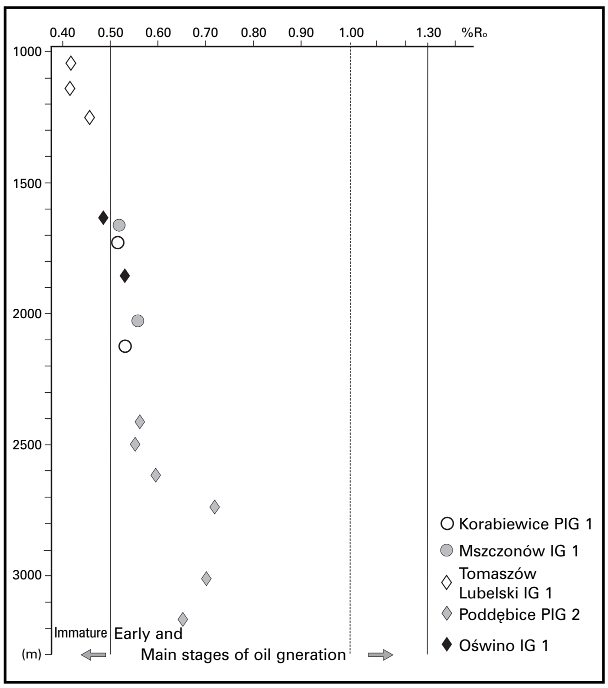

Fig. 1. Value of vitrinite reflectance index *versus* depth in the Upper Jurassic deposits.

In the Lower Cretaceous strata, important results of decreased porosity are due to compaction and cementing. In siliciclastic rocks, grains were

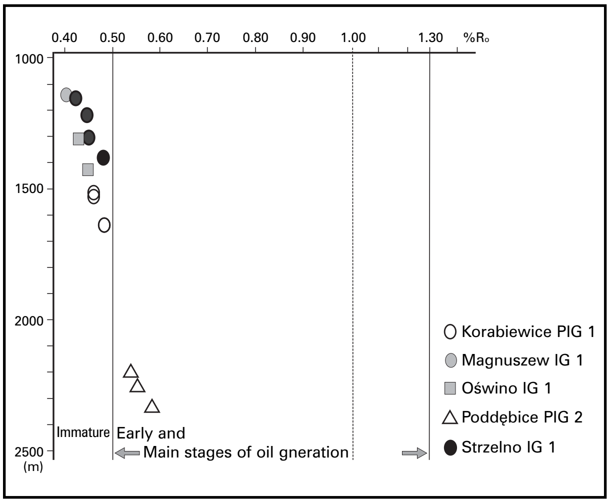

Fig. 2. Value of vitrinite reflactance index *versus* depth in the Lower Cretaceus deposits.

protected against destruction by compaction by their early diagenetic overgrowths of quartz and chlorite. In carbonates, the grains were similarly protected by calcite spar envelopes or micritic covers. While early cementation helped preserving primary porosity, late cementation led to blocking of the pores between grains and crystals. In arenites increased porosity was due to dissolution of unstable constituents, mainly feldspars. Through diagenesis, the Cretaceous sandstones obtained strongly porosity and permeable.

The studied Upper Jurassic and Lower Cretaceous strata contain organic matter, mainly humus type, with poor hydrocarbon generating potential. The degree of their transformation indicates immature (Lower Cretaceous) or early (Upper Jurassic) hydrocarbon generating stage (Figs 1, 2). Only the most changed Upper Jurassic rocks from the Poddębice PIG 2 borehole in their bottom part achieve the main stage of petroleum generation. Locally, they are enriched in organic carbon (>1.5% C_{org}), thus can be regarded as very poor or poor bedrock for oil generation.

Upper Jurassic rock studied showed low maturity of organic matter to hydrocarbon generation, with limited migration potential. The Cretaceous strata analyzed contain organic matter at the immature stage. However, noteworthy is the presence of sandstones with high filtration properties.

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