Generation potential of the Zechstein Main Dolomite (Ca2) carbonates in the Gorzów Wielkopolski–Międzychód–Lubiatów area: geological and geochemical approach to microbial-algal source rock

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A b s t r a c t. Source rocks of microbial-algal origin commonly occur in the Main Dolomite strata in the Gorzów Wielkopolski–Międzychód–Lubiatów area on carbonate platform slopes and on carbonate platforms. Oil-prone type II kerogen dominates with occasional amounts of type III or type I kerogens. Hydrocarbon generation processes followed two pathways. In the first pathway, generation was a single-stage process with full generation of hydrocarbon mass in a continuous progression of organic matter transformation, in late Triassic time. In the second pathway, the generation took place in two stages. Eighty to ninety percent of hydrocarbon mass was generated from kerogen by the end of the Jurassic period and the remaining generation was completed during post-Cretaceous time. As a consequence, oil accumulated in traps at the turn of the Triassic-Jurassic periods, and gas saturation of oil accumulations took place by late Jurassic time, with the final gas generation in the Paleogene or Neogene time. Hydrocarbons migrated only a few kilometres from source rocks to reservoir rocks within the Main Dolomite strata.

Key words: Zechstein Main Dolomite, Gorzów Wielkopolski–Międzychód–Lubiatów area, geological and geochemical characteristics of microbial-algal source rock, petroleum generation kinetics, modelling of hydrocarbon generation and expulsion processes, hydrocarbon potential

The Zechstein Main Dolomite unit is a lithostratigraphic unit composed of carbonates occurring at the base of the Zechstein PZ2 cyclothem (Wagner, 1994). Both source and reservoir rocks for hydrocarbons occur in the Main Dolomite carbonates (Wagner, 2004c). In 1961, the first Rybaki oil deposit was discovered in the Main Dolomite carbonates in the Polish Lowland (Karnkowski, 1999). Since then, more than 90 oil and gas deposits have been discovered (Karnkowski, 1999; Sikorski, 2002), including the large Barnówko-Mostno-Buszewo and Lubiatów-Międzychód- Grotów oil deposits near Gorzów Wielkopolski (Fig. 1) in 1992-1994 and in 2002-2006, respectively (Wolnowski, 2002, 2006; Sikorski, 2006). These numerous oil and gas deposits make the Main Dolomite strata one of the main targets of petroleum exploration in the Polish Lowland. Forming a closed hydrodynamic system isolated by evaporates on the top and on the bottom, the Main Dolomite unit is a good example of an evaporite petroleum-bearing formation.

The Gorzów–Międzychód–Lubiatów area is located in the northern edge of the Wielkopolska carbonate platform (Wagner et al., 2000), and it comprises the area of the Gorzów platform (without the Barnówko–Mostno–Buszewo deposit zone), the Noteć Bay with Krobielewko microplatform and the Grotów Peninsula (Fig. 1). The central sedimentary basin extends to the north and the east. Owing to a high/distant extension of shallow-water carbonate platforms into the central sedimentary basin, the basin has a specific paleogeographic situation, favourable for formation of hydrocarbon accumulations. Reservoir deposits on the slopes and carbonate platforms could have been supplied by migrating hydrocarbons. Additionally, hydrocarbons could be sourced from the platform plain (Kotarba &Wagner, 2006).

Petroleum exploration in the Zechstein Main Dolomite strata carried out in Poland is more difficult because of structural-geological conditions. To obtain satisfactory results, modern technical methods have to be employed, including 3D seismic surveys (e.g., Wolnowski, 2002, 2006) and geological and geochemical analyses of source rocks (Kotarba & Wagner, 2006).

This paper examines the utility of geological and geochemical methods for identification and evaluation of microbial-algal source rocks in the Zechstein Main Dolomite carbonates to direct petroleum exploration to the most perspective areas, i.e. areas of microbial-algal source rocks in the immediate vicinity of reservoirs located in the Gorzów Wielkopolski–Międzychód–Lubiatów area. As a consequence, their generation potential can be determined and genetic evaluation of undiscovered petroleum resources can be made.

The paper focuses on solving a number of issues: 1) identification of source rocks of microbial and algal origin by using geological methods, especially analysis of sedimentary structures, 2) determination of volume, genetic type, and thermal maturation of organic matter in source rocks by geochemical methods and 3) determination of petroleum generation kinetics of kerogen by isothermal hydrous pyrolysis. In addition, the application of a new indirect kinetic model for thermal maturation of kerogen in 1-D modelling of hydrocarbon generation and expulsion processes facilitated determination of the timing and the extent of oil generation from source rock.

Detailed geological and geochemical studies and 1-D modelling of petroleum generation and expulsion processes were performed on profiles of 26 wells. These wells are located as follows: 11 wells in area of the Grotów Peninsula (Chrzypsko-1, 2, 3; Grotów-1, 2; Lubiatów-1, 2; Międzychód-4, 5, 6 and Sowia Góra-1); and 15 wells in the eastern part of the Gorzów carbonate platform and the Noteć Bay (wells Krobielewko-2, Gorzów Wlkp.-2, Gorzów Wlkp. IG-1, Jeżyki-1, Baczyna-2, Buszewo-5, Ciecierzyce-1,

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Fig. 1. Paleogeographic map of the Main Dolomite strata on the Gorzów Platform and on the northern part of the Wielkopolska Platform

Dzierżów-1k, Gajewo-1, Marwice-3, Międzychód-2, Racław-1k, Santok-1, and Stanowice-2 and Stanowice-3) — Fig. 1.

The paper presents the results of works performed by specialist research teams from the Polish Geological Institute in Warsaw under Ryszard Wagner, and AGH-University of Science and Technology in Kraków under Maciej J. Kotarba, in co-operation with specialists from the Polish Oil and Gas Company, the Department of Petroleum Deposit Exploration, North Branch in Piła (Kotarba, 2000; Kotarba & Wagner, 2002–2004; Pokorski, 2004; Wagner, 2004a, 2004b, 2004c; Wichrowska, 2004).

Lithological and paleogeographical characteristics of the Main Dolomite strata

The paleogeography of the Main Dolomite unit is closely related to the basement development i.e. the anhydrite platform of the PZ1 cyclothem. Anhydrite platforms determined the morphology and inclination of the Main Dolomite carbonate platform slopes. Three depositional systems of paleogeographic relief of the Main Dolomite unit can be distinguished (Dadlez et al., 1998; Wagner, 1994, 2004a, 2004b; Wagner et al., 2000): 1) a basin plain, 2) a carbonate platform slope and 3) a carbonate platform. Depositional systems can be distinguished on the basis of microfacial and sedimentological analyses (Jaworowski & Mikołajewski — this issue; Jaworowski, 2004; Mikołajewski, 2004). Special attention was paid to sedimentological structures in particular paleo- geographic areas. This greatly aided definition and identification of source rocks.

Basin plain — **bays plain.** In the Main Dolomite unit a system of fragmented bays of Witnica and Rzepin was formed, separated by the Cychry, Chartów–Górzyca and Sulęcin microplatforms (Peryt & Dyjaczyński, 1991). This system formed southward of the Gorzów platform in the place where the Zielona Góra Bay developed during the PZ1 cycle. The deeply incised Noteć Bay, partly closed from the north by the Krobielewko microplatform, formed in the north between the Santok Peninsula and the Grotów Peninsula. Laminated carbonate mudstones with thin alternating microbial layers were deposited on the bay plain in low energy sedimentary conditions. Other sedimentary features such as flaser, lenticular and cross-bedding are rare. Overall the thickness of the Main Dolomite strata was up to 30 m in the bay area.

Carbonate platform slopes. Carbonate platform slopes continued the former slopes of the PZ1 sulphate platform. In the study area, slopes are steep and in the upper part they are escarpment-like. Escarpment height ranges from 40 m to 120 m, with an average 60–80 m. These slopes are also very narrow, usually several hundreds meters but less than 1 km in width.

Morphology of the slope is best shown by the paleotectonic cross-section of the western edge of the Grotów Peninsula (Fig. 2). This escarpment is 100 m high, and it contains terraces with accumulations of sediments (prisms) redeposited from the barrier.



Fig. 2. Paleotectonic cross-section at the top of the PZ2 cyclothem based on the A1 Międzychód–Sieraków 3D seismic section. Seismic section after Górska and Łukaszewski (2003)

Depositional slope systems were subjected to the influence of two different sedimentary environments: a shallow water, high-energy outer barrier edge (redeposited rocks from the barrier; rudstones, floatstones and packstones) and a relatively deepwater, low-energy area of the basin floor (mudstone and wackestone alterations). Highly variable thicknesses and facies of slope deposits resulted from the morphology of the carbonate platform edge, the slope angle, and sea currents flowing parallel to the platform slopes.

Slope deposits from the western edge of the Grotów Peninsula (Fig. 1) in several boreholes were best recognized. The lower part of the slope was examined in three well profiles: Lubiatów-1 and 2 as well as Sowia Góra 1. These profiles, 45.0 m to 56.0 m thick, are mostly comprised of a redeposited grain material and carbonate sands. Carbonate sands, in turn, are comprised of ooids and oncoids, incidental pisoids with admixtures of peloids forming main complexes of packstones alternated by floatstones, and rarely by rudstones. Visible in floatstones and rudstones are numerous intraclasts reaching up to 3 cm length, consisting of grainy rocks, mainly grainstones, mats, and microbial buildups. Grain elements and intraclasts probably originated from the barrier itself and/or from the outer barrier slope. They were transported to the deeper part of the basin by suspension currents and slumps resulting from storms and perhaps also by tectonic movements. Another possible process is from traction currents. These corrents could spread deposits in the deeper part of the slope, parallel to the platform edge, in accordance with the regional pattern of submarine currents (Wagner et al., 2000).

Laminated dolomitic and lime mudstones (rhythmites) alternating with redeposited deposits also occur in the slope profiles. Most of them were found in the Sowia Góra-1 well. They show that during calmer periods there was a reduced material supply available for deposition which is characteristic of the basin floor. In the slope deposits are indications of high biological activity of cyanobacteria. Numerous biolaminae stabilizing grainy deposits occur in packstones. Biolaminae in the rhythmites originated from phytoplankton falling out of suspension.

Carbonate platforms. The Main Dolomite carbonate platforms developed in vast terraces of shallow water sedimentation. Platforms such as Witnica, Rzepin and Noteć have very irregular outlines and are deeply incised. Also the platform morphology was variable from a very flat one to more variegated; their relief dependent on the underlying PZ1 sulphate platforms, and existing paleorelief. Thickness of the Main Dolomite strata in the platforms is about 30-40 m, reaching locally highs of 60-100 m. Water depth was generally shallow with dominant high-energy deposits. The salinity was somewhat higher than that of the open sea, and it influenced the organisms development. Algae and cyanobacteria evolved extensively and played a key role in the biomass accumulation from which hydrocarbons originated. Increased salinity possibly created the local oxygen-depleted environments at periods of intense development of cyanobacteria which could have protected the organic matter from destruction, thus facilitating their preservation.

The Main Dolomite platform deposits are characterized by the greatest diversity of sedimentary environments. In the platform two main facies can be distinguished: 1) barrier, and 2) platform flat of high-energy and of low-energy.

Barriers developed in areas of high water hydrodynamics and intense wave action. As a result, barriers were formed near the edges of outer carbonate platform areas. Resulting sedimentary macrostructures were shaped by their role acting of as a shield against the wave action. Barriers were mainly built of peri- and sublittoral carbonate sands as well as of microbial sediments. Cyanobacterial laminae commonly occur in the grainstone deposits stabilizing a loose grainy material. A similar role was played by microbial buildups — stromatolithes, and algal thrombolithes. Microbial deposits also occur as mats. Current action in the barrier areas is responsible for intraclasts of over 2 mm long, especially in the slopes, which build floatstone beds, and rarely rudstones. Wackestones and mudstones are very rare and occur locally in slope environments.

Carbonate barrier sediments also occur within the platform flat. Inner barriers developed on the locally elevated fragments of platform flat, dividing it into areas with low sedimentation. Barrier slopes can be divided into the outer and the inner slopes. Grainstones and packstones with a high contribution of microbial mats and domes generally occur in the outer slope. This sedimentary environment was high-energy. Thickness of the Main Dolomite strata is as much as 80 m. The inner slope was a lower-hydrodynamic energy environment than the outer slope and the barrier. Stable carbonate sands characteristically occur here during rapid episodes of sedimentation resulting in packstones and numerous microbial boundstones such as mats and biolaminae. Thickness of the Main Dolomite deposits varies from less than 40 m to over 94 m. Platform flats comprise the largest area in the platform and can be divided into high- and low-energy ones. Packstones are dominant in the high-energy area, rarely grainstones, and sometimes locally, wackestones. Boundstones are abundant mainly as microbial mats and biolaminae. An example of well developed flat is in the Grotów Peninsula. Deposit thicknesses are quite small, commonly less than 40 m, occasionally reaching 50 m. Low-energy flats occur in protected depressions of the platform flat. In these profiles wackestones and mudstones with intercalations of packstones and boundstones are dominant. Wackestones and packstones are commonly laminated forming rhythmites. Microbial mats and common biostabilization of sediments occurs. Thickness of the Main Dolomite strata in the platform flat environments is usually less than 40 m, sometimes even less than 30 m.

Geological characteristics of source rocks: microbial sediments and algae — types, environmental deposition, analysis of microbial organic matter preservation and thickness

For many years, source rocks in Main Dolomite strata were considered to be dark-grey laminated mudstones occurring in the central part of the basin. Our geological and geochemical data (see next chapter) proved that these series while having features of source rocks, cannot be the main source of hydrocarbons. This is because the rocks played only a limited role in generation, expulsion and migration of the hydrocarbons. Thus, reservoir rocks in the carbonate platform and its slope were charged by hydrocarbons generated from source rocks deposited tens and hundreds of kilometres away in source rock complexes from the central part of the basin. It was important to find different source rocks within the slope and carbonate platform deposits. Rocks of microbial and algal origin commonly occur in the Main Dolomite unit which could have been the source of organic matter (Wagner, 2004c; Wichrowska, 2004). It results from specific sedimentary and climatic conditions in the Main Dolomite Basin, where warm, shallow and highly saline waters of a mid-continental basin supported the flourishing development of cyanobacteria and algae. Increased salinity, though is deemed the most important for minimizing organic matter-consuming fauna thus allowing the biomass to accumulate.

Cyanobacteria make up a diverse and widespread group of microorganisms able to evolve in extreme environmental conditions. Periods of favourable development could involve local reducing conditions in shallow water zones which protect organic matter from destruction. Cyanobacteria are characterized by the ability to precipitate calcium carbonate in mucus — embracing cells. This is a very important feature influencing the deposition of the Main Dolomite carbonate rocks stabilizing grainy sediments in conditions of high hydrodynamic activity of sea waters and protecting the organic matter from oxidation.

In addition to cyanobacteria, red and green algae also occured during Main Dolomite deposition (Wichrowska, 2004), along with planktonic cyanobacteria and algae whose traces occur in the Main Dolomite strata. These planktonic forms of organic matter became a rich source particularly for sediments forming in deep parts of the basin (platform slopes and bay plains), where activity of benthic cyanobacteria and algae was limited.

Microbial structures in the Main Dolomite deposits were formed by many species of cyanobacteria, probably in cooperation with filamentous green and red algae which occur in several basic morphological groups (Wagner, 2004c). These are: 1) microbially-supported complexes microbial buildups and microbial mats, 2) dispersed microbial laminae, and 3) coated grains — oncoids.

Microbially-supported complexes. Microbially-supported complexes build regular and irregular structures which allow estimation of their thicknesses. Microbial buildups built of stromatolites and thrombolites can be distinguished as well as microbial mats built more or less of parallel laminated biolaminae.

Microbial buildups are composed of stromatolites and thrombolites. Stromatolites are mainly cyanobacterial structures with some filamentous laminated green algae forming mainly mound-like forms (Fig. 3). Stromatolites commonly occur with microbial mats, sometimes they are observed in a continuous transition with microbial laminae into stromatolitic structures. Thrombolites are probably a product of mainly red algae Rhodophyta from the genus Archeolithotamnion, an incrustation form with an irregular kidney-like outer fabric of complex inner buildup.

Microbial mats are built of sets of continuous biolaminae, flat-convex, regular and wavy-formed. In some places more irregular forms also occur which are more deformed and partly discontinuous. Single biolaminae have thicknesses from less than 1 mm to more than several millimetres, commonly 1–2 mm. Coated grains, ooids and oncoids, often occur in them. Microbial mats can achieve thicknesses ranging from 0.1 m to 6.9 m — Fig. 4.



Fig. 3. Columnar stromatolite, layer of microbial buildups and mats — a barrier environment (Dzierżów-1K well, depth — 3051 m). Photo courtesy of Z. Mikołajewski

Microbial mats and buildups commonly form mutual complexes in the carbonate platform interbedded with grainy deposits like grainstones and packstones, and they can attain a total thickness of up to 25.5 m.

Microbial clumps also occur in the Main Dolomite unit which are probably cyanobacterially-derived.

These clumps are oval with an irregular inner framework and several millimetres to several centimetres thick. They are quite common in the Main Dolomite profiles, together with microbial laminae and mats.

Dispersed microbial laminae. Dispersed microbial laminae are also cyanobacterial-like structures, similarly to microbial mats and probably have the same genesis. They differ by having a single to a few sets of biolaminae in rocks whose total thickness is not more than about 10 cm.

Thickness and shape of single biolamina is variable and depends on sedimentary conditions. In shallow water zones of the Main Dolomite basin, in the carbonate platform area, biolaminae are pale in colour, of slightly wavy shape and range from microns to several millimetres thick. The thickness commonly ranges from 1 mm to 3 mm, however, and not more than 5 mm. They usually occur in grainy deposits — grainstones and packstones — in very variable quantities (Fig. 5). Formation of biolamina takes a short period of low hydrodynamic activity which commonly occurs under shallow water conditions. Therefore it is difficult to estimate the total thickness of these biolaminae in



Fig. 4. Microbial mat, thin and parallel biolamination; initial forms of stromatolites in the lower part; layer of microbial buildups and mats — a barrier environment (Stanowice 2 well, depth — 3141 m). Photo courtesy of Z. Mikołajewski



Fig. 5. Carbonate sands (grainstones), stabilized by darker biolaminae. Dense biolamination — a barrier slope environment (Buszewo 5 well, depth — 3137.4 m). Photo courtesy of Z. Mikołajewski

studied profiles. Therefore method of counting sections of profiles at least 1 m thick we adopted. Using this method, biolaminae occur in four different ways: a) rare — composing up to 10% thickness of the whole interval, b) common — 10-20%, c) dense — 20-30%, and d) very dense — 30-40%.

It is concluded that microbial laminae represent a substantial percentage of total thickness of the whole profile. Of course, this method is not too precise and is to some extent subjective, but it accounts for variability in thickness of biolaminae occurrences in the Main Dolomite strata.

Coated grains — *oncoids.* Oncoids are usually coated grains in the Main Dolomite deposits. They commonly occur in the carbonate platform area building barriers and are dominant in profiles of the high-energy platform flat. Oncoids originated from filamentous cyanobacteria and green algae with which they coexist. They were probably the source of significant quantities of organic matter. However, a high hydrodynamic energy of environment in which they deposited probably prevented preservation of organic matter and hence these deposits are excluded from the source rocks classification.

Algae. The Main Dolomite deposits display variable amounts of algae fragments. Different genera and species of red and green algae, both benthic and planktonic ones are present (Wichrowska, 2004). Algae also were a rich source of organic matter but it cannot be estimated quantitavely. Algae fragments are only visible in thin sections and because these structures are very much susceptible to destruction during diagenetic processes their quantitative potential cannot be estimated.

Mudstones — **depositional environments and thickness.** In deep parts of the basin on the carbonate platform slope and bay plain, biolaminae are generally much thinner, usually less than 1 mm, and contain a dark clayey-organic matter (Fig. 6). They occur in mudstone and wackestone environments and suggest calmer sedimentary environments. Benthic cyanobacteria were a weak contributor to the formation of biolaminae because of the poor photic conditions. Planktonic algae and cyanobacteria played a more important role as they settled to the bottom. Most biolaminae in these zones probably had such a genesis, especially in the bay plain area.

Biolaminae difficult to distinguish from other sedimentary structures are current- and suspension-like. Therefore rhythmites are included with source rocks, knowing that most organic matter resulted from deposition of phytoplankton fragments (Wagner, 2004c).

In the slope area there is a problem of maturity of certain slump and debris deposits. They certainly contained large quantities of organic matter preserved in deposits moved to the deeper part of the basin such as fragments of microbial mats and buildups or grainy deposits with biolamination. It is very difficult to estimate the amount of organic matter moved by slumping, therefore values where used similar to those of the surrounding deposits.

Occurrence of microelements connected with the metabolism of algae and bacteria. The content of microelements connected with metabolism of algae and bacteria



Fig. 6. Rhythmites interbedded with packstones and thin dark biolaminae — a carbonate platform slope environment (Lubiatów-2 well, depth — 3312.0 m). Photo courtesy of Z. Mikołajewski

was analyzed in the Main Dolomite strata of 9 wells (Pokorski, 2004; Pokorski & Pokorska, 2003). Common components of living organisms as live micro- and macroelements, e.g. P, Mn, Cu, Cr, V, Ni and Zn can be indicative of intensity of organic life. Phosphorus content is most crucial for the interpretation of the range of rocks containing the organic matter. This element, apart from H, C, N, O and S occurs in significant quantities in every living organism and it is important for the metabolic processes of both the algae and the bacteria (Boyd & Lawrance, 1976; Stumm & Morgan, 1981). **Occurrence and estimation of source rock thickness.** Source rocks of microbial and algal origin commonly occur in carbonate rocks of the Main Dolomite strata (Fig. 7). They can be divided into two categories by their occurrence in specific paleogeographic areas and by biological composition: 1) source rocks of the shallow water zone where the main source of organic matter originated from benthic cyanobacteria and algae, and 2) source rocks of the deepwater zone where the main source of organic matter originated from planktonic cyanobacteria and algae.

Source rocks of the shallow water zone occur in the carbonate platform of the Main Dolomite unit. They comprise microbial rocks i.e. buildups, mats and dispersed laminae. Contribution of mudstones and wackestones is minimal.

The lowest thickness values are observed in the elevations of the barrier area, usually below 15 m, water depth, representing less than 20% of the whole profile thickness. The greatest thickness is found in the barrier slopes, both in the outer and the inner ones, where the source rocks are more than 15 m thick, usually 20 m, to a maximum of 24.3 m (Międzychód-6). The source rocks can comprise up from 30 to 50% of the profile thickness. These large thicknesses are rare in the low-energy platform flat environment. Thickness of source rocks in the shallow water zone cannot be precisely estimated. Source rocks of the very deepwater zone occur in the platform slope and the bay plain. They are represented by rhythmites with biolaminae, floatstones, and rudstones on the slope. Source rock thickness is highest in the carbonate platform slope reaching 30 m. Percentage contribution of source rocks there is over 50%, up to a maximum 65% (Sowia Góra-1 well). The bay area is recognized in one well (Gorzów Wlkp.-2), in which the entire 22.1 m section is the source rock.

Geochemical characteristics of source rocks

The attempts at making a genetic evaluation of dispersed organic matter in the Main Dolomite carbonates in the Polish Lowland were undertaken by Kotarba et al. (1998, 2000). Geochemical characteristics of organic matter (amounts, genetic types, its depositional environment and transformation degree) and evaluation of its generation potential in the Main Dolomite carbonates in the Gorzów Wielkopolski–Międzychód–Lubiatów area were based on the results of organic geochemical analyses (pyrolytic Rock-Eval, bitumen extraction, fraction distribution [saturates,



Fig. 7. Paleogeographic map of the Grotów Peninsula with thickness of the Main Dolomite source rocks



Fig. 8. Genetic characterization of bitumens from (**A**) slope of carbonate platform and (**B**) onlite reef barrier of the Main Dolomite carbonates from the Grotów Peninsula based on pristane/n-C₁₇ versus phytane/n-C₁₈ ratios

aromatics, resins and asphaltenes], biomarkers, stable carbon isotope compositions of bitumens, their fractions and kerogen, organic sulphur content in kerogen). Core samples for geochemical analyses were collected from 26 wells. Eleven wells are located in the Grotów Peninsula (wells Chrzypsko-1, 2, 3, Grotów-1, 2, Lubiatów-1, 2 Międzychód-4, 5, 6 and Sowia Góra-1), and 15 wells in the eastern part of Gorzów carbonate platform and the Noteć bay (wells Krobielewko-2, Gorzów Wlkp.-2, Gorzów Wlkp. IG-1, Jeżyki-1, Baczyna-2, Buszewo-5, Ciecierzyce-1, Dzierżów-1k, Gajewo-1, Marwice-3, Międzychód-2, Racław-1k, Santok-1, Stanowice-2 and Stanowice-3). Sampling intervals within the Main Dolomite profiles of these wells were determined basing on observations of sedimentary structures. Apart from the results of a large set of organic geochemical analyses for genetic interpretation, the results of vitrinite reflectance and maceral composition of dispersed organic matter measurements were employed (Grotek, personal communication). The geochemical characteristic was based on the analytical results of 864 core samples taken from the identified paleogeographical facies/units: carbonate platform, slope of carbonate platform, platform plain, oolite reef barrier, and a

high and a depression/bay within the basinal plain. From the analyzed population, 382 samples were selected. They met the criterion of being over the threshold of organic matter content for carbonates — TOC > 0.3 wt.%, as a starting condition for the assessment of original organic carbon content in individual paleogeographic facies/units of the Main Dolomite strata.

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Fig. 9. Genetic characterization and thermal maturity of organic matter from (A) slope of carbonate platform and (B) oolite barrier reef of the Main Dolomite carbonates from the Grotów Peninsula based on $(H/C)_{at}$ versus $(O/C)_{at}$ atomic ratios

The content of dispersed organic matter (total organic carbon) in the Main Dolomite strata is low, mainly ranging between 0.01 wt. % and 1.0 wt. %. Highest concentrations were noticed on the carbonate platform near the Gro-tów-2, Grotów-1, Międzychód-6, Chrzypsko-3, Gajewo-1, Ciecierzyce-1 and Santok-1 wells.

Evaluation of genetic type of kerogen and a degree of its thermal transformation was based on classic criteria by Espitalié & Bordenave (1993) and Hunt (1996). Oil-prone type II kerogen dominates with occasional amounts of type III or type I kerogens. Figure 8 shows the genetic characterization of bitumen from sediments of carbonate platform slopes and of oolite reef barriers from the Main Dolomite carbonates of the Grotów Peninsula based on pristane/n-C₁₇ versus phytane/n-C₁₈ ratios.

Thermal maturation of organic matter in the Main Dolomite strata was defined from Rock-Eval T_{max} temperature and indices of thermal maturation calculated from the distribution of *n*-alkanes, methylophenanthrenes and methylodibenzothiophenes as well as from the elemental composition of kerogen. The results of measurement of reflectance of vitrinite and bitumen were used as well (Grotek, personal communication). Rock-Eval T_{max} temperature values vary from 445 °C to 482 °C, which corresponds to thermal maturation of organic matter at levels of low- and high-temperature thermogenic generation processes ("oil winow" and "gas window"). Figure 9 illustrates the genetic characteristic and maturation of organic matter from sediments of carbonate platform slopes and oolite reef barriers from the Main Dolomite carbonates of the Grotów Peninsula based on $(H/C)_{at}$ versus $(H/C)_{at}$ atomic ratios.

Original total organic carbon (TOC₀) content was reconstructed with the use of Cornford method (1994). Calculated values of TOC₀ in the Main Dolomite sediments vary from 1 to about 5 wt.%. The highest values, exceeding 3% are found in deposits from the Grotów Peninsula in the vicinity of Międzychód and Chrzypsko (Fig. 10).



Simulation of hydrocarbon generation and expulsion processes — kinetic parameters of kerogen

Hydrocarbon generation is a non-reversible chemical reaction, which follows the laws of reaction kinetics. Kinetic parameters of kerogen (activation energy and Arrhenius frequency factor) can be determined by three methods. First, the classic method is the nonisothermal open-system dry pyrolysis (Rock-Eval) (e.g., Burnham & Braun, 1999; Ungerer & Pelet, 1987). A more recent method is isothermal closed-system hydrous pyrolysis (Lewan, 1985). Both methods differ in the experimental conditions, reaction products, and obtained kinetic parameters (Lewan, 1998; Lewan & Ruble, 2002). Hydrous pyrolysis is better than anhydrous pyrolysis (Rock-Eval analysis) for simulating hydrocarbon generation process because water always occurs in natural geological environments. Hydrous pyrolysis facilitates better adjustment of kinetic parameters for real kerogen, as compared to the Rock-Eval model, and it more reliably determines the extent and the timing of oil and gas generation from a source rock. Based on the method, Lewan & Ruble (2002) worked out a third, indirect method of determining kinetic parameters of kerogen, using organic sulphur content. They indicated that the mole fraction $S_{org}/[S_{org} + C]$ of immature kerogen correlates



Fig. 10. Map of original total organic carbon (TOC₀) content in the Main Dolomite carbonates from the Grotów Peninsula

with activation energy calculated from hydrous pyrolysis results. Figure 11 shows a comparison of total amounts of hydrocarbons generated and expelled from the Main Dolomite microbial-algal source rocks from the Dygo-



Fig. 11. Comparison of total amount of hydrocarbons generated and expelled from the Main Dolomite microbial-algal source rocks from the Dygowo-4 well (Pomerania region) calculated from (A and A') classic kinetic model, and (B and B') and (C and C') two variants of the new kinetic model for thermal maturity of kerogen at 0.6 and 0.8% in vitrinite reflectance scale, respectively. C — Carboniferous, Q — Quaternary, R_r — vitrinite reflectance, A — frequency factor, Ea — activation energy, S — organic sulphur content in kerogen

wo-4 well (Pomerania region). The results are from non-isothermal dry pyrolysis and two variants of the new kinetic model using isothermal hydrous pyrolysis with regard to organic sulphur content for thermal maturation of kerogen. Results from the simulation of the generation process indicated that the generation potential and the expulsion potential are 2 to 3 times higher in the new generation model than in the classic one. This kinetic model of the Main Dolomite kerogen was used for 1-D modelling of generation and expulsion processes in the Main Dolomite strata in the Gorzów Wielkopolski–Międzychód–Lubiatów area.

Modelling of hydrocarbon generation and expulsion processes and evaluation of hydrocarbon potential

Modelling of generation and expulsion processes within the Zechstein Main Dolomite carbonates in the Gorzów Wielkopolski–Międzychód–Lubiatów area were performed with the BasinMod[™] 1-D numerical program in profiles of 20 wells: Chrzypsko-3, Ciecierzyce-1, Dzierżów-1k, Gorzów-2, Grotów-1, 2, Krobielewko-2, Lubiatów-1, 2, Martwice-3, Międzychód-2, 4, 5, 6, Sowia Góra-1, Racław-1k, Santok-1, Sieraków-1, Stanowice-2 and Stanowice-3.

Theoretical bases of petroleum generation processes have been given in a number of publications, e. g. P. Allen & J. Allen (2005), Hunt (1996), Ungerer (1993), Bethke (1989), Tissot et al. (1987), England et al. (1987) and Lopatin (1983). Integrated petroleum analysis as a basis of numerical modelling of generation and expulsion processes, was presented by Ungerer et al. (1990) and Doree et al. (1993). The quantitative evaluation of hydrocarbon generation potential and expulsion potential was made employing proper parameters of kerogen for individual paleogeographic units.

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1-D modelling of hydrocarbon generation and expulsion processes in the Gorzów Wielkopolski-Międzychód-Lubiatów area indicated that microbial-algal source rocks of the Main Dolomite deposits entered the initial generation phase, exhausting by 25% of generation potential of kerogen, in the late Triassic and in the beginning of the early Jurassic. The main generation phase of liquid hydrocarbons, during which 65% of generation potential of kerogen was completed, depended on the location of a specific well at that time or slightly later, encompassing the span from the late Triassic, the early and the Middle Jurassic times up to the beginning of Late Jurassic. The final generation phase (late condensate and high-temperature thermogenic gas), during which 65 to 90% of generation potential of kerogen was completed, developed in a large time interval from the beginning of the Late Triassic to the end of the Late Jurassic, and sometimes even to the Late Cretaceous.

Hydrocarbon generation processes followed two pathways. In the first pathway, the generation process was a single-stage process with full generation of hydrocarbon mass in a continuous progression of organic matter transformation from the early to the late phase, in the late Triassic time. In the second pathway, generation took place in two stages, where 80 to 90% of hydrocarbon mass from kerogen was generated by the end of the Jurassic and the generation was completed in post-Cretaceous time. As a consequence, oil accumulated in traps at the turn of the Triassic and the Jurassic periods, and gas saturation of the oil deposit took place by the Late Jurassic, with final gas generation in the Paleogene and Neogene.

Generation potential of source rocks in the Main Dolomite strata in the Grotów Peninsula varies from 12.4 kg HC/m³ to 80.5 kg HC/m³ of source rock. For example, in the profile of the Lubiatów-1 well it is 28.0 kg HC/m³ of source rock (Fig. 12). The expulsion potential was calculated in a similar way. Its value varied from 7.6 kg HC/m^3 to 67.8 kg HC/m³ of source rock. The calculated unit surface hydrocarbon potential varies from 133 kg HC/m³ to 2052 kg HC/m² of structural surface of the Main Dolomite basin; e.g. in the profile of Lubiatów-1 well it was 804 kg HC/m^2 (Fig. 12). By referring the unit expulsion potential to the total thickness of microbial-algal source-rocks, a hydrocarbon mass transfer to migration may be defined. The calculated unit surface expulsion potential ranges between 128 kg HC/m³ and 1728 kg HC/m² of structural surface of the Main Dolomite basin, e.g. in the profile of Lubiatów-1 well it was 444 kg HC/m^2 (Fig. 12).

Conclusions — evaluation of prospective petroleum resources

Source rocks of microbial-algal origin commonly occur within the Main Dolomite strata in the Gorzów Wiel-



Fig. 12. Total amount of generated and expelled hydrocarbons from the Main Dolomite microbial-algal source rocks in the profile of Lubiatów-1 well: C — Carboniferous

kopolski-Międzychód-Lubiatów area. Largest thicknesses occur in the outer slopes of carbonate platforms, constituting more than 50% of the total thickness. Excellent conditions occur in this area for preservation of organic matter and the development of reservoir rocks. Total organic carbon (TOC) content varies from 0.01 wt.% to 1.0 wt.% (sporadically to 4 wt.%), and calculated original total organic carbon (TOC₀) content from 1.0 wt.% to about 5.0 wt.%. Oil-prone type II kerogen dominates with some admixture of type III and/or type I kerogens. Thermal maturation ranges from 0.7% to 1.3% on the vitrinite reflectance scale, which corresponds to the main and the final phases of low-temperature thermogenic processes ("oil window") and the beginning of high-temperature thermogenic processes ("gas window"). Carbonate platform slope facies seem to be the most prospective for petroleum exploration.

Microbial-algal source rocks also occur in shallow-water conditions on carbonate platforms. High salinity of sea waters was advantageous for the development of algae, and also had an influence on the formation of local reducting conditions, protecting organic matter from oxidation. Reservoir rocks are dominant in this sequence, but source rocks comprise from 20% to 50% of the profile. The total organic carbon (TOC) content varies from 0.0 to 0.5 wt.% (rarely up to 6 wt.%), and the calculated original total organic carbon (TOC₀) content from 0.8 wt.% to 2.0 wt.%. Oil-prone type II kerogen dominates sometimes with an admixture of type III or type I kerogens. Thermal maturation is from 0.8% to 1.3% on the vitrinite reflectance scale, which corresponds to the main and the final phases of low-temperature thermogenic processes ("oil window") and the beginning of high-temperature thermogenic processes ("gas window").

Microbial-algal source rocks of Main Dolomite strata in the Gorzów Wielkopolski–Międzychód–Lubiatów area entered the initial hydrocarbon generation phase in late Triassic time and in the beginning of the Early Jurassic. The main generation phase of liquid hydrocarbons occurred, depending on the location of a specific well, at that time or slightly later, covering the period from the late Triassic to the beginning of the late Jurassic. The final generation phase (late condensate and high-temperature thermogenic gas) developed in a large time interval from the beginning of the late Triassic to the end of the late Jurassic, and sometimes even to late Cretaceous time.

Hydrocarbon generation processes followed two pathways. In the first pathway, the generation process was a single-stage process with full generation of hydrocarbon mass in a continuous progression of organic matter transformation from early to late phase, in the Upper Triassic period. In the second scheme, the generation took place in two stages, where 80 to 90% of hydrocarbon mass from kerogen was generated by the end of the Jurassic period and the generation was completed in the post-Cretaceous. As a consequence, oil accumulated in traps at the turn of the Triassic and the Jurassic periods, and gas saturation of oil deposits took place by the late Jurassic time, with the final gas generation in the Paleogene and Neogene. Generation potential of source rocks in the Main Dolomite strata in the Grotów Peninsula varied from 12.4 HC/m³ to 80.5 kg HC/m³ of source rock. The expulsion potential,

calculated in a similar way, varied from 7.6 kg HC/m^3 to 67.8 kg HC/m^3 of source rock.

Geological and geochemical studies indicated that the routes of hydrocarbon migration from source rocks to reservoir rocks within the Main Dolomite strata were a few kilometres at most.

In the years from 1961 to 2000 the perspective petroleum resources have been estimated several times (Wolnowski, 2002). The petroleum resources prospective in genetic criteria with the use of results of geological and geochemical studies of microbial-algal source rocks in the Main Dolomite strata in the Gorzów Wielkopolski–Międzychód–Lubiatów area were estimated to be 228 million tonnes of hydrocarbons (Kotarba & Wagner, 2006).

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