



BALTICA Volume 35 Number 1 June 2022: 1–22 https://doi.org/10.5200/baltica.2022.1.1

Petrophysical characteristics of Silurian and Ordovician shale gas formations in the Baltic Basin (Northern Poland)

Jadwiga A. Jarzyna*, Paulina I. Krakowska-Madejska, Edyta Puskarczyk, Kamila Wawrzyniak-Guz

Jarzyna, J.A., Krakowska-Madejska, P.I., Puskarczyk, E., Wawrzyniak-Guz, K. 2022. Petrophysical characteristics of Silurian and Ordovician shale gas formations in the Baltic Basin (Northern Poland). *Baltica, 35 (1)*, 1–22. Vilnius. ISSN 0067-3064.

Manuscript submitted 27 November 2020 / Accepted 2 February 2022 / Available online 20 April 2022

© Baltica 2022

Abstract. This paper presents findings from the study into the relationships between the laboratory- and well log-derived data (including the comprehensive well-log interpretation data) on petrophysical properties of the Silurian and Ordovician shale gas formations in the Baltic Basin (North Poland). Approximately 70 samples of mudstone were examined in laboratory experiments to determine total and effective porosity; bulk, grain, and rock density; total organic carbon; physical permeability; total pore area, pore distribution; and mineral components. Some rock samples were further investigated using mercury injection porosimetry, helium porosimetry, dual liquid porosimetry, NMR, N₂ adsorption/desorption, rock-eval pyrolysis, and XRD to obtain the targeted petrophysical information from heterogeneous claystone/mudstone and their organic matter. Natural radioactivity, bulk density, total porosity, volume of kerogen, and other parameters were determined from the continuous curves plotted from the earlier depth matched well logging data, which were used to account for differences between vertical resolution of well logs and the point data obtained from the laboratory. The goal of this study was to provide a comprehensive characterization of the Silurian and Ordovician shale gas formations in Northern Poland to support the thesis about their heterogeneity.

Keywords: porosity and permeability; petrophysical model of shale with gas, Palaeozic shales, unconventional hydrocarbon deposits

☐ Jadwiga A. Jarzyna* (jarzyna@agh.edu.pl), [©] https://orcid.org/0000-0002-1803-8643, Paulina I. Krakowska-Madejska (krakow@agh.edu.pl), [©] https://orcid.org/0000-0002-8261-4350, Edyta Puskarczyk (puskar@agh.edu.pl), [©] https://orcid.org/0000-0001-5277-0507, Kamila Wawrzyniak-Guz (wawrzyni@agh.edu.pl) [©] https://orcid.org/0000-0001-6386-8171; AGH University of Science and Technology, Krakow, Poland, Faculty of Geology Geophysics and Environmental Protection

*Corresponding author

INTRODUCTION

Shale gas and tight gas reservoirs, which are considered to be unconventional hydrocarbon (HC) deposits, are heterogeneous geological formations that have very low permeability and a very complex pore space. Mudstones and claystones composing shale gas formations are fine-grained sedimentary rocks. They are both source and reservoir rocks in petroleum systems (Topór *et al.* 2017a, b; Aplin, Macquaker 2011). In the Baltic Basin (Northern Poland), such formations are represented by the Silurian and Ordovician shale gas rocks. When the total organic carbon (TOC) content is higher than 2 wt.% (2 mass percent), these shale gas formations become objects of prospecting interest (Poprawa 2010a, b; Rexer *et al.* 2014; Peters *et al.* 2015; Šliaupa *et al.* 2020).

Organic matter in shale gas rocks consists of kerogen (insoluble in organic solvents), bitumen, and solvent-soluble hydrocarbons. Being the product of the thermal maturation of solid organic matter components, gas is trapped in porous rock matrices. The large surface area and adsorption capacity of shales are related to the structure of clay minerals as well as to the primary (effective) and secondary porosity of the matrix (Topór *et al.* 2017a; Kuila *et al.* 2014; Mastalerz *et al.* 2013; Loucks *et al.* 2009). Therefore, in order to correctly determine the volume of free and adsorbed gas, it is necessary to consider the mineral composition and porosity. The organic matter content (gas in the considered forms) and clay minerals highly influence the density of the shaly rock.

In this study, a shale gas formation model was built based on the determined mineral components, porosity (total, effective), and surface area of the pore space. Two processes were considered: gas filling in micropores (< 2 nm) and gas adsorption on a specific surface in small pores (Ross, Bustin 2009; Zhou *et al.* 2000). Clay minerals influence the micropore volume and the capacity of methane adsorption (Heller, Zoback 2014; Rexer *et al.* 2014). The evaluation of shale composition and pore structure (pore volume and pore size distribution) is important for understanding methane adsorption and production in unconventional shale reservoirs (Topór *et al.* 2017b; Kuila *et al.* 2014).

In Poland, intensive studies of shale gas formations aimed at determining the potential hydrocarbon content have been conducted since the end of the 20th and the beginning of the 21st centuries (Fig. 1). Red and blue points in Fig. 1 show the efforts put in by the Polish institutions in shale gas prospecting, documentation and exploration for the purpose of designating an area for resources assessment. Many industrial investigations and research studies were undertaken to identify the specific geological structures and petrophysical parameters of the so called *sweet spots*, i.e.



Fig. 1 Location of the prospective shale gas formations in Northern Poland, Baltic Basin; the wells are marked W1, W2, and W3 (after Kiersnowski 2013; Jarzyna *et al.* 2019)

gas-enriched areas, defined as beds/formations of high total organic carbon (TOC) content (Podhalańska 2003; Modliński et al. 2006; Poprawa 2010a, b; Kiersnowski 2013; Topór et al. 2016, 2017a, b). Geological conditions of shale gas reservoirs in Poland differ from those in other countries, e.g. America, their distinctive features being deep burial (~3 km depth) and small thickness (maximum of 25 m) of the most prospective formations - sweet spots (Ja Mb and Sa Fm), high content of clay minerals (up to 50%) and relatively low porosity. Hence, the methodology elaborated for exploring foreign shale gas deposits cannot be directly adopted for exploring potential shale gas formations in Polish conditions. The shale gas formations found in the Ordovician and Silurian rocks in Poland represent an excellent example of hard, nonhomogeneous, and complex type of mudstone rock. They have not been subjected to any known equations, published descriptions, and models due to their old stratigraphic position, multi-mineral and highly variable lithology characterized by specific mineral admixtures, and deep or very deep siting.

GEOLOGICAL SETTING

The current study has investigated the Silurian and Ordovician shale formations in the Baltic Basin (Northern Poland). In three analyzed boreholes (W1–W3), the sequence of Pe, Pa, Pr, Sa and Ko formations was observed (Table 1). Boundaries between these formations are marked as lithological changes. Our attention was focused on two organic-rich, black shale objects: the Silurian Ja Member (Ja Mb) and the Ordovician Sa Formation (Sa Fm). Ja Mb belongs to the lower part of the Pa Fm and is composed of black bituminous claystone (Table 1). Its thickness is little (circa 12 m) and its average TOC value is equal to 3.0 wt.%. The highest TOC values are recorded in Sa formation (5.6 wt.% in Well 1 (W1) and 8.5 wt.% in Well 2 (W2). The average TOC in Sa formation is equal to 3.1 wt.%.

 Table 1 Sequence of the Silurian and Ordovician formations in the boreholes studied (after Jarzyna *et al.* 2019)

| Formation | Stratigraphy (age) | Type of rock |
|--|---|--------------------------------------|
| Pe (Pelplin) | Silurian, Ludlow, Wenlock | Claystone |
| Pa (Pasłęk) | Silurian, Llandovery | Claystone |
| Ja Mb (Jantar Mem- ber at the bottom of Pa Fm) | Silurian, Llandovery | Bituminous claystone |
| Pr (Prabuty) | Ordovician, Ashgil- lian | Marl, Limestone, Claystone |
| Sa (Sasino) | Ordovician, Carado- cian, Llanvirnian | Bituminous clay- stone, Claystone |
| Ko (Kopalino) | Ordovician, Llanvir- nian, Llandeilian | Limestone |

MATERIALS

The general description of the samples investigated for depth, stratigraphy, and lithology in the laboratory is presented in Table 2.

A wide variety of laboratory methods were applied for the examination of core plugs during the Blue Gas (MWSSSG) project (Jarzyna, Wawrzyniak-Guz 2017; Jarzyna et al. 2017a; Wawrzyniak-Guz et al. 2016) (Table 3). Our attention was focused on laboratory measurements of porosity and density because these parameters could be compared with the bulk density and total porosity that were continuously measured in wells or obtained from the comprehensive interpretation of well log data. The experiments were performed using specialized professional laboratory equipment. Before measuring the physical adsorption of nitrogen as well as before other experiments, the samples were degassed under vacuum at 473K overnight. The parameters measured in the laboratory experiments were subjected to statistical analysis.

The well logging data collected using the Halliburton or Schlumberger equipment were processed and subjected to interpretation employing appropriate interpretation systems. These used standard logs, such as natural gamma radioactivity (GR) and the spectral version of this log (SGR – URAN, THOR, POTA); bulk density and photoelectric absorption index (RHOB, PE); neutron porosity (NPHI); resistivity (LLD, LLS); and sonic log (DT). The results of the well log data subjected to the interpretation included total porosity (PHI); effective porosity (PHIE); volume of kerogen (VKER); volumes of lithological components in shale formations, and the volume of shale (VSH).

The interrelations between the determined parameters formed the basis for the shale gas model construction. The statistical relationships were also used for scaling continuous 1D well logging data by direct but point results from laboratory experiments. Selected interim results were presented at conferences and published (Wawrzyniak-Guz et al. 2016; Jarzyna, Wawrzyniak-Guz 2017; Jarzyna et al. 2017a, b, 2018, 2019; Puskarczyk 2019; Puskarczyk et al. 2019; Krakowska-Madejska, Jarzyna 2020; Jarzyna et al. 2020). The present paper presents the summarized findings of the performed study on petrophysical characteristics of the Silurian and Ordovician shale formations in the Baltic Basin, emphasizing the heterogeneous character of the studied formations and efficiency of the combined use of data from different information sources. Abundance of the compiled laboratory and well log data made it possible to disclose various relationships existing between them and to show difficulties arising in data processing and interpretation.

| | | Silu | irian | Ordovician | | | |
|------|---|-------------------|-----------|----------------------------|-----------|--|--|
| Wall | Depth interval | (Lland | lovery) | (Caradocian / Llanvirnian) | | | |
| well | [m] | Number of samples | Lithology | Number of samples | Lithology | | |
| | | 5 | mudstone | 16 | mudstone | | |
| W1 | 3198.1-3201.47 - Pa Fm, (Ja Mb) Llandovery; | | | 1 | limestone | | |
| | 3209.33-3234.4 - Pr Fm, Sa Fm, Ordovician | | | 1 | sandstone | | |
| | | | | 4 | tuff | | |
| | 280(2,2004 De Eng (Le Mh) Llanderson | 6 | mudstone | 17 | mudstone | | |
| W2 | 2896.3-2904 - Pa Fm (Ja Mb) Llandovery; 2018 22 2038 9 Sa Fm Caradocian/ Llanvirian | | | 1 | limestone | | |
| | 2)18.22–2)38,) – Sa Fili, Caradociali/ Elalivillar | | | 3 | tuff | | |
| | 2071 1 2002 2(| 7 | mudstone | 7 | mudstone | | |
| W3 | 28/1.1-2882.30 - Pa Fm (Ja Mb) Llandovery; 2885 54-2911 8 - Sa Fm Caradocian/ Llanvirian | | | 1 | limestone | | |
| | | | | 3 | tuff | | |

 Table 2 Laboratory data set: depth interval, number of samples, lithology, and stratigraphy

| | | Laboratory Method (in parenthesis – institutions, where the measurements were performed) | Parameter (measured applying this method) |
|---|---|--|---|
| | 1 | Water immersion porosimetry (WIP) (dual liquid porosim- etry); a prototype set for water/light kerosene immersion porosimetry (dual liquid porosimetry) (Topór <i>et al.</i> 2016) | Grain density (GD_WIP), Total porosity (Φ_WIP) |
| | 2 | Mercury injection porosimetry (MIP); AutoPore IV 9500, Micromeritics Instrument Corporation (AGH UST) | Bulk density (BD_Hg), skeletal density (SD_Hg), total pore area (TPA), effective porosity (Φ _Hg) |
| | 3 | Pressure decay permeability (PDP); PDP Terra Tek Schlum- berger Reservoir Laboratory | Permeability (K_PDP), bulk density (BD_PDP) |
| ĺ | 4 | He pycnometry; AccuPyc 1330 (AGH UST) | density (D_He) |
| | 5 | NMR; Maran Ultra 23 MHz spectrometer (AGH UST) | Total porosity (Φ _nmr_tot), effective porosity (Φ _nmr_eff), irreducible water saturation (Sw irr) |
| | 6 | Physical adsorption of nitrogen; Quantachrome Autosorb-1C automatic gas adsorption apparatus (AGH UST) | Specific surface (S_BET), total pore volume with diameters < 350 nm - V_tot) |
| | 7 | Rock-Eval pyrolysis; Rock-Eval 8 (AGH UST) | Total organic carbon (TOC) |

METHODS

The laboratory experiments that were conducted in this study for obtaining the targeted information (mainly on density and porosity) on properties of shale gas formations were based on various physical phenomena.

Mercury injection porosimetry (MIP) (Webb 2011) was used to measure porosity (total and effective), density (bulk and specific) and total pore area, which are especially important for understanding rock formation structure. The pore diameter determined using MIP was found to range from approximately 0.3 μ m to 360 μ m.

Gas sorption and mercury injection porosimetry are complementary techniques. **Physical adsorption** / **desorption of nitrogen at 77 K** were used to examine the porous texture, i.e., the pore size distribution and specific surface area, providing especially important data on pores, from extremely small (nanometer level) to approximately 0.00035 mm-sized pores. The Brunauer-Emmet-Teller (BET), Barrett-Joyner-Halenda (BJH), and quenched solid density functional theory (QSDFT) techniques were used for the interpretation of nitrogen adsorption isotherms (Thommes *et al.* 2015; Rouquerol *et al.* 2014; Gor *et al.* 2012; Thommes 2010).

NMR petrophysical experiments performed in the laboratory and in boreholes are based on nuclear magnetic relaxation of protons in hydrogen atom nuclei. In sedimentary reservoirs, hydrogen is present in the pore space as formation water, and hydrocarbons, as OH groups and bound water in clay minerals. Hydrogen is also present in chemically bound water (for instance, in gypsum). In NMR experiments, the proton signal amplitude, spin-lattice relaxation time T_{1} , and spin-spin relaxation time T₂ are measured to provide information on porosity, permeability of reservoir rocks, the porous space structure, and the type of the liquid filling rock pores (Coates et al. 1999). Individually selected T₂ cut-offs adopted in the quantitative interpretation of NMR signals enable the calculation of the proper bound water volume and movable media in reservoirs (Puskarczyk 2011). NMR signals registered in the first few hundred milliseconds are very important because shales have fast relaxation times. In organic shales, hydrogen is observed in the bounded part of porosity. Also, kerogen- and clayassociated microporosity is visible in NMR signals (Coates et al. 1999; Kleinberg 1999), thus surface relaxation dominates the measured T_2 relaxation time. Due to high heterogeneity of shales and separation between the smallest and largest time scales, broad NMR spectra are observed (Watson, Chang 1997). Additionally, the presence of internal gradients can affect the accuracy of the measured signal and result in the overestimation of the NMR porosity determined from T_2 (Washburn 2014; McPhee *et al.* 2015). Two evolution times (TAU = 200 and 1000 µs) were adopted to obtain the broadband T_2 distributions for all the samples and to compare them with the standard evolution time. Standard cutoffs were used for the interpretation (Coates *et al.* 1999).

Pressure decay permeability method (PDP) was employed to provide data on matrix permeability, which, together with bulk density, is measured from the crushed grains of shale or mudstone (TRA Glossary 2016). Crushing of shales/mudstones provides access to the pore space and enables removal of artifacts or unnatural features from the rock under study, thus enhancing the accuracy of the data obtained. However, pressure decay is only partly valid for silty, laminated shales, and is not valid for sand-stones or tight gas sandstones.

Water immersion porosimetry (WIP) based on deionized water in combination with light kerosene immersion porosimetry (KIP) (Topór et al. 2016) was employed to perform total porosity measurements. The combination of WIP and KIP methods and the use of kerosene and water as saturation-immersion liquids form the basis of the porosity measurement technique called dual-liquid porosimetry (DLP). Using WIP, the rock grain density (GD) together with rock porosity was determined. The experiments were performed at the Research Centre of the Institute of Geological Sciences of the Polish Academy of Sciences in Krakow. The reason why the grain density determined applying the KIP method was lower than that obtained using WIP was incomplete pore saturation with kerosene due to the presence of residual water in small diameter pores. This effect indicates the maximum volume of liquid hydrocarbons in pores of geological formations (Topór et al. 2016).

Gas pycnometer (AccuPyc 1330) was used for rock density determination (AccuPyc 2001). Helium gas has a minimal particle size, is free from reaction with other substances, and adsorbs at room temperature thus, its use enables the investigation of rock samples with highly complicated pore systems.

The Rock-eval pyrolysis method is well described in many papers (among others Kotarba *et al.* 2014). This method is used to provide data on: total organic carbon (TOC), free hydrocarbons (S1), hydrocarbons generated through thermal cracking (S2), and also on other parameters useful in characterizing rock formations rich in organic matter.

RESULTS

The geological formations composing the Silurian and Ordovician deposits discussed in this study are heterogeneous, which is, on the one hand, due to the impact of geological, sedimentological, mineralogical, geochemical, and petrophysical factors, and on the other, due to the impact of factors associated with the construction of well logging devices. It is difficult to assess the combined impact of these factors on the heterogeneous character of the geological formations under study. Therefore, in this study, numerous laboratory measurements of the same part of the rock were performed employing various, different physical phenomena-based methods, based on which the most probable relationships between the obtained parameter values were predicted. These were further validated by the relationships between the respective parameters derived from well logging. The obtained results illustrate existence of the interaction among the investigated lithological variables, shale gas reservoir parameters, hydrocarbon production potential, and other variables characterizing shale rock formations.

Results – density

This paper presents results of the comparison made between the rock density data obtained applying different laboratory methods, i.e. grain density determined by water immersed porosity (GD WIP), bulk density determined by mercury injection porosimetry (BD Hg), rock density determined by helium pycnometer (D He), and bulk density determined by pressure decay permeability (BD PDP) (Fig. 2). The amount of correlated data is limited to the smallest number of PDP results, which are presented on the horizontal axis in the plot. The best matching is observed between the grain density GD WIP and the rock density data D He. Data scattering in this group is distinctly lower than in the group of the bulk density data obtained applying MIP. The lowest density values were obtained by mercury injection porosimetry, and the highest ones by water immersed porosimetry. These results confirm that helium pycnometer and water immersed porosimetry can provide grain/ rock density and MIP - bulk density.

The BD_Hg values are very similar to those of the bulk density derived applying the pressure decay permeability method (BD_PDP). Scattering of the BD_Hg values implies that Hg particles penetrate the pore space in the rock incompletely (Jarzyna *et al.* 2017b).

A similar comparison was made between the bulk density log values (RHOB) and those determined in the laboratory (Fig. 3). In both wells W2 and W3, the



Fig. 2 Relationship between the bulk density determined by MIP, BD_Hg (dark blue), grain density derived by the water immersed porosity method, GD_WIP (green), and density derived by helium pycnometry, D_He (red), and the bulk density derived by pressure decay permeability method (BD_PDP) (Jarzyna *et al.* 2017b)





Fig. 3a Collective plot of laboratory-derived densities in W2 ν s. bulk density log data

Fig. 3b Collective plot of laboratory-derived densities in W3 *vs.* bulk density log data

| Table 4 | Simple d | lensity s | tatistics | derived | from we | ell l | logs and | laboratory | measurements and | la | boratory | TOC | values |
|---------|----------|-----------|-----------|---------|---------|-------|----------|------------|------------------|----|----------|-----|--------|
|---------|----------|-----------|-----------|---------|---------|-------|----------|------------|------------------|----|----------|-----|--------|

| | RHOB [g/cm ³] | | | BD_Hg [g/cm ³] | | | D_He [g/cm ³] | | | GD_WIP [g/cc] | | | TOC [wt.%] | | |
|-----|---------------------------|------|------|----------------------------|------|------|---------------------------|------|------|---------------|------|------|------------|------|------|
| | W1 | W2 | W3 | W1 | W2 | W3 | W1 | W2 | W3 | W1 | W2 | W3 | W1 | W2 | W3 |
| Min | 2.23 | 2.41 | 2.37 | 2.23 | 2.23 | 2.33 | 2.56 | 2.56 | 2.55 | 2.57 | 2.46 | 2.50 | 0.06 | 0.1 | 0.01 |
| Max | 2.74 | 2.68 | 2.70 | 2.61 | 2.60 | 2.53 | 2.74 | 2.75 | 2.72 | 2.74 | 2.79 | 2.74 | 4.98 | 6.35 | 7.15 |
| Avg | 2.57 | 2.55 | 2.57 | 2.42 | 2.42 | 2.43 | 2.65 | 2.66 | 2.68 | 2.66 | 2.64 | 2.67 | 1.52 | 2.06 | 1.70 |

bulk density values derived by MIP were the lowest and highly scattered. In W3, the two groups of data were almost comparable; the values of the grain density GD_WIP and those of the rock density D_He were slightly higher than the RHOB values derived from logging runs. In W2, the D_He and GD_WIP values were distinctly higher than those of RHOB. Such results suggest that in the investigated formations (Ja Mb and Sa Fm) in both wells, gas originates in different ways. It partially fills effective pore spaces in the matrix and organic matter, and is partially adsorbed on the skeleton.

The rock density values obtained applying the helium pycnometer method (D_He) showed the greatest similarity with the minimum, maximum and average rock density log values from three wells (Table 4), which can be partly explained by the method applied and partly by similarity in the composition of the investigated samples' matrix. The average value of the bulk density derived by MIP is close to that recorded in the three wells explored, but the minimum and maximum values differ. The greatest differences were observed in the grain density (GD WIP). Rock density values are depth-dependent, which is because of the pressure impact. However, in the formations studied, the impact of depth was indistinct, because the investigated depth intervals were similar (Table 2). The volume of organic matter also belongs to the parameters affecting rock density. The average value of TOC in W2 was the highest, and it may be concluded that the lowest maximum value of BD Hg in this well is due to the high organic matter volume. Also, it is assumed that organic matter partially fills the porous space. Different plots presented in Figs 3a and b confirm that characteristics of shale formations in two wells differ.

Results – porosity

The petrophysical parameter values of the studied rock formation samples (mudstones and tuff) derived in the laboratory applying MIP, NMR, and N_2 adsorption/desorption methods are presented in Table 5. The current study was performed on the samples representing the heterogeneity of the studied rock formations.

The results obtained by applying the MIP method are presented in Fig. 4. There are four graphs for each sample with the horizontal axis showing the pore diameter, and the vertical axes displaying the total pore volume, total pore area, incremental pore volume, and the incremental pore area, respectively.

Results of the NMR experiment are provided in Fig. 5. Time in microseconds is presented on the horizontal axis, and the amplitude of a signal is given in conventional units on the vertical axis. Exemplary T₂ relaxation times recorded using TAU = 200 μ s (blue) and TAU = 1000 μ s (red) are presented in Fig. 5a to show the importance of the proper adoption of the signal evolution time. The NMR signal recorded using short TAU shows a distinctly higher amplitude, indicating higher total and effective porosities. Such a result may be explained by the fact that the major part of the signal was generated by hydrogen in bound water in nano- and micropores of shales (in some cases, it is the total signal). All samples (recorded with TAU $= 200 \text{ } \mu\text{s}$) were subjected to the interpretation. Total and effective porosities were calculated together with the volume of irreducible water (Table 5). A collective plot of T₂ distributions in W1–6 and W2–4 rock samples (mudstones of Ja Mb) as well as in W1-15 and W2-13 rock samples (mudstones of Sa Fm) is presented in Fig. 5c. For comparison, similar plots of Sa Fm mudstone (W2-13), Pr Fm mudstone (W3-7), and Sa Fm tuff (W3-14) are shown in Fig. 5e. The respective cumulative signals are presented in Figs 5d and f. These plots and the parameter values presented in Table 5 support the thesis that the shales studied are highly heterogeneous.

Figure 6 presents N2 adsorption/desorption isotherms and the pore size distributions obtained by combining MIP-derived results with those of N2 adsorption (BJH and DFT models). Shales display mesoporosity and the nitrogen adsorption isotherms are ascribed to Type IV (isotherms with hysteresis loop) according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Donohue, Aranovich 1998). Nitrogen volume plots as a function of relative pressure at standard temperature and pressure (STP) are presented in Figs 6a, c, e, and g. The volume increment per increment of pore diameter as a function of pore diameter is presented in Figs 6b, d, f, and h. A significant amount of gas adsorbed at low relative pressure is linked to microporosity of the formation (Figs 6a, c, e, and g). When relative pressure increases to about 0.85, the volume of adsorbed gas significantly increases, and the monolayer adsorption begins shifting towards the multilayer type. At a relative pressure above 0.85, the volume of adsorbed gas increases again due to capillary condensation, and the adsorption and desorption branches of the isotherm do not coincide. As a result, a hysteresis loop is formed and its shape depends on the pore structure. The observed shapes of hysteresis loops are complex, which is probably due to the combination of several pore types. The isotherm shapes of all the studied rock samples were similar. The height of the shift between the adsorption and desorption curves (Figs 6a, c, e, and g) is different and depends on the volume of mesoporosity. The pore size distributions obtained applying the nitrogen adsorption method and the mercury intrusion method show good correlations, and the most promising approach seems to be DFT. QSDFT, which takes into account differences in pore geometry, makes it possible to specifically describe both micro- and mesopores without reference to the adsorption mechanism. As can be seen from all the plots (Figs 6b, d, f, and h), the initial part of the DFT curve starts at very small pore diameters. The combined application of the two methods made it possible to extend the investigated pore diameter interval to 0.8 nm and reveal additional maxima in

Table 5 Petrophysical parameters of the selected rock samples (mudstones and tuff): Ja Mb, Sa Fm, and Pr Fm

| Method | | М | IP | | | NMR | N ₂ ads/des | | |
|-----------------------|----------------------|----------------------|------|---------------------|----------------|------------------|------------------------|-----------|----------------------|
| Parameter/ | BD_Hg | SD_Hg | Φ_Hg | TPA | Φ_nmr_tot | Φ_{nmr_eff} | Swirr | S_BET | V_tot |
| sample | [g/cm ³] | [g/cm ³] | [%] | [m ² /g] | [%] | [%] | [%] | $[m^2/g]$ | [cm ³ /g] |
| W1-6/Ja Mb; mudstone | 2.54 | 2.57 | 1.06 | 1.81 | 3.32 | 1.11 | 66 | 9.4 | 0.027 |
| W2–4/Ja Mb; mudstone | 2.34 | 2.38 | 1.77 | 3.07 | 3.35 | 0.34 | 90 | 8.2 | 0.024 |
| W1-15/Sa Fm; mudstone | 2.52 | 2.55 | 1.26 | 2.80 | 9.66 | 2.22 | 77 | 21 | 0.031 |
| W2–13/Sa Fm; mudstone | 2.36 | 2.42 | 1.92 | 4.34 | 6.53 | 0.76 | 88 | 7.2 | 0.023 |
| W3–14/Sa Fm; tuff | 2.49 | 2.54 | 1.83 | 4.69 | 3.07 | 1.16 | 62 | 6.8 | 0.020 |
| W3–7/Pr Fm; mudstone | 2.58 | 2.62 | 1.43 | 3.09 | 2.36 | 0.77 | 67 | 7.1 | 0.024 |



Fig. 4a Cumulative pore volume [mL/g] vs. pore diameter [μ m]



Fig. 4b Cumulative pore area $[m^2/g]$ vs. pore diameter $[\mu m]$



Fig. 4c Incremental pore volume [mL/g] vs. pore diameter [μ m]



Fig. 4d Incremental pore area $[m^2/g]$ vs. pore diameter $[\mu m]$

the section with the smallest diameters. Large anomalies in Figs 6b, d, f, and h indicate a large group of small pores included in the gas movement network. It is important to note that only the DFT model provides additional information about the microporosity of the formation.

The examined samples represent Ja Mb and Sa Fm mudstones from wells W1 and W2. The MIP-derived



Fig. 5a T, distribution in W1-6 sample, Ja Mb



Fig. 5b T_2 distribution in W1-15 sample, Sa MbFig. 5c. Collective presentation of T_2 distributions in selected samples of Ja Mb and Sa Fm



Fig. 5c Collective presentation of the cumulative signals' amplitude in selected samples of Ja Mb and Sa Fm

effective porosity shows the highest values for the mudstone samples W2-4 and W2-13. These samples also exhibit high values of porosity as determined by the NMR experiment (Φ _nmr tot and Φ _nmr eff) (Table 5). However, the highest NMR porosities were recorded in W2-13 sample. The highest cumulative volume of pores in this sample is shown in Fig. 4a. The NMR signals from these samples are also the



Fig. 5d Collective presentation of T_2 distributions in selected samples of Sa Fm and Pr Fm



Fig. 5e Collective presentation of the cumulative signals' amplitude in selected samples of Sa Fm and Pr Fm



Fig. 5f Collective presentation of the cumulative signals' amplitude jn selected samples of Sa Fm and Pr Fm



Fig. 6a $\rm N_2$ adsorption/desorption isotherms, W1-6 sample, Ja Mb



Fig. 6b Pore size distribution derived from the combined results of N_2 adsorption (BJH model), MIP, and density functional theory, W1-6 sample, Ja Mb



Fig. 6c $\rm N_2$ adsorption/desorption isotherms, W2–4 sample, Ja Mb



Fig. 6d Pore size distribution derived from the combined results of N_2 adsorption (BJH model), MIP, and density functional theory, W2-4 sample, Ja Mb



Fig. 6e $\rm N_2$ adsorption/desorption isotherms, W1-15 sample, Sa Fm



Fig. 6f Pore size distribution derived from the combined results of N_2 adsorption (BJH model), MIP, and density functional theory, W1-15 sample, Sa Fm



Fig. 6g $\rm N_2$ adsorption/desorption isotherms, W2-13 sample, Sa Fm



Fig. 6h Pore size distribution derived from the combined results of N_2 adsorption (BJH model), MIP, and density functional theory, W2-13 sample, Sa Fm

largest (Figs 5c and d). The total pore area of sample W2-4 is the largest, while pore area values in other samples, apart from the W1-6 one, are comparable (Fig. 4b). As shown in Table 5, the W2-4 and W2-13 samples exhibit the highest values of TPA. Swirr values were also found to be high. Sample W1-15 also showed high values of Φ nmr tot and Swirr, and the highest value of S BET. Also, this sample had a high NMR signal amplitude and the highest value of V tot. The relatively high MIP-derived effective porosity and NMR-derived total porosity indicate that pores of the examined rock sample range widely in size and include micro- and meso-pores. Plots of the incremental pore volume (Fig. 4c) and incremental pore area (Fig. 4d) show similar features, although the W2-4 sample is distinguished by higher amplitudes. The highest values of S BET (21 m^2/g) and V_tot (0.027 ccm/g (Table 5) in sample W1-15 are visually confirmed in Fig. 6h by the maximum at 0.966 nm. In Fig. 6a, sample W1-6 (1.05 nm) shows a similar spike, but figures on the vertical axis differ: 0.0151 and 0.0043, respectively. S BET and V tot values in W1-6 sample are also high: 9.4 m²/g and 0.021 cm/g, respectively.

Results – mineral composition

The mineral composition of the studied rock formations was determined based on XRD measurements following the methodology described by Środoń et al. (2001). Powder rock samples were milled in methanol for 5 min with 10% ZnO used as an internal standard addition. Side loading was applied to ensure the most reproducible clay particle disorientation. A Thermo X'TRA diffractometer was used to record data. Measurements and interpretation employing a domestic computer program were performed in the Research Centre in Krakow, Institute of Geological Sciences, PAS, (Jarzyna, Wawrzyniak-Guz 2017). The main goal of the interpretation program was to compare the real result recorded for the sample with the sum of standard patterns obtained for the minerals that were assumed to compose the investigated rock. This comparison was repeated to obtain the minimal difference (Omotoso et al. 2006). The following minerals were determined in the studied rock samples: quartz, orthoclase, plagioclases, calcite, dolomite, pyrite, hematite, anatase, a group of illite and smectite, and chlorite, as well as organic matter.

Figure 7 presents histograms illustrating the mineral composition of the following samples: W1-6, Ja Mb; W-15, Sa Fm; W2-4, Ja Mb; W2-13, Sa Fm; W3-7, Pr Fm and W3-14, Sa Fm. Table 5 shows the petrophysical parameters of the same samples, and Figs 4–6 present MIP, NMR, and N_2 adsorption/desorption plots for the samples. The volumes and sums

of the minerals are presented as follows: 1 – quartz, 2 - orthoclase + plagioclases, 3 - carbonates (calcite + dolomite), 4 - iron- and titanium-containing minerals (pyrite, hematite, anatase), 5 - clay minerals (sum of the illite and smectite group and chlorite), and 6 organic matter. As confirmed by the values presented in Table 6, the mineral composition of the examined rock samples differs markedly. Differences between the hydrocarbon productivity potential in Ja Mb and Sa Fm (as sweet spots) determined on the basis of organic matter and compared with Pr Fm are presented. The estimated volume of quartz in the investigated rock samples is also very different. In Sa Fm alone, the volume of quartz was found to vary from 27.5% (W1-15) to 64.6% (W3-14). The minimum percentage of quartz was recorded in marls and carbonates of Pr Fm. The



1 2 3 4 5 6

Fig. 7 Simplified presentation of the mineral composition in the selected rock samples; first row: left pie chart – sample W1-6, Ja Mb, right pie chart – sample W1-5, Sa Fm; second row: left pie chart – sample W2-4, Ja Mb, right pie chart – sample W2-13, Sa Fm; third row: left pie chart – sample W3-7, Pr Fm, right pie chart – sample W3-14, Sa Fm; 1 – quartz, 2 – orthoclase + plagioclases, 3 – carbonates (calcite + dolomite), 4 – iron- and titanium- containing minerals (pyrite + hematite + anatase), 5 – clay minerals (sum of illite and smectite group and chlorite), 6 – organic matter

| Sample | Depth [m] | Quartz [%] | Orthoclase + plagioclases [%] | Calcite ^A + dolomite ^B [%] | Pyrite + hema- tite + anatase [%] | Clay Minerals ^c [%] | Organic matter [%] |
|--------------|-----------|---------------|-------------------------------------|--|---|--------------------------------------|--------------------|
| W1-6, Ja Mb | 3209 | 33 | 3.1 | 5.7 | 1.4 | 56.4 | 0.5 |
| W1-15, Sa Fm | 3225.5 | 27.5 | 4.8 | 2.1 | 2.7 | 62.5 | 0.4 |
| W2-4, Ja Mb | 2900 | 23.1 | 2.8 | 2.8 | 3.7 | 60.5 | 7.1 |
| W2-13, Sa Fm | 2925 | 28.5 | 3.8 | 4.2 | 2.4 | 57.7 | 3.3 |
| W3-14, Sa Fm | 2911 | 64.6 | 1.7 | 3.5 | 2.5 | 27.2 | 0 |
| W3-7, Pr Fm | 2885 | 24.1 | 3.3 | 33.9 | 2.3 | 36.1 | 0.4 |

Table 6 Mineral composition in the selected samples of shale

^A including magnesium calcite; ^B sum of dolomite + low Fe ankerite + high Ca dolomite;

 c sum of the mixed layer clay mineral illite-smectite + illite + dioctahedrite Al smectite + dioctahedrite Al mica (like muscovite) + chlorite + trioctahedrite layer mineral 1:1 type + mixed layer variety of the latter two minerals.

proportion of quartz, plagioclases, and carbonates to clay minerals is also different, which implies that conditions for their fracturing were different. Mudstone sampled from W2-4, Ja Mb, exhibited the lowest bulk and specific densities (Table 5), which was related to the highest porosity. However, that sample was also found to contain the highest volume of iron-bearing minerals and the lowest volume of organic matter. All these components influence both bulk and specific densities. The W3-7, Pr Fm sample contained a high volume of carbonates, a relatively low volume of quartz, and a very low volume of clay minerals (the lowest is characteristic of W3-14, Sa Fm). Organic matter volume in that sample was estimated at level 0.4, the same as in the mudstone sample W2-4. Tables 5 and 6 and the plots in Figs 4–7 illustrate a great diversity of the studied shales.

Results – permeability

Physical permeability of the rocks under study was determined using the following methods: mercury injection porosimetry, pulse decay permeability (plug method), and pressure decay permeability (matrix permeability measured on crushed crumbs of mudstone). The obtained permeability results cannot be directly compared due to differences in measurement approaches and technical difficulties arising in plug cutting. The MIP-derived permeability is calculated on the basis of porosity and density measurements, assuming that pores have a certain shape. The pressure decay method measures the minimum permeability of shale/mudstone, while pulse decay permeability measures the maximum permeability of the silt portion of the laminated shale system. A direct proportionality was observed to exist between the permeability derived applying pressure decay method (higher values) and the permeability derived applying MIP (lower values). However, the correlation between the above mentioned results was weak although the order of magnitude was the same. High

data scattering was observed, similar to that of the discussed density data (Fig. 2). The highest values of permeability were obtained applying the plug method. However, they were affected by natural fractures if they were present, and contained no natural artifacts/microfractures from coring and cutting procedures that could artificially increase permeability values. The relationship between the total volume of pores with diameters < 350 nm (V tot) derived by the N₂ adsorption/desorption method and the pressure decay-derived permeability (K PDP) is given in Fig. 8a, and the relationship between the sum of clay minerals (illite, smectite group, and chlorite) and K PDP is presented in Fig. 8b. The number of samples was limited by PDP measurements. The presented relationships showed that permeability is inversely related to the total volume of pores with diameters < 350 nm and the clay content, and there is a direct proportionality between the volume of organic matter (OM) and K PDP (Fig. 8c). Inverse proportionality between V_tot and K_PDP means that volumes of micro/nanopores are not involved in media flow, and that gas may be inside. Direct proportionality between OM and permeability implies that secondary porosity resulting from organic matter maturity is included in the connected pores network.

Results – relationships between laboratory and well log results

Correlations between the data obtained applying different methods (laboratory and well logging) were examined to show that the data obtained from these two information sources are compatible and can extend the knowledge of shale formations. Laboratory data were derived from the examination of small or very small rock samples collected from the selected core depth intervals. In contrast, well logging data are continuous but averaged and can be distorted by the investigation radius and the vertical resolution of the logging devices used.



Fig. 8a Relationship between the total pore volume with diameters < 350 nm (V_tot) derived applying the N₂ adsorption / desorption method and the pressure decay-derived permeability



Fig. 8b Relationship between the sum of clay minerals and the pressure decay-derived permeability



Fig. 8c Relationship between the volume of organic matter and the pressure decay-derived permeability

Figure 9 shows the determined correlation between the laboratory-derived TOC and bulk density data (RHOB) based on well logs. The data in Table 5 and in the plots presented in Fig. 9 confirms that characteristics of the two *sweet spots* under study differ. The laboratory-derived TOC in Ja Mb is higher and the Ja Mb data are more consistent (the determination coefficient for the Ja Mb relationship is almost twice as high as that for Sa Fm). Data scattering in the Sa Fm plot is more distinct, indicating higher heterogeneity of this formation.

Similar formation characteristics are indicated by the data presented in Fig. 10, where the total porosity data obtained using dual liquid porosimetry (Φ DLP) are compared with the well log-derived bulk density data, and, also, by the data given in Fig. 11, where the grain density (GD WIP) data are compared with the bulk density (RHOB) data. As can be seen from the plot, the Sa Fm data are highly scattered, while the Ja Mb data are assembled along the trend line. The direct proportionality determined between the porosity and bulk density data (higher determination coefficients for GD WIP) implies that such organic matter as kerogen and gas is associated with porosity and matrix. In Ja Mb, this relationship was found to be stronger than in Sa Fm, leading to the assumption that in Sa Fm, organic matter is also present in the matrix.

It is also of interest to consider the relationships between the volume of kerogen (VKER) and total porosity (PHI) or shaliness (VSH) determined based on the comprehensive interpretation of the respective log data. On this basis, it is possible to assume that kerogen and hydrocarbons are associated with porosity, i.e., organic matter partially fills the pores, or that organic matter is related to shaliness, which is understood to be the volume of clay minerals and uranium closely related to them. Figure 12 presents the relationship between Φ DLP and VKER as an exponential function, with the determination coefficient equal to 0.44 for Ja Mb. A higher porosity and lower VKER means that part of the pore volume is occupied by organic matter. The gas produced as a result of kerogen maturation may also accumulate in the pore space. The Sa Fm data are scattered, with no regular dependence between the compared data.

Robustness of shale gas models depends on all the factors involved in these relationships. Figures 13 and 14 illustrate the relationships between laboratory data and those derived from the interpretation of log data for three wells, i.e., between laboratory measurements of TOC and the well log-derived volume of kerogen (VKER) and shaliness (VSH), respectively. A direct proportionality was observed to exist between the data presented in Fig. 13, i.e., an increase in VKER was observed to cause an increase in TOC, the determination coefficient of this dependence being 0.54 for the data from Ja Mb and Sa Fm processed together. The data presented in Fig. 14 exhibit a similar dependence; however, no direct proportionality is observed to exist between these data. It should be noted that data of the comprehensive well log interpretation also confirm the presence of kerogen (VKER) and shaliness (VSH). The presented results show that in the formations under study, especially in Sa Fm, organic matter is associated not only with clay minerals.

Figure 15 shows the relationship between the volume of pores with diameters < 350 nm (V_tot), de-



Fig. 9 Relationships between the laboratory-derived TOC content and the bulk density derived from the density log (RHOB) for three wells: W1, W2, and W3



Fig. 10 Relationships between the total porosity data derived using dual liquid porosimetry (Φ _DLP) and the bulk density derived from the density log (RHOB) for three wells: W1, W2, and W3



Fig. 11 Relationships between the grain density data derived using water immersed porosimetry (GD_WIP) and the bulk density derived from the density log (RHOB) for three wells: W1, W2, and W3



Fig. 12 Relationship between the total porosity data obtained using dual liquid porosimetry (Φ _DLP) and the volume of kerogen derived from the comprehensive well log interpretation



Fig. 13 Cross-plot of the laboratory-derived TOC vs. the well log-derived volume of kerogen (VKER)



Fig. 14 Cross-plot of the laboratory-derived TOC vs. the well log-derived shaliness (VSH)



Fig. 15 Relationship between the total volume of pores with diameters < 350 nm derived from N₂ adsorption/desorption isotherms (V_tot) and the volume of kerogen (VKER) derived from the comprehensive well log interpretation

termined using N_2 adsorption/desorption isotherms and the volume of kerogen (VKER) derived from the comprehensive well log interpretation. A decrease in the pore volume with an increase in the kerogen volume implies that insoluble organic matter (kerogen) has not filled in very small diameter pores.

The plots presented in Figs 9–15 are constructed based on the data for three wells. Figure 16 presents plots based on the data for only one well (W1) and Sa Fm. A distinct inverse proportionality is observed to exist between the laboratory-derived TOC and shaliness (VSH) derived from the comprehensive well log interpretation, and a direct proportionality between the laboratory-derived TOC and the total porosity (PHI) derived from the comprehensive well log interpretation. The decrease in TOC with an increase in VSH means that gas has filled in the pore space. The increase in TOC with that in PHI also confirms the assumption that gas has filled in the pores.

The three red points at the largest TOC values (Fig. 16b) do not follow the general trend, which means that in the Sa Fm, kerogen or adsorbed gas may also be present in the matrix. This is confirmed by the relatively low density in the Sa Fm matrix (Table 4).



Fig. 16a The laboratory-derived TOC *vs.* the volume of shale (VSH) derived from the comprehensive log interpretation for well W1 in Sa Fm



Fig. 16b The laboratory-derived TOC *vs.* the total porosity derived from the comprehensive log interpretation for well W1 in Sa Fm

It is known from the macroscopic description of these samples that graptolites occur in these less calcareous mudstones. A relatively low volume of quartz and a high volume of pyrite are also recorded. No other minerals identified in this formation are present in anomalous volumes.

Relationships between the kerogen volume (derived from the comprehensive interpretation of well logging) and GR log as well as between the kerogen volume and URAN log are presented to demonstrate the importance of natural radioactivity logging for indicating the presence of organic matter. GR or spectral GR is a good indicator of organic matter. Both logs can be used interchangeably, although the correlation is higher for URAN (Fig. 17). Similar relationships were recorded in other wells.

Figure 18 presents the kerogen volume against total porosity, PHI (Fig. 18a, c), and effective porosity, PHIE (Fig. 18b, d) in wells W2 and W3, respectively. Values of both porosity types were determined from the comprehensive interpretation results. Two branches are observed in Fig. 18a for low values of total porosity (< 3%), and both branches exhibit the same dependence: lower VKER values are recorded



Fig. 17a Relationships between the kerogen volume derived from the comprehensive well log interpretation and natural radioactivity in well W1



Fig. 17b Relationships between the kerogen volume derived from the comprehensive well log interpretation and URAN content in well W2

at higher values of PHI for both formations (Ja Mb and Sa Fm). An increase in the kerogen volume with porosity suggests the presence of kerogen in the pore space of the shale formation. Splitting of Ja Mb data into two distinct groups shows that two different volumes of kerogen can be detected at the same porosity. This means that kerogen in Ja Mb is present in two forms, i.e., it partially fills in the pore space and exists in the matrix as organic matter (Fig. 18a).

There is no visible, distinct relationship observed to exist between the above-mentioned parameters at the porosity value ranging between 3% and 4%. Two values of the kerogen volume at the same total porosity value can be explained by the fact that in the rock, organic matter is present in two forms, i.e., as a pore space filler and as a constituent part of the matrix. As can be seen from the plot, relationships between VKER and PHI data for Ja Mb and between the data for well W3 in Sa Fm are similar. In this plot, only one branch is visible. The plot showing the VKER vs. PHIE relationship (Fig. 18b) for well W2 presents a different picture for Sa Fm. In this plot, data scattering is great compared with that in Figs 18a and c. Effective porosity (PHIE) is considered as the value



Fig. 18a Cross-plot of the kerogen volume (VKER) *vs.* total porosity (PHI); W1 well



Fig. 18b Cross-plot of the kerogen volume (VKER) *vs.* effective porosity (PHIE); W2 well



Fig. 19a Comparison of the kerogen volume data derived from the ULTRA comprehensive interpretation and those from GEM log calculations, W3 well, Ja Mb

unaffected by shaliness. Elimination of the shaliness effect on porosity partially reduces the presence of organic matter related to clay minerals in the rock matrix structure. Data for the W3 well display a different picture (Fig. 18d). Scattering of the data does not allow observing any of the above discussed correlations.

A special comparison can be made of the dataset obtained from the W3 well, where the kerogen vol-



Fig. 18c Cross-plot of the kerogen volume *vs.* total porosity, W3 well



Fig. 18d Cross-plot of the kerogen volume *vs.* effective porosity, W3 well



Fig. 19b Comparison of the kerogen volume results from the ULTRA comprehensive interpretation and those from GEM log calculations, W3 well, Sa Fm

ume was calculated from the comprehensive well log interpretation using the ULTRA program (Halliburton) and the one derived from the GEM log interpretation (Fig. 19).

Basic relationships between the parameters determined in laboratory experiments and those obtained from well logs and their comprehensive interpretation were analyzed as 2D functions of two or three variables. A wide spectrum of the parameters considered enabled the examination of their interactions and interrelationships. 3D presentation is an additional way of visualizing results, enabling the observation of parameters in a selected coordinate system.

The 3D presentation of shale volume (VSH), kerogen volume (VKER), and neutron porosity (NPHI) (Fig. 20a) provides additional clarity. A distinct separation of the Ja Mb and Sa Fm data can be seen based on shaliness. Larger VKER values are observed at larger values of VSH and NPHI. The Ja Mb data are concentrated within the VSH range 0.25–0.65, while the Sa Fm data are clustered within the VSH range 0-0.35. Higher VKER values are observed at higher values of NPHI, which is explained by the presence of HC. In both formations, the lower kerogen volume correlates with the higher bulk density and higher transit interval time (Fig. 20b). This trend is more obvious in the Ja Mb data, which means that in the matrix of these rocks, kerogen occurs more frequently. The situation in Sa Fm is similar. Relationships between the log-derived parameters are similar to those existing between the laboratory-derived data. Fig. 20c presents 3D relationships between well-log and laboratory parameters. Laboratory-derived values of organic matter (OM) correlate with those of bulk density and shaliness (Fig. 20c). An increase in the volume of kerogen with an increase in the organic matter volume is characteristic of Ja Mb. Low NPHI and low OM recorded in several depth sections from Sa Fm indicate the presence of gas in pores.

The presented examples illustrate diversity of mudstones in Ja Mb and Sa Fm and show that various measurements are necessary to reveal the complexity of shale structure, petrophysical properties, elemental and mineral composition. Analyses document the presumptive mutual interrelations between various parameters. All of them are influenced by the highly variable mineral composition of the studied mudstone rocks as well as by the low number of the samples studied.

CONCLUSIONS

The current study has proved that the use of diverse methods and methodologies for gaining comprehensive information on heterogeneous shale formations is highly expedient. The goal of this study was to characterize the heterogeneous shale gas mudstones that can be considered to be potential shale gas plays. There is a great many of not yet discovered relationships that can be revealed and clarified using modern measurement methods as well as innovative data processing and interpretation procedures. Analysis of the data obtained from laboratory tests in combination with those obtained from comprehensive well log interpretation is particularly fruitful. Laboratory data were obtained from the planned sophisticated laboratory



Fig. 20a 3D presentation of interrelations between shaliness (VSH), neutron porosity (NPHI), and volume of kerogen (VKER)



Fig. 20b 3D presentation of interrelations between intensity of natural radioactivity (GR), transit interval time (DT), bulk density (RHOB), and volume of kerogen (VKER)



Fig. 20c 3D presentation of interrelations between the laboratory-derived volume of organic matter (OM), shaliness (VSH), neutron porosity (NPHI), and volume of kerogen (VKER)

measurements performed only at the specified depth for the purpose of gaining very detailed information. Meanwhile, well logging data represent rock formation characteristics continuously recorded at selected depth intervals, which, however, were affected by environmental conditions and response functions of the log devices employed. Scientific researchers perform measurements making use of numerous sophisticated methods that are constantly being improved. It is important to note that the physical bases of the methods employed differ in regard to physical phenomena. Hence, the information provided using each of them is unique. Skillful combination of the data obtained from different sources is a non-substitutable platform for creating rock models that combine geological, mineralogical, and petrophysical data.

Various plots presented in this paper show that the analyzed sweet spots, i.e. gas-enriched high total organic carbon formations of Ja Mb and Sa Fm, differ in their petrophysical characteristics. The Ja Mb data are more consistent and are more closely interrelated than the Sa Fm data. Small thickness of the Ja Mb formation supports the assumption that duration of sedimentation in this formation was shorter and conditions were stable. In contrast, the greater thickness of the Sa Fm formation suggests the extended period of sedimentation and possible changes in conditions, which is evidenced by a larger scattering of almost all parameter values. The presented results show typical relationships between petrophysical properties, which confirm that the high heterogeneity of shale gas formations requires that a wide spectrum of laboratory methods be employed for gaining an adequate understanding of their characteristics. Density (bulk, specific, grain, and rock, depending on the petrophysical definition and method of measurement) and porosity (total, effective, dynamic) are the main petrophysical parameters of the shale gas formations of interest. These parameters can be measured in different ways, including laboratory tests and geological field techniques, e.g., well logging. Our results illustrate the importance of using all these methods together for gaining multi-dimensional information. Comparison of various data and analysis of differences in the results obtained are highly recommended. Simple statistics and mostly 2D relationships (in special cases, 3D relationships) were used as quick tools enabling the identification of the basic trends.

ACKNOWLEDGMENTS

This study was performed within the framework of the Blue Gas project entitled "Methodology for the determination of sweet spots based on geochemical, petrophysical and geomechanical properties in connection with correlation of laboratory tests with well logs and the 3D model generation" (MWSSSG) Polskie Technologie dla Gazu Łupkowego (2013–2017) and was financed by the NCBiR (National Centre for Research and Development), Warsaw, Poland. Access to data for this study was provided by the Polish Oil and Gas Company, Warsaw, Poland. The authors thank Dr. Roman Semyrka, AGH UST for mercury injection porosimetry measurements and Prof. Dr. Leszek Czepirski's scientific research group AGH UST for performing N₂ adsorption/desorption experiments. Also, we express our gratitude to Prof. Dr. Arkadiusz Derkowski and Dr. Tomasz Topór from the Research Centre in Krakow of the Institute of Geological Sciences of the Polish Academy of Sciences for the performed dual liquid porosimetry measurements and XRD mineralogical analyses. The authors would like to thank two anonymous reviewers and Editors for their work to improve the article.

LIST OF THE ABBREVIATIONS USED IN THE ARTICLE

NMR – experiment (here laboratory measurement) based on nuclear magnetic resonance phenomenon,

XRD – X-Ray Diffraction, a non-destructive test method used for analyzing the structure of crystalline materials,

HC – hydrocarbons,

TOC - total organic carbon,

W1, W2, W3 – short names of wells in the study,

Pe, Pa, Pr, Sa and Ko – abbreviations of names of the Pelplin, Pasłęk, Prabuty, Sasino and Kopalino formations in the W1-W2 geological profiles,

Ja Mb – Silurian Jantar Member of the Pa Fm,

Sa Fm - Ordovician Sasino Formation,

WIP - Water immersion porosimetry,

KIP – Kerosene immersion porosimetry,

MIP – Mercury injection porosimetry,

PDP – Pressure decay permeability,

GD_WIP Grain density from the Water immersion porosimetry,

 Φ _WIP Total porosity from the Water immersion porosimetry,

BD_Hg, SD_Hg, TPA, Φ _Hg – Bulk density, skeletal density, total pore area, effective porosity from the Mercury Injection Porosimetry, respectively,

K_PDP, BD_PDP – permeability and bulk density from the Pressure decay permeability experiment,

D He – density from the He pycnometry,

 Φ _nmr_tot, Φ _nmr_eff, Sw irr – total porosity, effective porosity, irreducible water saturation from the NMR experiment, respectively,

S_BET, V_tot – specific surface (Brunauer-Emmet-Teller-method), total pore volume with diameters < 350 nm from the Physical adsorption of nitrogen, respectively, BET, BJH and QSDFT – Brunauer-Emmet-Teller, Barrett-Joyner-Halenda and quenched solid density functional theory techniques of processing and interpretation of the Physical adsorption of nitrogen experiment results,

GR - natural gamma radioactivity log,

SGR – URAN, THOR, POTA – curves from the spectral gamma log,

RHOB, PE – bulk density and photoelectric adsorption index from the Density (gamma-gamma) log,

NPHI – neutron porosity log,

LLD, LLS – resistivity logs of far and medium radius of investigation,

DT – P-wave slowness from the sonic log,

PHI, PHIE, VKER, VSH – total porosity, effective porosity, volume of kerogen, volume of shale – results of the comprehensive interpretation of well logging, respectively,

S1 and S2 – free hydrocarbons and hydrocarbons generated through thermal cracking from rock-eval pyrolysis,

ULTRA – Halliburton co. program for the comprehensive interpretation of well logs,

GEM – geochemical well logging device,

OM - organic matter volume.

REFERENCES

- AccuPyc. 2001. AccuPyc[™] 1330 Pycnometer Operator's Manual.
- Aplin, A.C., Macquaker, J.H.S. 2011. Mudstone diversity: Origin and implications for source, seal, and reservoir properties in petroleum systems. *Bulletin of the American Association of Petroleum Geologists 95*, 2031– 2059, doi:10.1306/03281110162.
- Coates, G.R., Lizhi Xiao, Prammer, M.G. 1999. NMR logging. Principles and Interpretation. Huston, Texas: Halliburton Energy Service.
- Donohue, M.D., Aranovich, G.L. 1998. Classification of Gibbs adsorption isotherms. *Advances in Colloid and Interface Science* 76–77, 137–152.
- Gor, G.Y., Thommes, M., Cychosz, K.A., Neimark, A.V. 2012. Quenched solid density functional theory method for characterization of mesoporous carbons by nitrogen adsorption. *Carbon 50 (4)*, 1583–1590.
- Heller, R., Zoback, M. 2014. Adsorption of methane and carbon dioxide on gas shale and pure mineral samples. *Journal of Unconventional Oil and Gas Resources 8*, 14–24, doi:10.1016/j.juogr.2014.06.001.
- Jarzyna, J., Wawrzyniak-Guz, K. (eds) 2017. Adaptation to the Polish conditions of the methodologies of the *sweet spots* determination on the basis of correlation of well logging with drilled core samples: methodology to determine *sweet spots* based on geochemical, petrophysical and geomechanical properties in connection with correlation of laboratory test with well logs and gen-

eration model 3D. *Monography*, 500 pp., GOLDRUK Wojciech Golachowski Printing House (In Polish).

- Jarzyna, J.A., Bała, M., Krakowska, P.I., Puskarczyk, E., Strzępowicz, A., Wawrzyniak-Guz, K., Więcław, D., Ziętek, J. 2017a. Shale Gas in Poland, Chapter 9. In: Hamid Al-Megren (ed.) Advances in Natural Gas Emerging Technologies. Open access peer-reviewed volume. ISBN: 978-953-51-3434-3. IntechOpen.
- Jarzyna, J.A., Czepirski, L., Krakowska, P.I., Puskarczyk, E., Szczurowski, J. 2017b. Petrophysical Model of Polish Shale Gas Rocks on the Basis of Various Laboratory Experiments. 79th EAGE Conference and Exhibition 2017, Paris, France, EarthDoc, doi: 10.3997/2214-4609.201701268.
- Jarzyna, J.A., Krakowska, P.I., Puskarczyk, E., Wawrzyniak-Guz, K., Zych, M. 2018. Comprehensive interpretation of the laboratory experiments results to construct model of the Polish shale gas rocks. *E3S Web of Conferences*, ISSN 2267-1242, 35, 03009, pp. 1–8, available online since 2018-03-23, proceedings of the POL-VIET 2017 – Scientific-research cooperation between Vietnam and Poland, Krakow, Poland, November 20–22, 2017, https://www.e3sconferences.org/articles/ e3sconf/pdf/2018/10/e3sconf polviet2018 03009.pdf.
- Jarzyna, J.A., Krakowska, P.I., Puskarczyk, E., Wawrzyniak-Guz, K., Zych, M. 2019. Total organic carbon from well logging – statistical approach. Polish shale gas formation case study. *International Journal* of Oil Gas and Coal Technology 22 (2), 140–162. ISSN 1753-3309. Available online since 2019-10-03, DOI: 10.1504/IJOGCT.2019.102784.
- Jarzyna, J.A., Krakowska, P.I., Puskarczyk, E., Wawrzyniak-Guz, K. 2020. Petrophysical investigations of shale gas formations in Poland. Aspects in Mining & Mineral Science 5 (3), 582–584, ISSN 2578-0255, available online since 2020-08-12, https://crimsonpublishers.com/amms/pdf/AMMS.000611.pdf.
- Kiersnowski, H. 2013. Geological Environment of Gas-Bearing Shales. In: Nawrocki, J. (ed.), *Shale gas as seen by Polish Geological Survey*. Polish Geological Institute – National Research Institute, 26–31 pp.
- Kleinberg, R.L. 1999. Nuclear Magnetic Resonance. In: Po-zen Wong (ed.) *Methods in the Physics of Porous Media*, 35, 337–385. Academic Press, ISSN: 1079-4042/ 99, ISBN: 0-12-475983-3, doi: 10.1016/S0076-695X(08) 60420-2.
- Kotarba, M.J., Lewan, M., Wiecław, D. 2014. Shale gas and oil potential of Lower Palaeozoic strata in the Polish Baltic Basin by Hydrous Pyrolysis. Presented at the Fourth EAGE Shale Workshop. *Shales: What do they have in common? 6–9 April, 2014.* Porto, Portugal.
- Krakowska-Madejska, P.I., Jarzyna, J.A. 2020. Diverse scale data for shale gas formation description why is digital shale rock model construction difficult? The Polish Silurian and Ordovician rocks case study. *Minerals 10 (108)*, 1–20, ISSN 2075-163X, available online since 2020-01-27, https://www.mdpi.com/2075-163X/10/2/108/pdf.

- Kuila, U., McCarty, D.K., Derkowski, A., Fischer, T.B., Prasad, M. 2014. Total porosity measurement in gas shales by the water immersion porosimetry (WIP) method. *Fuel 117*, 1115–1129, doi: 10.1016/j.fuel.2013.09.073.
- Loucks, R.G., Reed, R.M., Ruppel, S.C., Jarvie, D.M. 2009. Morphology, genesis, and distribution of nanometerscale pores in siliceous mudstones of the Mississippian Barnett Shale. *Journal of Sedimentary Research 79*, 848–861, doi: 10.2110/jsr.2009.092.
- Mastalerz, M., Schimmelmann, A., Drobniak, A., Chen, Y. 2013. Porosity of Devonian and Mississippian New Albany Shale across a maturation gradient: Insights from organic petrology, gas adsorption, and mercury intrusion. Bulletin of the American Association of Petroleum Geologists 97, 1621–1643, doi: 10.130/04011312194.
- McPhee, C., Reed, J., Zubizarreta, I. 2015. Chapter 11 – Nuclear Magnetic Resonance (NMR). In: McPhee, J.R.C., Izaskun, Z. (eds). *Developments in Petroleum Science*, Elsevier Volume 64, 655–669, doi: 10.1016/B978-0-444-63533-4.00011-1.
- Modliński, Z., Szymański, B., Teller, L. 2006. The Silurian lithostratigraphy of the Polish part of the Peri-Baltic Depression (N Poland). *Przegląd Geologiczny 54 (9)*, 787–796 (In Polish, summary in English).
- Omotoso, O., McCarty, D.K., Hillier, S., Kleeberg, R. 2006. Some successful approaches to quantitative mineral analysis as revealed by the 3rd Reynolds Cup contest. *Clays and Clay Minerals* 54, 748–760.
- Peters, K.E., Xia, X., Pomerantz, A.E., Mullins, O.C. 2015. Geochemistry applied to evaluation of unconventional resources. In: Ma, Y.Z., Holditch, S.A. (eds), Unconventional Oil and Gas Resources Handbook: Evaluation and Development, Elsevier Inc., doi: 10.1016/B978-0-12-802238-2.00003-1.
- Podhalańska, T. 2003. Late Ordovician to Early Silurian transition and the graptolites from Ordovician/Silurian boundary near the SW rim of the East European Craton (northern Poland). *Series Geological Correlation 18*, 165–172.
- Poprawa, P. 2010a. Shale gas hydrocarbon system North American experience and European potential. *Przegląd Geologiczny 58 (3)*, 216–225 (In Polish, summary in English).
- Poprawa, P. 2010b. Shale gas potential of the Lower Palaeozoic complex in the Baltic and Lublin-Podlasie basins (Poland). *Przegląd Geologiczny 58 (3)*, 226–249 (In Polish, summary in English).
- Puskarczyk, E. 2011. Assessment of Reservoir Properties of Rock through Nuclear Magnetic Resonance Phenomenon Application. Ph.D. Thesis. Main Library of AGH UST, Krakow, Poland (In Polish, summary in English).
- Puskarczyk, E. 2019. Artificial neural networks as a tool for pattern recognition and electrofacies analysis in Polish Palaeozoic shale gas formations. *Acta Geophysica* 67, 1991–2003, https://doi.org/10.1007/s11600-019-00359-2.

- Puskarczyk, E., Jarzyna, J.A., Wawrzyniak-Guz, Krakowska, P.I., Zych, M. 2019. Improved recognition of rock formation on the basis of well logging and laboratory experiments results using factor analysis. *Acta Geophysica* 67 (6), spec. iss., 1809–1822, ISSN 1895-6572, https://link.springer.com/content/ pdf/10.1007%2Fs11600-019-00337-8.pdf.
- Rexer, T.F., Mathia, E.J., Aplin, A.C., Thomas, K.M. 2014. High-pressure methane adsorption and characterization of pores in Posidonia Shales and isolated kerogens. *Energy Fuels 28*, 2886–2901, doi: 10.1021/ef402466m.
- Ross, D.J.K., Bustin, M.R. 2009. The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. *Marine and Petroleum Geology* 26, 916–927, doi: 10.1016/j.marpetgeo.2008.06.004.
- Rouquerol, F., Rouquerol, J., Sing, K.S.W., Llewellyn, P., Maurin, G. 2014. Adsorption by Powders and Porous Solids: Principles. Methodology and Applications. Academic Press, 2014.
- Środoń, J., Drits, V.A., McCarty, D.K., Hsieh, J.C.C., Eberl, D.D. 2001. Quantitative XRD analysis of clayrich rocks from random preparations. *Clays and Clay Minerals* 49, 514–528.
- Šliaupa, S., Lozovskis, S., Lazauskienė, J., Šliaupienė, R. 2020. Petrophysical and mechanical properties of the lower Silurian perspective oil/gas shales of Lithuania. *Journal of Natural Gas Science and Engineering 79* (103336).
- Thommes, M. 2010. Physical Adsorption Characterization of Nanoporous Materials. *Chemie Ingenieur Technik*, *82 (7)*, 1059–1073.
- Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W. 2015. Physisorption of gases with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry 87 (9–10)*, 1052–1069.
- Topór, T., Derkowski, A., Kuila, U., Fischer, T.B., McCarty, D.K. 2016. Dual liquid porosimetry: a porosity measurement technique for oiland gas-bearing shales. *Fuel 183*, 537–549, http://dx.doi.org/10.1016/j.fuel.2016.06.102.
- Topór, T., Derkowski, A., Ziemiański, P., Marynowski, L., McCarty, D.K. 2017a. Multi-variable constraints of gas exploration potential in the Lower Silurian shale of the Baltic Basin (Poland). *International Journal of Coal Geology 179*, 45–59, doi: http://dx.doi.org/10.1016/j.coal.2017.05.001.
- Topór, T., Derkowski, A., Ziemiański, P., Szczurowski, J., McCarty, D.K. 2017b. The effect of organic matter maturation and porosity evolution on methane storage potential in the Baltic Basin (Poland) shale-gas reservoir. *International Journal of Coal Geology 180*, 46– 56, doi: http://dx.doi.org/10.1016/j.coal.2017.07.005.
- TRA Glossary. 2016. Terra Tek Schlumberger Reservoir Laboratory, Glossary.
- Washburn, K. 2014. Relaxation mechanisms and shales.

Concepts in Magnetic Resonance Part A, 43A, 57–78, doi: 10.1002/cmr.a.21302.

- Watson, A.T., Chang, C.T.P. 1997. Characterizing porous media with NMR methods. *Progress in Nuclear Magnetic Resonance Spectroscopy* 31, 343–386, doi: 10.1016/S0079-6565(97)00053-8.
- Wawrzyniak-Guz, K., Jarzyna, J.A., Zych, M., Bała, M., Krakowska, P.I., Puskarczyk, E. 2016. Analysis of the heterogeneity of the Polish shale gas formations by Factor Analysis on the basis of well logs. In: *Extended Abstracts 78th EAGE Conference & Exhibition incor-*

porating, 30 May – 2 June 2016. Vienna, Austria.

- Webb, P.A. 2011. An introduction to the physical characterization of materials by mercury intrusion porosimetry with emphasis on reduction and presentation of experimental data. Norcross, Georgia: Micrometrics instruments corp.
- Zhou, L., Zhou, Y., Li, M., Chen, P., Wang, Y. 2000. Experimental and modeling study of the adsorption of supercritical methane on a high surface activated carbon. *Langmuir* 16, 5955–5959, http://dx.doi.org/10.1021/la991159w.