SEM and FIB-SEM investigations on potential gas shales in the Dniepr-Donets Basin (Ukraine): pore space evolution in organic matter during thermal maturation

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Abstract. Porosity and permeability are essential parameters for reservoir rocks. Techniques developed for conventional reservoir rocks characterized by large pores, cannot be applied to study gas shales. Therefore, high resolution techniques are increasingly used to determine reservoir quality of shale gas plays. Within the frame of the recent study, Upper Visean black shales (“Rudov Beds”) from the Dniepr-Donets-Basin (DDB, Ukraine) were characterized by X-ray diffraction, conventional SEM imaging and FIB/BIB-SEM.

According to SEM and FIB/BIB-SEM data, nanopores are not abundant in primary macerals (e.g., vitrinite) even in overmature rocks, whereas they develop within secondary organic matter (bitumen) formed mainly at gas window maturity. Frequently occurring sub-micrometre porosity, probably related to gas generation from bituminous organic matter, was detected within mudstones at a vitrinite reflectance > 2.0 % Rr. However, such pores have also been detected occasionally in solid bitumen at oil window maturity (0.9 % Rr). Authigenic nanoscale clay minerals and calcite occur within pyrobitumen at gas window maturity.

Furthermore, Rudov Beds can be subdivided into mineralogical facies zones by SEM imaging and X-ray diffraction. A basin-centred, brittle siliceous facies is most likely caused by increased contribution from deeper water radiolaria and is separated from a marginal clayey and carbonate-rich facies.

1. Introduction

Despite major achievements in the investigation of organic matter-hosted pores in the nanometre scale [1], storage capacity and production behaviour of gas shales are still poorly understood [2]. Visualisation of nanopores from conventionally (mechanically) polished surfaces is impossible, whereas FIB/BIB-SEM techniques generate undisturbed surfaces without preparation-induced artefacts, allowing imaging of nanopores in the range of > 10 nm in equivalent diameter. Such pores might contribute largely to storage capacity and release behaviour, although recent findings support a significant influence of nanopores even below the resolution of modern FE-SEM devices (< 5 nm) [1].
Great progress has been made in the understanding of the evolution of nanopores in organic matter. Nevertheless, it is still unclear if, at which maturity, and to which amount, nanopores form within primary or secondary organic matter. Furthermore, most previous studies focussed on kerogen type II, whereas the behaviour of vitrinite-rich kerogen (mixed type III-II) is poorly investigated.

Taking into account the high total organic carbon (TOC) contents (average 5.5 %) and original hydrogen index values of 270 mg HC/ g TOC [3], the Upper Visean “Rudov Beds” (V-23) in the Dniepr-Donets Basin (DDB; Ukraine; figure 1) offer a unique possibility to study organic-rich rocks with a kerogen type III-II at different maturities. While their significance as source rocks for a high number of conventional hydrocarbon deposits found in Upper Visean clastic rocks [4-6] is apparent, their potential for unconventional production of shale gas/liquids is currently underinvestigated. Apart from the general generation potential, production parameters like permeability and fraccability are largely influenced by the mineralogical facies as well as type and distribution of pores within the fine-grained rocks. Furthermore, types of organic matter porosity and its evolution during thermal maturation are of great interest for the evaluation of an unconventional hydrocarbon play.

Figure 1. (a), (b) Regional setting of the Dniepr-Donets-Basin (DDB) in Eastern Europe. (c) Chrono- and lithostratigraphy of the Palaeozoic succession [7]. Age data follow [8].
The Rudov Beds cover a large area in the DDB. The best source rocks, however, are found within the Srebnen Bay, a low-energy basin surrounded by a reef belt (figures 2a,b; [9]). Siliceous, clayey, and carbonate-rich facies zones have been defined by Gavrish et al. [10] and Machulina and Babko [11]. However, apart from bulk mineralogical parameters, understanding the habitus and distribution of brittle and ductile mineral phases is important. Apart from that, the visualisation of organic matter and its arrangement within the mineral matrix was a main interest of the current study. For that purpose, SEM imaging of freshly broken surfaces was performed to characterize both organic and inorganic facies changes.

2. Geological setting
The DDB is an about 650 km long, Late Devonian rift-basin, located within the East-European Craton (figure 1a, b). Chrono- and lithostratigraphy of the DDB are shown in figure 1c.

Middle Devonian pre-rift deposits represent the oldest strata in the DDB (figure 1c). The Late Devonian syn-rift succession is up to 4 km thick and includes clastic deposits, carbonate rocks, extensive salt deformed to salt domes, and volcanic rocks [12].

The Carboniferous post-rift succession with a maximum thickness in excess of 10 km is represented by cyclic successions of siliciclastic and minor carbonate rocks deposited in fluvial, shallow-marine, and lagoonal environments. Water depth was typically low and exceeded 200 m only in the axial part of the basin. Typically each cycle, up to 50 m in thickness, includes a sand interval ("productive unit") and a shallow marine, organic-rich shale interval ([13]; see figure 1c). The Rudov Beds (up to 70 m thick) form the base of the Upper Visean section and mark the most prominent black shale horizon.

Basin-wide Lower Visean and Bashkirian carbonate platforms were the result of major transgressions from the south-east. The percentage of fluvial and deltaic sands increases in the Upper Serpukhovian succession. Serpukhovian to Moscovian coal seams, extensively mined in the Donbas Foldbelt, extend into the DDB. Clastic deposits, carbonate rocks, and evaporite rocks prevail in the Permian section. The Mesozoic and Cenozoic sediments unconformably overlie the Paleozoic series.

Petroleum systems in the DDB [6] are based on multiple source rocks [7, 14]. Visean and Serpukhovian black shales (incl. Rudov Beds) together with Serpukhovian to Moscovian coaly layers are potential source rock horizons. Oil window maturity (~0.65 % Rr; random vitrinite reflectance in oil) in the north-western part of the basin is reached at around 3,500 m depth, but at shallower depth in the inverted SE part of the DDB [5, 15, 16]. Hydrocarbon generation occurred predominantly during Permian deep burial, according to previous basin modelling studies [16]. Additionally, a potential generation of hydrocarbons is suggested for Mesozoic to Cenozoic burial stages. Carboniferous and Permian clastic rocks are the dominant reservoir lithology [6]. Small quantities of hydrocarbons occur in Lower Carboniferous and Lower Permian carbonates. Oil fields prevail in the north-western part of the basin as well as along the basin flanks.

3. Samples and methodology
Samples were obtained from wells with cored Upper Visean shales. Two sample sets have been selected. (1) For the investigation of the organic matter evolution due to thermal maturation, samples were chosen according to their vitrinite reflectance (measured following established procedures [17]). (2) A second sample set with comparable (marginal to oil window) maturity was obtained from different locations throughout the basin, to characterize lateral changes in the depositional environment and maceral composition. The location of sampled wells within the DDB is illustrated in figure 2a.

For conventional SEM investigations, freshly broken surfaces of rock samples have been coated with an Au layer to enhance conductivity. To prevent charging effects, relatively even surfaces were chosen for investigation. Investigations were conducted with a Zeiss Evo MA 10 SEM, equipped with a secondary electron (SE) and a backscattered electron (BSE) detector, as well as a Bruker Nano XFlash 430M energy-dispersive X-ray (EDS) detector.
Figure 2. a) Position of studied wells in relation to the “Srebnen Bay”. b) Lateral facies map (modified after [11]). Isopachs indicate thickness of V-23 interval. The schematic cross-section (insert; after [18]) shows the syncline surrounded by a reef belt. “Rudov Beds” (V-23) are deposited in the central depression, overlying a Lower Visean platform. c) Vertical change of mineralogy, total organic carbon and calcite equivalent content (calculated from total inorganic carbon) within basinal well Yantarna (Yan). d) Mineral assemblages of shale samples from X-ray diffractometry. The composition of gas-bearing, siliceous Barnett Shale is shown for comparison.
For FIB-SEM investigations, the specimen surfaces were prepared using a JEOL IB-09010 broad ion beam (BIB) cross-section polisher with an Ar ion beam (5 kV; 6 h), followed by an Au coating to make the specimen conductive for high resolution imaging. For the final polishing of the investigated surface, a FEI Versa 3D Dual focussed ion beam (SEM-FIB) microscope was used. The particular area of interest was polished with a Ga ion beam at 30 kV for 30 s at low current (10 pA or less). With the electron beam of the microscope, the image surface was investigated at 5 kV and 10 kV using SE and BSE detectors. The gradient distribution of pores to depth within the organic matter was obtained by progressive ion polishing and image capturing.

EDS analysis was done with an Octane silicon drift detector (SDD) from EDAX and a Genesis software package. In order to decrease the interacting volume, measurements were performed with 6 kV.

X-ray diffraction (XRD) measurements of texture-free and textured powder mounts were done following established procedures [19]. Measurement parameters were set at a goniometer speed rate of 0.5° 2θ/minute and a registration range from 2° to 66° 2θ. Particularly for the analyses of clay minerals, textured mounts were measured four times at a goniometer speed rate of 0.5° 2θ/minute with a registration range from 2° to 42° 2θ in the following order: (1) in untreated condition, (2) after solvation with ethylene glycol (12 h, 60 °C), after thermal treatment (2 h) at (3) 350 °C and (4) at 550 °C. The quantification followed the method of Schultz [20]. The results were cross-checked using the ADM software (Version 6.22) of Wassermann Röntgenanalytik (Germany) which is based on the Rietveld method. To verify the quantitative analysis, a comparison between the percentage-composition based on XRD-data of the shale samples, XRD-data of quartz standards and data of calcimeter measurements in accordance with the method of Scheibler [3] took place.

4. Results

4.1. Mineralogy
Facies zones were established by Gavrish et al. [10] and Machulina and Babko [11] for parts of the north-western DDB (Srebnen Bay; figure 2b). Within the frame of the present study, investigated samples cover basinal (siliceous), transitional (siliceous-carbonaceous-clayey), and clayey reef facies (for locations see figures 2a,b).

As a consequence of lateral facies zones, the mineralogical composition is strongly variable throughout the V-23 interval. Apart from lateral variations, highly variable vertical composition has been observed for well Yantarna (Yan, see figures 2c,d).

4.1.1. Basinal siliceous facies. Samples from the basin-centred well Yantarna show strong vertical variations in mineral assemblages, with a quartz-rich composition in the lowermost (~ 65 wt%) and central part (40 - 55 wt%), downwards decreasing contents of kaolinite as well as minor amounts of feldspar, pyrite, and detrital mica (< 5 - 10 wt%). Expandable clay minerals (ECM) are present in trace amounts in the upper part of the sampled interval. One sample exhibits a remarkably high calcite content (~ 50 wt%), corresponding to a significantly lower quartz content than observed in surrounding areas. A kaolinite-rich sample (~ 70 wt%) with total clay minerals exceeding 80 wt% was investigated in the uppermost part of the stratigraphic section. The cumulated amount of brittle mineral phases (quartz + feldspar + carbonates + pyrite + marcasite) exceeds 60 wt% in the Yantarna well, except of the uppermost sample.

SEM imaging shows that quartz is mainly microcrystalline with grain sizes < 5 µm (figures 3g,h), whereas rhombohedral carbonate minerals reach sizes of several tens of µm. Clay minerals are randomly arranged, therefore, a layering is not visible at the given magnification. Trace amounts of apatite have been detected from EDS measurements, occasionally occurring as fine layers or randomly distributed, isolated crystals. Organic matter mainly occurs as dispersed vitrinite grains (10 - 30 µm), sharp-edged, partly branched inertinite (up to 300 µm), or irregularly shaped, bituminous (?) organic matter (several tens of µm; figure 3h).
Figure 3. SEM (SE) images of selected Rudov (V-23) samples from marginal (Zimnistka; a-b), transitional (Selyukhov, Kompanska, Lelyakov; c-f) and basinal (Yantarna; g-h) wells, showing facies variations. White bar represents a width of 10 µm. bit – bitumen; cc – calcite; cm – clay minerals; dol – dolomite; qrz – quartz; py – pyrite; vit – vitrinite.
4.1.2. Marginal carbonate and clay rich facies. Within wells from the calcareous and clayey reef facies (Ostapovska; Zimnitska), the content of total clay minerals ranges between 45 and 85 wt%. The clay mineral fraction of both samples from Ostapovska consists of variable amounts of ECM, identified as an illite-dominated illite-smectite mixed layer mineral, detrital mica, illite, and kaolinite. In one sample, the dominant non-clay mineral is calcite. In the second, deeper sample, the content in kaolinite is ~ 45 wt%, whereas the quartz content is < 15 wt%. Samples from Zimnitska show high clay mineral and only minor quartz contents. The dominant mineral phase is kaolinite, although the percentages vary. Small amounts of chlorite are present in all samples. Two samples contain trace amounts of marcasite. One sample exhibits a total carbonate content > 30 wt%, including a significant proportion of siderite. Plagioclase occurs in trace amounts in all samples. Within the transitional and clayey facies, the content of brittle mineral phases generally ranges below 60 wt%.

A fine layering of clay minerals is visible within samples from the clayey facies zone in SEM images (figures 3a,b), elongated mineral grains as well as fine, carbonate-rich layers frequently occur within the clayey matrix. In contrast, within the transitional zone, samples exhibit both blocky, layered carbonates as well as finely dispersed partly rhombohedral crystals (figures 3c-f). In carbonate rich samples, the layering of clay minerals is obscured by partly authigenic, mainly microcrystalline (< 5 - 10 µm) carbonate.

Vitrinite is present as layers or elongated grains embedded into the clay matrix (see figures 3a, b). In samples with high content of inertinite macerals, irregularly branched particles, up to several 100 µm in size, have been detected. According to their habitus, they are suggested to represent higher plant material, which has been oxidized during syn-depositional wildfires.

4.2. Maturity related evolution of organic matter
Four samples with thermal maturity from 0.9 to 2.7 % Rr were picked for FIB-SEM and SEM imaging to create a maturity profile of organic matter evolution (for locations see figure 2a).

4.2.1. Oil window (N. Pogarshchinska). Organic matter in an oil mature sample (0.9 % Rr; ~ 5,100 m) from well N. Pogarshchinska (Npog) appears as primary (vitrinite) macerals as well as (secondary) solid bitumen, generated by thermal alteration of kerogen. Both types could be visualized by SEM imaging of freshly broken surfaces (figures 4a-d). Primary macerals occur as layers or isolated, equidimensional grains, while occasionally visible solid bitumen is preferentially found near larger rigid grains indicating precipitation in pre-existing pore space. Vitrinite macerals exhibit a homogeneous, pore-free surface. In contrast, solid bitumen hosts (sub-)micrometre open pores (figures 4c,d).

FIB-SEM imaging on primary macerals confirms their homogeneous composition without visible nanopores (figures 4e,f). Occasionally, pores in the sub-micrometre range occur at the border between maceral compounds and surrounding clay sheets, but not within the organic matter itself.

4.2.2. Wet gas window (Rodnikova). A sample from the wet gas window (1.35 % Rr) was obtained from well Rodnikova (Rod) at a depth of ~ 5,500 m, southeast of the Sreben Bay. Maceral composition is dominated by primary vitrinite and inertinite fragments. According to SEM (figures 4g,h) and FIB-SEM measurements, no sub-micrometre pores are present in these macerals. Solid bitumen with secondary pores has not been detected (see figures 4i,j). Nevertheless, clay matrix-hosted nanopores, partly occurring at the borders between organic matter and clays, are clearly visible in the FIB-SEM image. Furthermore, nanometre-scale flakes of clay minerals (?), fully incorporated into solid bitumen, have been detected in few cases. However, EDS mapping could not be performed on such inhomogeneities due to very small particle sizes.

4.2.3. Dry gas window and overmature (Komyshovatska). Dry gas mature (2.1 % Rr; ~ 3,800 m) and overmature (2.7 % Rr; ~ 4,300 m) samples from well Komyshovatska (Kom), located in the inverted south-eastern part of the basin, host both non-porous, primary macerals (vitrinite; inertinite), and
Figure 4. SEM (SE) and FIB-SEM (SE) images of non-porous, homogeneous vitrinite, non-porous as well as porous bitumen at a vitrinite reflectance of 0.9 - 1.35 % Rr. White bar represents a width of 2 µm.
nanoporous, secondary organic matter (pyrobitumen). While primary macerals mainly form isolated, randomly dispersed grains within the clay- and quartz-rich matrix (figures 5a-g), secondary bitumen often forms elongated or irregularly shaped bodies or fillings along large mineral grains (figures 5b,e,k). Two types of “inclusions” within bitumen have been detected, (1) pores down to 10 nm in size (figures 5c,d,i,j,l) and (2) clay flakes or calcite nodules in the nanometre-scale (figures 5e,f,k). In case of the latter, EDS measurements show Al, Si and low amounts of K, Mg or Fe (clay), or Ca (calcite) enrichments with well-defined borders within the organic carbon. Although a quantification of those minerals using the required small spot size is not possible, the qualitative identification within a large-scale organic phase without present inorganic elements is reliable. FIB milling was performed and confirmed that the inorganic phases are fully incorporated into the secondary organic matter and not part of the surrounding clay matrix. In contrast, primary vitrinite or inertinite macerals exhibit a homogeneous, pore-free fabric without included inorganic elements (see figure 5h). In case of the overmature sample, merging nanopores partly form micrometre-scale, irregularly shaped connected pores within pyrobitumen (figure 5l).

5. Discussion

5.1. Facies zones
The obtained results agree with the facies zones established by former studies [10, 11]. Nevertheless, XRD measurements revealed a highly variable mineralogical composition within Rudov Beds, both in lateral and vertical direction. Even within the basinal, siliceous facies, one sample exhibited a clay mineral portion of > 80 wt%. A good estimation of mechanical properties can be established according to the accumulated content of brittle mineral phases, which should exceed 60 wt% for unconventional HC production. This value is reached by all samples from the siliceous basinal facies except one, whereas no sample from transitional (carbonate-dominated) or clayey facies shows such a high amount of brittle phases.

Apart from that, a higher permeability can be suggested for the basinal samples rich in microcrystalline quartz grains, compared to their fine-layered, clay rich counterparts recovered from distal positions. The decrease of such microcrystalline, slightly elongated quartz particles towards the basin rim is most likely a result of decreasing contribution from deeper water radiolaria. The change from siliceous and clay dominated facies is marked by a transitional zone, often rich in carbonates. The amount of inertinite macerals formed by wildfires also increases towards the basin margin. Carbonates occur both as fine layers as well as authigenic rhombs of dolomite and calcite.

The presence of ECM to depths of > 5,000 m argues for a low heat flow during burial, consistent with the low gradient of vitrinite reflectance to depth within the north-western part of the basin. Mineral pores of sub-micrometre-scale were frequently observed within Rudov Beds, especially in the oil and wet gas mature samples. However, illitic shales are commonly suggested to be strongly water wet, whereas kaolinite-rich clays might impart a higher possibility for shales to become oil/gas wet [21]. Therefore, the clay mineral ratio (illite/kaolinite) might be a useful parameter for production behaviour from shale reservoirs.

In general, pore geometries and distribution in the mineral matrix might be strongly related to clay mineral composition; therefore, assignment of pore classes to certain clay phases could reveal valuable insights.

5.2. Thermal evolution of organic matter
Organic matter within the investigated black shale samples can be separated into (1) primary macerals and (2) secondary (pyro-)bitumen, formed by thermal alteration of the primary kerogen. Jarvie [22] distinguishes between earlier solid bitumen (oil window) and later pyrobitumen generated at gas window maturities. Depending on the type of kerogen, porous bitumen might occur already at oil window maturity (>0.9 Rr; see also [23, 24]), but in most cases is not abundant below 1.4 % Rr [25, 26]. Porous pyrobitumen was frequently observed within samples showing thermal maturity
Figure 5. FIB-SEM images (SE and BSE), showing organic matter porosity and inhomogeneities within pyrobitumen as well as non-porous, homogeneous vitrinite at a vitrinite reflectance of 2.1 % Rr (a - f) and 2.7 % Rr (g - l). White bar represents a width of 2 µm. OMP – organic matter porosity.
corresponding to the dry gas window (2.1 % Rr). The mostly equidimensional nanopores show limited connectivity, whereas, in zones with enhanced porosity, connected (former) nanopores form irregularly shaped pores in the micrometre-scale. The size and abundance of connected micrometre-scale pores increases within the overmature (2.7 % Rr) sample. Oval pores up to micrometre-scale occur at the boundaries between organic matter and clay matrix, possibly also holding gas storage potential. Apart from that, elongated, sharp-edged pores occasionally have been visualized at the interface of organic particles with the surrounding matrix. Klaver et al. [27] interpreted such features as artificial micro-cracks formed probably during or after coring.

Milliken et al. [28] observed that variations in TOC have a stronger influence on organic matter-hosted pores than thermal maturity. However, the present study suggests that apart from kerogen type, the presence of organic matter-hosted porosity is strongly controlled by the maturity related generation of (pyro-)bitumen.

Another feature observed within the maturity profile was the development of authigenic clay flakes and calcite nodules, often in the scale of < 100 nm, within pyrobitumen. This was not observed within the least mature sample (0.9 % Rr), rarely observed within the wet gas mature sample (1.35 % Rr) and frequently observed within the dry gas (2.1 % Rr) and overmature (2.7 % Rr) samples. The growth mechanisms of such mineral phases during thermal evolution of organic matter need further investigation. However, similar findings have been described by Reed et al. [23], who observed pellets of mixed organic-clayey composition, even if the clay flakes in those pellets were an order of magnitude larger than in this case, and seemed not to be fully incorporated into bitumen.

The possible presence of nanopores in primary kerogen was discussed controversially and is subject to an ongoing debate [23, 29]. However, we did not identify nanoporous organic matter that likely can be referred to as kerogen.

6. Conclusions

SEM is used as a standard method for the characterisation of rock fabrics within conventional reservoir rocks. However, also within the field of unconventional reservoir rocks with small grain sizes, SEM imaging performed on freshly broken surfaces reveals valuable insights for the understanding of rock properties like fracability and permeability. Large variations, especially in the content of brittle mineral phases, have been observed within the investigated Rudov samples in lateral extent. Furthermore, strongly variable XRD data also suggests high variations in vertical direction. Siliceous, transitional and clayey facies could be distinguished from SEM imaging. Therefore, mechanical properties of Rudov Beds and Upper Visean time equivalents outside of the Srebnen Depression have to be considered highly variable in both lateral and vertical extent.

As already reported by Wüst et al. [30], the characterisation of organic matter by SEM on freshly broken surfaces depends on its specific properties and also on the hosting mineral fabric. Primary macerals and bituminous pore filling appeared more often in rock samples with a higher content of brittle mineral phases (e.g., quartz, calcite), whereas they might be easily obscured in laminated, clay-rich shales. However, OM was identified in all rocks investigated with conventional SEM and bituminous organic matter hosting micrometre-scale pores could be easily discriminated from primary vitrinite within the oil mature sample from well N. Pogarshchinska.

FIB-SEM and BIB-SEM proved to be a valuable tool for the investigation of sub-micrometre porosity within the organic matter hosted by shales (see also [23, 25, 26, 29, 31-33]). OM-hosted nanopores are restricted to secondary bituminous organic matter within Rudov Beds. Their frequency strongly increases at a vitrinite reflectance of > 2.0 % Rr, corresponding to a dry gas window maturity. Furthermore, nanoscale features like authigenic clay and calcite particles within pyrobitumen at gas window maturity have been visualized. At a vitrinite reflectance of 0.9 % Rr, sub-micrometre pores to nanopores have been detected only in very few cases within bituminous pore fillings. Most investigated particles did neither host nanopores, nor did they host mineral inclusions. Therefore, in case of Rudov Beds, minor generation of nanopores within bitumen, due to hydrocarbon generation
and release, might already start at oil window maturity, but the main stage of development occurs at maturities between 1.35 % Rr and 2.0 % Rr.

The performed investigations showed that non-invasive preparation techniques like BIB milling further improve processing due to fast coverage of larger areas within a single sample and lower possibility of creating artefacts caused by improper FIB milling conditions. Working on organic matter with a FIB-SEM, handling parameters like the acceleration voltage of the ion beam turned out to be a crucial influencing factor possibly even causing the concealment of pores. In contrast, clay minerals seem less sensitive to beam damage. Reduced working distance as well as the use of a microscope equipped with a field emission electron source enhanced the maximum resolution down to < 10 nm of equal pore diameter, helping to visualize even the smallest features within the studied kerogen.

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