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POROSITY EVOLUTION IN THE CHALK: AN EXAMPLE FROM THE CHALK-TYPE SOURCE ROCKS OF THE OUTER CARPATHIANS (POLAND)

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The development and evolution of pore space in the impure chalk-type source rocks of the Oligocene Grybów Marls (Outer Carpathians, Poland) have been investigated using high-resolution petrographic techniques (FESEM/BS/CCI). Evidence suggests that the Grybow Marls are the products of the re-deposition of shelf sediments in deeper parts of the Outer Carpathian Basin during the final stages of its closure. The initial shelf sediments had variable levels of clay content ranging from fairly pure to impure chalks. After redeposition, the diagenetic history was similar to that of chalk sediment modified during the initial stages of diagenesis and controlled by the clay content. Stress-induced micro-cracks are restricted mainly to foraminiferal tests. Most coccolith shields were unaffected by compaction as they were protected from crushing by the presence of clay cement; the cement was re-organized under stress, forming less porous lamellar aggregates. The timing of diagenetic processes indicates that the origin of the clay and the eogenetic overgrowth calcite cement influenced the pathway of burial diagenesis and, thus, the pore-space evolution in the impure chalk.

1. Introduction

The cause of low permeability in chalk is of considerable interest (*e.g.* Scholle, 1977; Hardman, 1982; Brasher and Vagle, 1996; Fabricius, 2007; Mallon and Swarbrick, 2008; Hu *et al.*, 2012; Jeans *et al.*, 2014). These rocks can become seals or reservoirs or source rocks by a combination of factors related to the depositional environment, composition of sediments, and their diagenetic pathways. The present study deals with the evolution of pore space in Oligocene clay-rich and organic-matter-rich chalk deposits that are thought to be the source rocks for the Outer Carpathian oil and gas deposits (Ślączka *et al.* 2006). Oligocene organic-rich deposits from the Outer Carpathian region are considered to be high-quality source rocks, with mainly type II kerogen and significant petroleum potential, and a maturation level corresponding to the oil window (Kotarba and Koltun, 2006). Although geologic, lithological, biostratigraphic, and organic geochemistry studies of these rocks have been published (see Ślączka *et al.*, 2006; Kotarba and Koltun, 2006; Górniak, 2011 and references therein), petrographic data are needed. The present study is the first report of the

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microtexture imagery and petrology of these rocks. The aim of the present study was to establish whether high-resolution microscopy of the pore space in these chalks can provide a better understanding of the diagenetic history and consequently impart the ability to predict the permeability potential of the rocks.

2. Materials and methods

The rocks studied are the Grybów Marls collected from a complex tectonic region (Górniak, 2011, pp. 240–247, table 16, figures 2 and 16) of the Grybów Tectonic Unit. During the Miocene the strata were folded strongly, overthrusted, thrust faulted, and uprooted during the closing stage of the Carpathian Basin. The Grybów Marls were deposited in the Fore-Magura Basin during the maximum shallowing of the sea in the Outer Carpathian Basin when it was cut off from the global oceans. This caused restricted water circulation and a deficit of oxygen in the sedimentary environment. Sedimentologically, the Grybów Marls are turbidites. They represent a synorogenic chalk facies (Górniak, 2011, pp. 286–290) re-deposited by mass flow from the shelf into the deeper part of the basin (see Górniak, 2011, and references therein). The range of Ghibaudo's facies recognized within the lithologic-sedimentological features of the Grybów Marls are mud-sand couplets (MS) and mud-silt couplets (MT) with a distinct dominance of non-arenaceous marly units, and mud beds (M). These indicate the deposition of mainly fine-grained material and may represent the upper part of the Bouma sequence. According to the analysis of the internal structure of 56 beds, they represent depositional events composed of sedimentation by traction and suspension settling mechanisms (Górniak, 2011, pp. 281–283, table 20). The Grybów Marls are estimated to be up to 400 m thick consisting of a poly-lithic sequence. In addition to marls the sequence also includes beds referred to as limestones and Fe-dolomites; the Fe-dolomite formed within the precursor sediments of the Grybów Marls during early diagenesis (Narębski, 1957). These marls are black to brown in color and either non-arenaceous or arenaceous. The non-arenaceous variety is fairly hard, structureless, with a slabby parting and occurs in beds of variable thickness (from 2 cm to 10 m). The arenaceous variety is hard, parallel laminated with a flaggy parting and may be thin-bedded and represents a basal facies of the non-arenaceous marl beds (Górniak, 2011, pp. 241–245, figure 16).

Analysis has been carried out at scales from outcrop to submicroscopic levels. An FEI Quanta 200 field emission scanning electron microscope (FESEM, FEI, Hillsboro Oregon, USA) equipped with an EDAX energy-dispersive spectrometer Genesis 4000 (EDAX, Mahwah, New Jersey, USA) was used to examine marls in their natural state. The instrument was equipped with a back-scattered electron (BSE) detector Centaurus which can resolve 0.05 μm-sized grains. The polished equivalents of 13 thin sections (sample: Gr-I-2, 3, 4; Gr-II-3, 8, 13, 14, 16, 17, 18, 19A,B, 20; see figure 16 in Górniak, 2011) were examined by electron microscopy using BSE and charge-contrast imaging (CCI). For the purpose of making thin sections, each rock chip was impregnated with epoxy resin.

X-ray diffraction (XRD) was used to examine bulk rocks (13 samples) and the fine clay fraction (<0.2 μm) in a mono-ionic state isolated from representative carbonate-depleted samples. The XRD analyses were performed using a Philips APD X'Pert PW 3020 diffractometer with CuKα radiation and a graphite monochromator. The XRD patterns were recorded for 1 s per 0.05°2θ step from random-powder back-loaded specimens and oriented preparations of the fine clay fraction in both the air-dried state and when solvated with ethylene glycol (Figure 1). External standards obtained from selected Outer Carpathian marl samples were used to estimate the semi-quantitative mineralogy — this was conducted following the procedure of Schultz (1964) and Moore and Reynolds (1997).

3. Results and discussion

3.1. Mineralogical analysis (XRD, optical microscopy, FESEM/BSE)

Mineral analysis of the non-arenaceous variety of Grybów Marls indicates the following compositional ranges: carbonates 19–48% (calcite 12–48%: dolomite ≤10%); clay minerals 31–50%, dominated by illite-smectite (I-S); quartz 8–18%; feldspar 3–8%; pyrite 7–10%; and organic matter average ~2% (estimated by thermogravimetry/Evolved Gas Analysis). Microscopic observation (FESEM/BSE) revealed the presence of euhedral biotite (Figure 2) and apatite crystals.

The grain size of a representative marl sample is 50% clay, 49% silt, and <1% sand. Silt-sized grains are mostly calcareous fossils (48%) and scarce non-calcareous material (1%), while clay-sized particles are mostly non-calcareous in composition (clay minerals and rare micrometer-sized quartz) with minor amounts of micrometer-sized calcite grains (micarb). The clastic material does not exceed 0.06 mm in size.

The XRD patterns of the carbonate-free <0.2 μm particle size fractions in a homoionic Na-saturated state (Figure 1) are similar to those of highly illitic ordered illite-smectite (~82% illite in I-S).

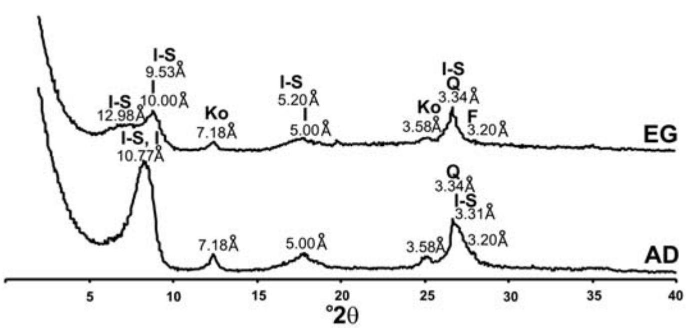

Figure 1. Representative XRD patterns of the fine clay fraction (<0.2 μm) isolated from the Grybów Marl sample (G-II-3). AD – air-dried; EG – ethylene glycol solvated; I-S – illite-smectite, I – illite, Ko – kaolinite, Q – quartz.

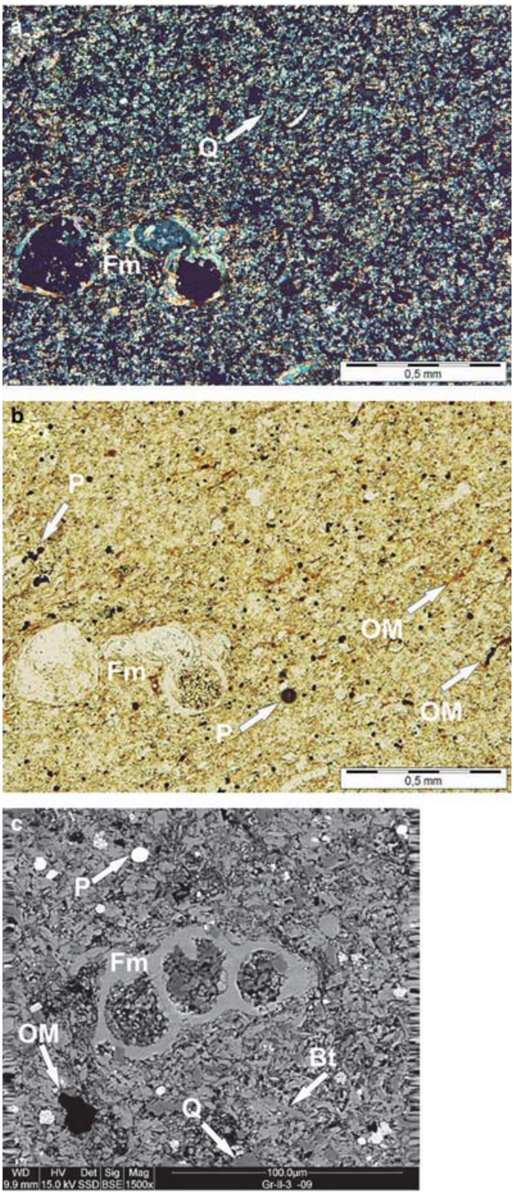

Figure 2. Microfabric of the Grybów Marls (sample Gr-II-3). Individual foram test (Fm), silt-size quartz grains (Q), biotite (Bt), pyrite framboids (P), and organic matter (OM), which are disseminated in the background. Thin-section micrograph (a – crossed polars; B – plane polarized light). c – coccolith fragments (white) and clay in the background captured in an FESEM/BSE image.

The average structural formula: $K_{0.42}Na_{0.09}(Al_{1.64}Mg_{0.23}Fe^{3+}_{0.23}Fe^{2+}_{0.08})[(Si_{3.48}Al_{0.52})O_{10}](OH)_2$, calculated from FESEM/EDX chemical analyses supplemented by the Fe^{3+}/Fe^{2+} ratio determined by Mössbauer spectroscopy, suggests dioctahedral compositions with similar octahedral Mg and Fe^{3+} contents. The clay minerals in some Carpathians chalk-type rocks are thought to have originated, at least partially, from altered volcanic material (see Bromowicz and Górniak, 1988; Górniak, 2011, 2015). The chemistry of the I-S octahedral sheet, along with the presence of pyroclastic grains such as biotite (Figure 2) and apatite in the rocks studied, suggests that the clay in the Grybów Marls may have a volcanic origin.

3.2. Petrography (optical microscopy, FESEM/BSE/CCI)

The thin-section images of the Grybów Marls show a dark brown background with very varied amounts of fine-grained siliciclastic material, bioclasts, pyrite framboids, and areas of organic matter (Figure 2a–c). Both siliciclastic and bioclastic grains are scattered throughout the background, and appear less commonly concentrated in indistinct silt-defined laminae. Individual dolomite microspars occur scattered throughout the background.

The Grybów Marls have a wackestone texture with the groundmass composed mostly of coccolith fragments and clay; they are classified as impure chalks. Coccolith

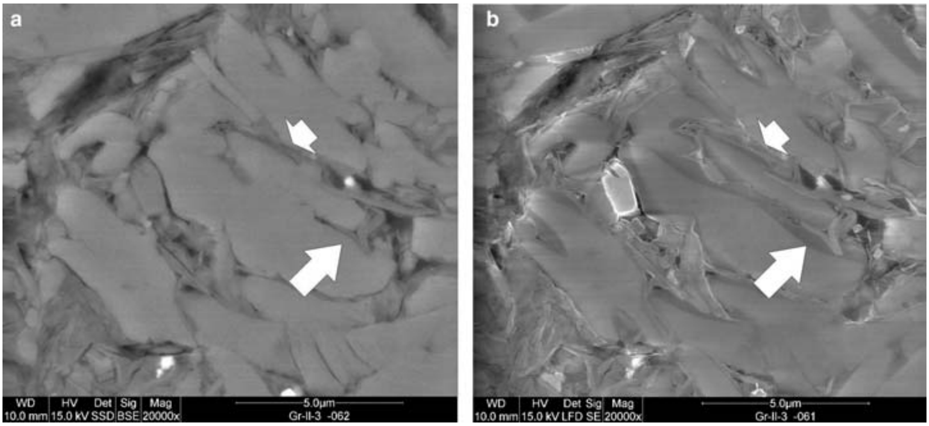

Figure 3. Interstices between coccolith shields partially cemented by pore-lining clay which postdate the overgrowth cement (longer arrows). Note the lamellar clay aggregates squeezed between overgrown coccoliths (shorter arrows). Grybów Marls, sample Gr-II-3: (a) FESEM/BSE and (b) CCI images.

shields are thickened by calcite overgrowths and only rarely is evidence of the dissolution of the central region with the resulting micrometer-sized rounded crystals (micarbs) found. The overgrowth cement links together adjacent coccoliths, locally, forming a framework. Clay occurs locally as contact, pore-lining, and pore-filling cements. The clay flakes display lamellar arrangements (Figure 3a–b).

3.3. Deposition and diagenesis

The coccolith shields with calcite overgrowths are separated by clay (Figure 3a–b), which seems likely to have post-dated the formation of coccolith overgrowths. Overgrown coccoliths were re-deposited along with clay (pore-filling clay) and the starting material (possibly volcanic ash) for clay neoformation (pore-lining clay).

3.4. Compaction

Compaction is indicated by broken foraminifer chambers (Figure 4), deformed coccospheres, coccolith shields altered by pressure-solution and crushed, as well as slightly flattened pyrite framboids. Clay aggregates are bent, but not spectacularly, around adjacent more rigid grains. In the majority of clay aggregates, however, the clay flakes are in close contact with nearly face-to-face associations, probably as the result of mechanical compaction.

3.5. Porosity

The intergranular, intragranular, and intrabiotic porosity within groundmass constituents, pyrite framboids, and foraminiferal tests, respectively, have been recognized. The evolution of pore space in the Grybów Marls is suggested to result from a combination of factors such as: (1) the origin of components, *i.e.* minute bioclasts along with

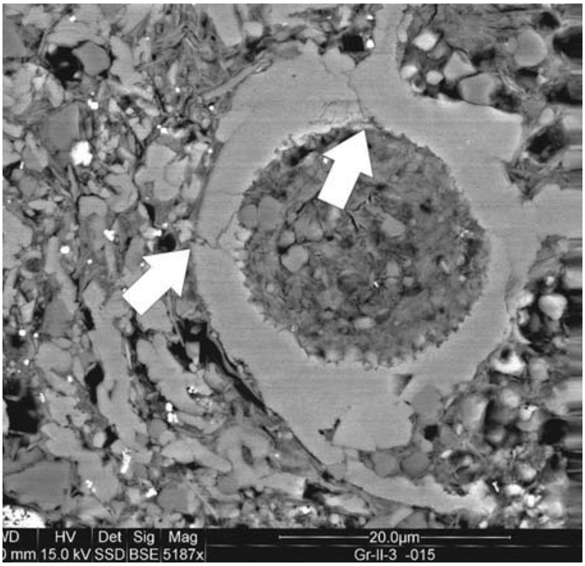

Figure 4. Fractured foraminineral test (arrows). FESEM/BSE image from the Grybów Marls, sample Gr-II-3.

smectite originating from the alteration of dispersed volcanic glass shards and altered subsequently during diagenesis to highly illitic I-S; (2) an organic acid-rich sedimentary environment which facilitated the eogenetic re-distribution of calcite; and (3) compaction-induced clogging of pore space reducing porosity within the clay flake associations and resulting in the formation of lamellar clay aggregates.

In addition to reports by Fabricius (2007) and by Mallon and Swarbrick (2008) that porosity loss in chalk-type rocks was caused by diagenetic burial-induced processes (chemical diagenesis in chalk; early mechanical compaction and dissolution in impure chalk), the present study suggests that the origin of the clay and the early diagenetic overgrowth of coccolith debris may also influence the pore-space evolution in these rocks. The timing of diagenetic processes revealed by microscopic investigation indicates that eogenetic overgrowth cementation influences the pathway of burial diagenesis in impure chalk. The eogenetic cementation in chalk was also documented by isotopic trace-element studies performed by Hu *et al.* (2012) and by Jeans *et al.* (2014).

4. Summary and conclusions

A possible pathway for the evolution of porosity in the Grybów Marls is as follows: (1) deposition of coccoliths in oxygen-depleted conditions in a sedimentary basin with limited water circulation; (2) dissolution and recrystallization of coccolith shields due to calcite redistribution in sediments rich in organic matter with the localized formation of coccolith clusters; (3) periodic addition of volcanic material and scarce terrigenous particles to the biogenic mud followed by the initial alteration of volcanic glass fragments to clay; (4) re-deposition by turbidity currents of the shelf sediments consisting of recrystallized coccolith shields along with siliciclastic material which acted subsequently as a pore-filling cement; (5) burial-induced compaction, which brought about: (i) closer relationships between coccolith shields and the formation of pore-lining clay along with scarce pore-filling micro-quartz cements from the dissolution of disseminated volcanic glass fragments; and (ii) the smectite-to-illite alteration that was accompanied by the re-organization of clay flakes into less porous aggregates; and (6) stress-induced micro-cracks (secondary porosity) created mostly in foraminiferal tests, as the majority of coccolith shields were protected from crushing by the presence of clay cement. As the result of the increasing stress, the clay cement underwent re-organization, forming lamellar aggregates causing the loss of primary porosity.

The pore space, viewed using high-resolution microscopy, which is accessible to fluid and gas migration in the impure chalks of the Grybów Marls is within: (1) pyrite framboids; (2) central areas of the interstices which are partially cemented by pore-lining clay, and (3) secondary fractures within allochems.

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