Characteristics of diagenesis, isotopic relations and reservoir properties of the Middle Miocene sandstones in the Carpathian Foredeep (Poland and Ukraine)

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INTRODUCTION

Changes in reservoir characteristics of the Middle Miocene strata of the Carpathian Foredeep are important for the interpretation of the geological history and as regards evolution of oil and gas potential and hydrocarbon prospects. Hence, detailed sedimentological, petrological, mineralogical, isotopic and fluid inclusion studies on the Upper Badenian and Sarmatian rocks from southeastern Poland and western Ukraine have been carried out in the last two decades (e.g., Dzidzio, 2000; Maliszewska et al., 2001a, b, 2004; Jasionowski and Peryt, 2010; Jarmolowicz-Szulc et al., 2011; Kozłowska et al., 2011; Kuberska et al., 2011; Lis and Wysocka, 2012; Jasionowski et al., 2012; Wysocka et al., 2012; Peryt et al., 2014; Galamay et al., 2014). Isotopic analysis and particularly strontium isotopic analyses have proven a powerful chronostatigraphic tool (e.g., McArthur et al., 2001, with references therein). Furthermore, isotopic composition of δ18O and 87Sr/86Sr can provide useful information about the origin, mixing processes (Cendón et al., 2008; Garcia-Veigas et al., 2013, 2015, amongst many others) and diagenetic evolution of formation waters (Sheppard, 1986; Schulz et al., 1989; Armstrong-Altrin et al., 2009). However, diagenesis can alter 87Sr/86Sr ratios from their original values, so a detailed understanding of alteration processes is needed to validate such studies (e.g., Kasprzyk et al., 2007).

Miocene deposits from twenty one boreholes are the subject of the present synthetic study (Fig. 1). Their location is shown in Figure 1.

The aim of the present study is to analyse mineral compositions of the sandstones and their cements and the relationships between various diagenetic processes and the sedimentary environment, and to describe the characteristics of the hydrocarbon reservoir rocks. Attention was focused on observing processes over the entire study area. Over one hundred samples of siliciclastic rock were examined, the results being presented both in earlier works of the authors and in the present paper. These rocks are underlain by the evaporitic succession of the Middle Miocene basin (Oszczypko et al., 2006; Peryt, 2006). Earlier results obtained for the Middle Miocene sandstones from boreholes in the Tamnogród area (Maliszewska et al., 2001a) have been used for comparison and discussion. The presently analysed rock samples are mainly the sandstones referred by Garecka and Olszewska (2011) to the Late Badenian and Sarmatian.
GEOLOGICAL SETTING AND DEPOSITIONAL ENVIRONMENTS

The Carpathian Foredeep is a large sedimentary basin developed on the Carpathian front from the Danube River in Austria to the Iron Gates in Romania (Oszczypko et al., 2006). The foreland basin developed as a result of Carpathian front movement towards north during Early to Middle Miocene. The inner part of the Carpathian Foredeep is located beneath the Carpathian nappes whereas the outer one is placed in front of the orogen (Ney et al., 1974; Oszczypko et al., 2006).

According to seismic, magnetotelluric and borehole data (Oszczypko et al., 2006), the Carpathian Foredeep is asymmetrical as a whole, with an erosional boundary in the north and a tectonic boundary to the south. It is filled in with predominantly clastic strata of Miocene age. The molasse deposits underlain by the basement of the East European Platform are overlain by Permain-Mesozoic terrestrial and shelf strata and locally by Paleogene deposits. The platform basement with the Miocene molasse dips southwards beneath the Outer Carpathian units (Oszczypko et al., 2006). The Early to Middle Miocene Carpathian Foredeep developed as a peripheral foreland basin related to the moving Carpathian front. The Paleozoic–Mesozoic, Paleogene and Neogene strata of the Carpathian Foredeep are oil and gas productive (e.g., Fedyshyn, 1998; Karnkowski, 1999; Kurovets et al., 2004, respectively). The latest Badenian–Early Sarmatian deposits formed in a variety of depositional environments, from deep marine (basin plain) to shallow marine (Lis and Wysocka, 2012). They represent the Machów Formation in the Polish part (Jasionowski, 1997; Oszczypko et al., 2006) and the Kosiv and Dashava formations in the Ukrainian part (Andreyeva-Grigorovich et al., 2008). In general, the section consists of mudstones and fine-grained sandstones deposited predominantly from gravity flows. Proximal facies contain huge sandstone packages, while the distal ones are dominated by mudstones and claystones with thin sandstone beds. The orogen was the main source area for the material deposited in the Carpathian Foredeep Basin. The sedimentary record is interpreted as terrestrial to marine and consists predominantly of fine-grained sandstones, claystones and mudstones (Peryt and Piwocki, 2004, with references therein). Lis and Wysocka (2012) distinguished fourteen lithofacies in the Middle Miocene deposits within the Polish and Ukrainian parts of the study area. Generally, the sandstones are characteristic of deltaic and shallow marine environments.

METHODS

53 core samples of sandstones from the depth interval of 300–2500 m from 8 boreholes from Poland and 49 samples from the depth interval of 1250–3200 m from 10 boreholes from Ukraine were collected. Sedimentological descriptions of cores and well-log correlation panels for both parts of the Carpathian Foredeep are given by Lis and Wysocka (2012). Analytical procedures comprised several stages: preparation, microscopic evaluation, petrological and mineralogical assessment and isotopic and fluid inclusion analyses.

All petrological samples were vacuum-impregnated with blue resin prior to thin section preparation in order to investigate, optically, the porosity. Sandstones underwent mineral counting using a counter PRIOR model G. Modal compositions of the sandstones were obtained by counting 300 points per thin section using a polarizing microscope Nikon Eclipse LV 100 Pol. The pore percentage in sandstones was calculated. Sandstone microlithofacies were distinguished using the Pettijohn et al. (1972) classification (a version of the Dott classification, modified). Thin sections were stained by Evamys solution in order to identify the carbonates. Textural features, grains of feldspar and cements of carbonates, quartz and kaolinite were observed in selected polished thin sections analysed within cathodoluminescence (CL) using the equipment with a cold cathode CCL 8200 mk 3, Cambridge Image Technology Ltd.

Studies of crystal habit, occurrence and paragenetic relationships were performed on gold-coated samples chips using a LEO 1430 scanning electron microscope (SEM) with energy-dispersive X-ray analyser. Back-scattered electron (BSE)
images were also obtained with the same SEM. The chemical composition of carbonates and feldspars was determined on twenty-two polished, carbon-coated thin sections using a JEOI JSM-35 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyser. Mineralogical composition of the <2 μm fraction of the sediment (clay minerals) was determined by X-ray diffraction (XRD), using a Philips X'Pert PW 3020 diffractometer (Cu Kα radiation and semiconductor detector). The analyses were performed on oriented air-dried and subsequently glycol-saturated samples, heated at 550°C. The fluid inclusion analysis was conducted on authigenic carbonates in selected samples in twenty-double-polished thin sections. Thermometric studies were performed using a Linkam THMS600 heating-cooling stage mounted on a polarizing microscope (Nikon Eclipse LV 100 Pol). In the heating mode they lead to determination of temperatures of mineral crystallisation, since it is assumed that the homogenisation temperature of the primary aqueous inclusions represents a minimum temperature of fluid trapping during mineral precipitation (Roedder, 1984). The estimation of the pressure and temperature conditions of the formation of minerals based on the crossing isochore technique using coexisting carbon dioxide and aqueous inclusions, followed the method introduced by Kalyuzhnii (1982; Jarmolowicz-Szulc et al., 2011). Isochores for the carbon dioxide were calculated with both the Flincor program (Brown, 1982) and the FLUIDS package (Bakker, 2003).

Carbon and oxygen stable isotope analyses were performed on forty-seven calcite- and eighteen dolomite-cemented sandstone samples. Measurements were conducted at the Maria Curie-Skłodowska University in Lublin (e.g., Halas, 1982). For the isotopic analyses, carbon dioxide gas was extracted from the samples by reaction of carbonate with H3PO4 at 50°C in a vacuum line for at least 24 hours (according to the procedure by McCrea, 1950). The gas was purified of water on a P2O5 trap and collected on a cold finger. Isotopic compositions were analysed using a triple collector mass spectrometer equipped with a gas ion source. After subsequent normalization to measured international standards, the isotopic composition was expressed in per mille relative both to VPDB and VSMOW standards. Analytical precision of both δ13C and δ18O in samples and in standards was better than ±0.08‰.

Strontium analyses were performed on eight sandstone samples with carbonate cements (10–15 vol.% calcite) at the Isotope Geochemistry Laboratory of the Polish Academy of Sciences in Cracow. Standard procedures have been described, e.g., by Peryt et al. (2010), or by Peryt and Anzczkiewicz (2015). Powdered rock samples were dissolved on a hot plate in HCl. Dissolved samples were first loaded on a standard cation column (DOWEX 50W-X2 15 resin). The collected Sr fraction was further purified on Eichrom Sr-spec resin. After converting to nitrates, analyses of the strontium isotopic ratio (87Sr/86Sr) were performed in a static mode on the MC ICPMS Neptune with reference to frequent analyses of the SRM987 standard. The measured ratios were instrumentally corrected to fractionation effect using the values of 87Sr/86Sr=0.1194 and normalized with 87Sr/86Sr = 0.710248 (Oslick et al., 1984). Precision of individual ratios refers to the last significant digits and is at 2σ level (Thirwall, 1991).

 Petrophysical measurements of porosity, permeability and the pore space parameters: porosimetric porosity, the percentage of pores with a diameter >1 μm, size of threshold diameter and hysteresis were conducted at the Oil and Gas Institute in Kraków.

**SANDSTONE PETROGRAPHY**

The sandstones, as packages or layers of different thickness, form interlayers in thick mudstone-claystone thick successions. Sandstone features for both parts of the study area are shown in Table 1.

**FRAMEWORK GRAIN COMPOSITION**

The sandstones are very fine- to medium-grained, moderately to poorly sorted. The grains are angular to subrounded. The sandstones studied represent subarkosic and sublithic arenites and wackes (Fig. 2).

The quartz, the content of which ranges from 18.7 to 70.6 vol.%, is the main component of the rock (Table 1). Monocrystalline quartz predominates over polycrystalline quartz, which includes fragments of chert (on average ~1 vol.%). The quartz grains commonly have sharp edges, and only those of the fraction of 0.25 mm are partly rounded. Feldspars occur in all sandstone samples analysed in amounts varying from 1.0 to 12.3 vol.%. They are mainly potassium feldspars which show a blue color in cathodoluminescence. The plagioclase, characterized by a green color in CL, is less frequent (Fig. 3A, B). The partial or total replacement of some feldspar grains by albite (non-luminescent in CL) and/or calcite as well as dissolution of feldspar is observed (Fig. 3C). Micas occur in various amounts in both segments of the basin, with a distinct muscovite predominance over biotite. Their percentage is low in the east, only occasionally exceeding 10 vol.%. In the western part of the study area, mica content reaches about 18 vol.%. Lithoclasts occur in the sandstones studied in amounts of up to 11.6 vol.% in the Ukrainian and up to 18.3 vol.% in the Polish segments. They are mainly sedimentary rock fragments (mudstones, very fine-grained sandstones, claystones, carbonate rocks in the eastern, and mainly limestone, rarely claystones, siltstones and sandstones in the western part of the basin). The fragments of metamorphic rocks (mica and quartz-mica schists), and the fragments of igneous rocks (granitoids and eruptive rocks, mainly volcanic glass) are less frequent. Calcite bioclasts were observed in the sandstones analysed, from 0 to 3.3 vol.% Foraminifers are the most common bioclasts (Fig. 3D), while fragments of bivalve and brachiopod shell and echinoderm and branches of bryozoans are less frequent. Other components of sandstones with <2 vol.% in the sandstones are: organic matter, accessory minerals (mainly zircon andapatite), ooids and glauconite. The glauconite is common and forms oval, green grains of various size that appear affected by varying degrees of chloritisation and pyritisation. Locally, ooids with diameter <0.5 m are observed (e.g., the Pruchnik 22 borehole).

Both the matrix and the cement in the Middle Miocene sandstones are present in variable amounts. The matrix is composed of fine grains of quartz mud and detrital flakes of clay minerals, plus locally iron hydroxides, organic matter and pyrite. XRD analyses of clay minerals have shown the presence of smectite, illite, chlorite, and kaolinite. Cements are mainly built of carbonates, while quartz and clay mineral cements are less frequent.

**CEMENTS AND REPLACIVE MINERALS**

Various diagenetic minerals in the Middle Miocene sandstones (Fig. 3A, B, E–H) were earlier described by Maliszewska...
Table 1

<table>
<thead>
<tr>
<th>Sandstone features</th>
<th>Western part (Poland)</th>
<th>Eastern part (Ukraine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz [vol.%]</td>
<td>19.0–70.6</td>
<td>18.7–68.0</td>
</tr>
<tr>
<td>Feldspar [vol.%]</td>
<td>1.7–12.3</td>
<td>1.0–9.3</td>
</tr>
<tr>
<td>Lithoclast [vol.%]</td>
<td>0–18.3 (mudstones, very fine grained sandstones, claystones, carbonate rocks, rarely mica schists, quartz-mica schists, granitoids and volcanic glass)</td>
<td>0.3–11.6 (limestones, rarely claystones, siltstones, sandstones, mica schists, quartz-mica schists, granitoids and volcanic glass)</td>
</tr>
<tr>
<td>Micas [vol.%]</td>
<td>0–17.7</td>
<td>0–13.3</td>
</tr>
<tr>
<td>Bioclasts [vol.%]</td>
<td>0–3.3</td>
<td>0–2.7</td>
</tr>
<tr>
<td>Ooids [vol.%]</td>
<td>0–0.7</td>
<td>0</td>
</tr>
<tr>
<td>Glaucnite [vol.%]</td>
<td>0–1.3</td>
<td>0–5.3</td>
</tr>
<tr>
<td>Accessory minerals [vol.%]</td>
<td>0–1.7</td>
<td>0–0.7</td>
</tr>
<tr>
<td>Matrix [vol.%]</td>
<td>0–49.7</td>
<td>1.7–33.7</td>
</tr>
<tr>
<td>Authigenic quartz [vol.%]</td>
<td>0–2.4</td>
<td>0–6.3</td>
</tr>
<tr>
<td>Carbonates [vol.%]</td>
<td>3.0–39.7 (calcite, dolomite, ankerite, siderite, rhodochrosite)</td>
<td>4.8–49.3 (calcite, dolomite, ankerite)</td>
</tr>
<tr>
<td>Authigenic clay minerals [vol.%]</td>
<td>0–0.3</td>
<td>0–1.7</td>
</tr>
<tr>
<td>δ¹³C in dolomite cement [% VPDB]</td>
<td>n.d.</td>
<td>-0.59–2.11</td>
</tr>
<tr>
<td>δ¹⁸O in dolomite cement [% VPDB]</td>
<td>n.d.</td>
<td>-8.25–(-1.70)</td>
</tr>
<tr>
<td>δ¹³C in calcite cement [% VPDB]</td>
<td>-5.72–(-1.71)</td>
<td>-7.76–(-1.03)</td>
</tr>
<tr>
<td>δ¹⁸O in calcite cement [% VPDB]</td>
<td>-8.61–(-5.51)</td>
<td>-8.80–(-3.46)</td>
</tr>
<tr>
<td>⁸⁷Sr/⁸⁶Sr in calcite cement</td>
<td>n.d.</td>
<td>0.708661–0.709255*</td>
</tr>
<tr>
<td>Th [°C] in calcite cement</td>
<td>&lt;50</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Salinity wt.% eq. NaCl</td>
<td>13.52</td>
<td>7.53–16.24</td>
</tr>
<tr>
<td>Porosity in thin section [vol.%]</td>
<td>0–29.4</td>
<td>0–19.3</td>
</tr>
<tr>
<td>Effective porosity [%]</td>
<td>14.03–34.76</td>
<td>0.61–28.33</td>
</tr>
<tr>
<td>Pores &gt;1 μm [%]</td>
<td>47–91</td>
<td>4–90</td>
</tr>
<tr>
<td>Threshold diameter [μm]</td>
<td>3–50</td>
<td>0.2–30</td>
</tr>
<tr>
<td>Hysteresis [%]</td>
<td>21–84</td>
<td>43–82</td>
</tr>
<tr>
<td>Permeability [mD]</td>
<td>0.62–332.27</td>
<td>0.10–294.40</td>
</tr>
</tbody>
</table>

Data from Jarmo³owicz-Szulc et al. (2011), Koz³owska et al. (2011) and Kuberska et al. (2011); * – new data; n.d. – not determined

Fig. 2. Plot of the mineral composition of the Miocene sandstone (arenites, wackes) samples in the classification triangle of Pettijohn et al. (1972); data from Koz³owska et al. (2011) and Kuberska et al. (2011)
et al. (2001a, b), Koźłowska et al. (2011) and Kuberska et al. (2011).

The carbonate cements in the study area are represented mostly by calcite, dolomite andankerite (Figs. 4–9). The siderite was identified only in the western part of the study area. Two types of the calcite cement can be distinguished: micro- and coarsely crystalline. The microcrystalline calcite occurs on the surface of grains and in primary pores. The coarsely crystalline to poikilitopic calcite cement occurs in intergranular and intragranular position in the sandstones studied (Fig. 3A, B).

Additionally, this cement replaces feldspar grains and rock fragments, often forming pseudomorphs. The coarsely crystalline calcite post-dates quartz overgrowths and dolomite and ankerite rhombohedra (Fig. 3E). The chemical composition of calcite is: 92.2–99.4 mol.% CaCO$_3$, 0–4.6 mol.% FeCO$_3$, 0–2.5 mol.% MgCO$_3$ and 0–2.5 mol.% MnCO$_3$ (Fig. 4). It represents mainly Fe-bearing calcite characterized by red-orange and orange-yellow colors in CL (Fig. 3A, B). The δ$^{18}$O values for calcite range from –8.80 to –3.46‰ VPDB, and the δ$^{13}$C values from –7.76 to –1.03‰ VPDB (Table 1; Figs. 5 and 6). Strontium values in the calcite are shown in Tables 1 and 2, Figures 8 and 9. The $^{87}$Sr/$^{86}$Sr ratios in the sandstones studied with predominantly calcite cements range from 0.708661 to 0.709255 (2σ = 0.000011, Table 2; Figs. 8 and 9). Fluid inclusions in the calcite cement in the sandstones are mostly one-phase and either transparent or dark in color. Their size ranges from 1 to 2 µm. The one-phase character of the inclusions indicates low temperatures of cement formation – at about 50°С (Shepherd et al., 1985; Burruss et al., 1987; Jarmo³owicz-Szulc et al., 2011). The dolomite and the ankerite occur in sandstones as pore-filling rhombohedra (Fig. 3A, E–G). Some of the crystals show zoning, with the core poorer in iron than the rims. The chemical composition of the dolomite minerals is: 52.4–61.4 mol.% CaCO$_3$, 18.1–45.0 mol.% MgCO$_3$, 0–21.0 mol.% FeCO$_3$ and 0–2.0 mol.% MnCO$_3$ (Fig. 4). The dolomite and ankerite crystals are surrounded by Fe-bearing calcite. The δ$^{18}$O values for dolomite are between –8.25 and –1.70‰ VPDB, while the δ$^{13}$C values range from –5.99 to –2.11‰ VPDB (Table 1; Figs. 5 and 7). The siderite occurs as scattered microcrystalline crystals. Siderite varies widely in composition, being enriched in magnesium, and represents sideroplasite (Fig. 4).

The quartz cement occurs commonly in amounts below 1 vol.% of the whole rock, only rarely reaching up to 2.4 vol.%. It occurs as partial or complete syntaxial overgrowths around the quartz grains. The boundary between the overgrowths and the detrital core is either poorly defined or delineated by fluid inclusions or thin clay coatings. The quartz overgrowths show dark-brown luminescence or no luminescence, while the quartz grains have brown and blue colors (Fig. 3B). The authigenic quartz overgrowths are rhombohedral crystals and prisms on detrital quartz grains as observed in SE images (Fig. 3H).

The authigenic clay minerals observed under the polarizing and scanning electron microscopes are kaolinite, chloride and illite. The kaolinite occurs as booklets and vermicular stacked...
pseudohexagonal crystals, the latter being locally distributed in intergranular and intragranular space of the Middle Miocene sandstones. Blocky habits were also noticed in some samples. The kaolinite is surrounded by quartz overgrowths, so it pre-dates the quartz. Rarely, it replaces detrital feldspar or muscovite. Chlorite was identified only locally. Chlorite/chlorite-smectite minerals occur as small flakes developed into a honeycomb-like texture that coats the framework grains. Iron content is there higher than that of magnesium (Kozłowska et al., 2011). Platy and filamentous crystals of illite cover the authigenic quartz and calcite and infill the pore space in the sandstone (Fig. 3H).

Minor diagenetic minerals include pyrite, feldspars and rhodochrosite. The pyrite occurs as scattered frambooids filling primary and secondary pores (dissolved bioclasts) in the rock. Authigenic K-feldspars occur as overgrowths on partly to completely albited and argillitised plagioclase grains. These overgrowths are surrounded by, and hence pre-date, the quartz overgrowths. The rhodochrosite in nodules was identified only in samples from the western part of the area.

Fig. 6. Plot of the results obtained from pore water in the calcite cement in the δ18O versus temperature diagram (see Friedman and O’Neil, 1977); data from Kozłowska et al. (2011) and Kuberska et al. (2011); temperature of 50°C obtained from Fl (Jarmolowicz-Szulc et al., 2011)

Fig. 7. Plot of the results obtained from pore water in the dolomitic cement in the δ18O versus temperature diagram (see Dutton and Land, 1985); data from Kuberska et al. (2011)

### INTERPRETATION AND DISCUSSION

#### EVOLUTIONARY PATHWAYS OF DIAGENESIS

In the present paper, a classification of diagenetic stages after Choquette and Pray (1970) has been applied. As shown below, two diagenetic stages (eo- and mesodiagenesis) have been distinguished.

The eodiagenesis corresponds both to the formation of clay mineral rims (mostly chlorite rims on the detrital grains) and mechanical compaction, observed as undulous mica flakes or as local grain re-arrangement. At this stage the crystallisation of the microcrystalline calcite and calcite and infill the pore space in the sandstone (Fig. 3H).

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<table>
<thead>
<tr>
<th>Borehole</th>
<th>Depth [m]</th>
<th>δ13C [% VPDB]</th>
<th>δ18O [% VPDB]</th>
<th>87Sr/86Sr</th>
<th>2se (measurement precision)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanivka 1</td>
<td>1456.3</td>
<td>–2.40</td>
<td>–5.76</td>
<td>0.708842</td>
<td>0.000011</td>
</tr>
<tr>
<td>Makuniv 1</td>
<td>1847.0</td>
<td>–5.55</td>
<td>–7.66</td>
<td>0.708927</td>
<td>0.000011</td>
</tr>
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<td>Nykovych 26</td>
<td>1250.5</td>
<td>–1.30</td>
<td>–4.66</td>
<td>0.708661</td>
<td>0.000011</td>
</tr>
<tr>
<td>Nykovych 26</td>
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<td>–4.39</td>
<td>–7.19</td>
<td>0.708859</td>
<td>0.000009</td>
</tr>
<tr>
<td>Podil’tsi 1</td>
<td>1231.8</td>
<td>–5.95</td>
<td>–7.24</td>
<td>0.708823</td>
<td>0.000011</td>
</tr>
<tr>
<td>Skhidne Dovhe 3</td>
<td>1714.3</td>
<td>–7.76</td>
<td>–8.27</td>
<td>0.708953</td>
<td>0.000009</td>
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<tr>
<td>Skhidne Dovhe 3</td>
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<td>–6.56</td>
<td>–8.80</td>
<td>0.708887</td>
<td>0.000012</td>
</tr>
<tr>
<td>Susoliv 5</td>
<td>2100.5</td>
<td>–1.95</td>
<td>–6.11</td>
<td>0.708783</td>
<td>0.000007</td>
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<td>Susoliv 5</td>
<td>2528.2</td>
<td>–2.78</td>
<td>–6.09</td>
<td>0.709256</td>
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<tr>
<td>Voloscha 1</td>
<td>2091.2</td>
<td>–6.91</td>
<td>–5.59</td>
<td>0.709163</td>
<td>0.000011</td>
</tr>
</tbody>
</table>
 tion of the calcite cements, the dissolution and albition of plagioclases, or the illitisation of the smectite may have been sources for Ca and Fe in the coarsely crystalline calcite in the sandstones studied (Boles and Franks, 1979; Milliken, 1998; Morad, 1998). Progressive mesodiagenesis led to a continued dissolution of feldspars, lithoclasts and components of the earlier cements resulting in the formation of secondary, intergranular and intragranular, porosity. Moreover, effects of the illitisation of kaolinite can be observed. The formation of authigenic illite took place at temperatures of about 100°C (Kantorowicz, 1990). All these processes have been accompanied by limited compaction.

**DIAGENETIC CONDITIONS OF CARBONATE CEMENTATION**

Fluid inclusions (FI) in the calcite cement in the sandstones studied by means of microthermometry indicate a temperature dependence. The eutectic temperature for these inclusions is generally ~<21°C and the ice melting temperature is between ~6.5 to ~5.9°C (see: Jarmo³owicz-Szulc et al., 2011). Microthermometric data of the fluid inclusions in the coarsely crystalline calcite cement studied in the west of the area (e.g., in the Pruchnik 22 borehole; Koz³owska et al., 2011) point to low temperatures of cement formation ~<50°C (Shephard et al., 1985; at maximum 80°C, Jarmo³owicz-Szulc et al., 2011). The eutectic temperatures suggest the NaCl-CaCl₂-MgCl₂-H₂O system, while the ice melting temperature indicates fluid salinity of ~13.52 wt.% NaCl eq. (Brown, 1982; Burruss, 1987; Bodnar, 1990; Jarmo³owicz-Szulc et al., 2011). In the eastern part of the study area, the microthermometric results of one-phase inclusions (Skhidne Dovhe 3, Lanivka 1) suggest salinities of ~9 wt.% NaCl eq., densities of ~1.1 g/cm³ trapping conditions <60°C and pressures of about 375 bars (see Jarmo³owicz-Szulc et al., 2011).

**CARBON AND OXYGEN ISOTOPES**

The generally positive δ¹³C values of dolomite in the study area in Ukraine in the interval from ~0.59 to 2.11‰ VPDB and its enrichment in iron suggest derivation of the carbon from microbial methanogenesis of organic matter (Burns et al., 1988; Morad, 1998). The δ¹⁸O values for dolomite change most frequently from ~4.0 to ~2.0‰ VPDB (Jarmo³owicz-Szulc et al., 2011; Kuberska et al., 2011). From the fractionation equation of Dutton and Land (1985) the authors have used δ¹⁸O values (mainly from ~4.62 to ~1.70‰ VPDB) and assumed a crystallisation temperature of about 40–50°C (Fig. 7). The data indicate the precipitation of dolomite from porewater showing δ¹⁸O VSMOW values between about ~3.5 to 1.0‰ which further points to a mixture of marine and meteoric waters. El-Ghali et al. (2013) obtained similar isotopic compositions of porewater and they assumed that dolomite precipitated from brackish to marine porewaters.

The δ¹³C values of calcite, with an average of about ~4.0‰ VPDB, suggest the microbial methanogenesis of organic matter as a source of the carbon. The FeCO₃ content in calcite (0.0–4.6 mol.%; average 2.0 mol.%) suggests precipitation in the suboxic zone where the porewaters were depleted in oxygen during progressive burial (El-Ghali et al., 2013). According to Glasmann et al. (1989), the high iron and manganese concentrations in the calcite indicate precipitation from pore waters in reducing conditions. The δ¹⁸O values for calcite change from ~8.80 to ~3.46‰ VPDB. If the fractionation equation of Friedman and O’Neil (1977) is adopted, a temperature of 50°C for precipitation of the coarsely crystalline calcite is indicated.
A certain relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.708661 to 0.709255) in calcite and the sampling depth can be noticed (Fig. 8 and Table 2). In general, the deeper is the sample, the higher are the values of isotopic ratios. The points corresponding to $^{87}\text{Sr}/^{86}\text{Sr}$ values seen in the figure (Fig. 8) plot on an almost linear trend for the Ukrainian samples, with one exception (the sample from the Podil’tsi borehole). The samples show distinctly lower values than those obtained by Jasionowski and Kurzawa (1990) for the calcite from the anhydrite succession of the Wola Różaniecka borehole. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the carbonates from the depth between 1112.9 and 1118.8 m are between ~0.70276 and 0.71148. In that context, a decreasing tendency eastwards may be observed in regional comparisons of the strontium ratios in carbonates. The present paper data (0.708661 to 0.709255) also differ from the $^{87}\text{Sr}/^{86}\text{Sr}$ value reported by Dickson et al. (2001) for contemporaneous marine carbonates. According to Schultz et al. (1989), the carbonate cements have the same strontium ratio as those of the pore water at the time they precipitated. The ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater during the Late Miocene to Early Pliocene lies between 0.7089 and 0.7091 (Holdell et al., 1991). According to Pulver et al. (2001) depicted $^{87}\text{Sr}/^{86}\text{Sr}$ ratio variation in the Phanerozoic, seawater values lower than about 0.7083 were characteristic for the time period from the Early Devonian to the earliest Miocene. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio value in the Badenian seawater is reported as 0.708698–0.708817 (Kasprzyk et al., 2007). The samples studied show average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios values of about 0.708915, which is higher than those of the Badenian seawater quoted above. This difference can suggest that the calcium cements were formed from brines containing non-marine Sr, or with significant meteoric water inputs, and also by bacterial sulphate reduction. In general, the non-marine waters are characterized by higher $^{87}\text{Sr}/^{86}\text{Sr}$ values as compared with values of the normal Miocene seawater (Palmer and Edmond, 1985). In a closed basin system, the local, altered plagioclase and smectite could have been a possible source of strontium for the calcite which crystallised at a later stage of diagenesis. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in plagioclase (average of ~0.70663) are lower than those in smectite (average of ~0.71073) which can affect the $^{87}\text{Sr}/^{86}\text{Sr}$ value in calcite (Schultz et al., 1989). In the calcite studied, there is an increase in strontium ratios as compared with the Badenian seawater values.

In the present case, therefore, the plagioclase cannot be a source of strontium. The samples studied have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the contemporary seawater, indicating a significant input of the radiogenic $^{87}\text{Sr}$ to the system after deposition (Armstrong-Altrin et al., 2009). The radiogenic strontium may have been supplied during diagenesis by meteoric waters draining the continental area. Glasmann et al. (1989) stated that the high radiogenic strontium level indicates an interaction of the pore-fluid with continental silicates. As shown in Figure 9, there is a general trend towards higher negative $^{87}\text{Sr}$ and higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This confirms that continental waters or a mixture of marine and continental waters were responsible for these relationships.

Such an interpretation is in agreement with the values of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained recently in the Badenian primary gypsum from two boreholes in the Polish Carpathian Foredeep Basin (Peryt and Anczkiewicz, 2015) and with the fluid inclusion and isotopic studies in the Badenian evaporates that suggest a mixed marine /meteoric origin for brines resulting in evaporite precipitation (Cédon et al., 2008). Peryt and Anczkiewicz (2015) found out that strontium ratios are higher than the contemporary seawater value due to significant non-marine contribution of radiogenic strontium. The high-grade Archean and Paleoproterozoic igneous rocks of the Ukrainian shield are regarded as the source of the higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios recorded in the primary gypsum.

**Diagenesis and Porosity**

The porosity and the permeability data obtained for numerous Polish and Ukrainian sandstone samples shows variability as shown by Kozłowska et al. (2011) and Kuberska et al. (2011) and in Table 1. The results of laboratory determinations of effective porosity factor oscillate from 0.61 to 34.76%. According to the classification of Jenyon (1990), the Miocene sandstones can be regarded as having a good and a very good porosity. Curves of capillary pressure were constructed and a threshold diameter determined (from 0 to 50 μm). Values of <3 μm indicate very low properties, while higher values point to good or very good filtration abilities of the sandstones analysed. The values of the hysteresis change in general from 21 to 84%, being less scattered eastwards. From analysis of these values some regularity in development of the pore space may be noticed. The percentage of pores with a diameter >1 μm varies and changes from 4 to 91% (exceeding 50% in most samples). The majority of the Ukrainian samples show a low permeability ~<1 mD. In some samples the permeability is of some dozens mD, occasionally >200 mD. On the other hand, most of the Polish samples are characterized by a very high permeability, above 100 mD, according to the classification of Levorsen (1956).

The porosity measured in thin sections reaches at maximum 19.3 vol.% (in the eastern part of the area studied) and 29.4 vol.% in the west and corresponds mainly to a primary intergranular porosity. Secondary intragranular pores were primarily associated with the dissolution of detrital feldspars (Fig. 3C) and rock fragments and minor bioclasts and calcite cement. Some secondary pores are inside foraminifer shells (Fig. 3D). Intercrystalline porosity (micropores) may be associated with the presence of clays.

A successive deterioration of porosity in the sandstones studied with increasing depth is observed (Kozłowska et al., 2011; Kuberska et al., 2011). The primary porosity of sandstones decreased due to compaction and cementation. Later, it increased by dissolution.

The mechanical compaction includes grain re-arrangement and plastic deformation of mica and ductile grains. Point and linear contacts between quartz grains were the only ones observed in the sandstones. The carbonates, the quartz and the authigenic calcite minerals play the most significant role among the cements of the sandstones. The calcite cement is predominant. Locally, it strongly reduces the porosity and decreases permeability down to zero. The early fringe cements as the clay
CONCLUSIONS

1. The Middle Miocene sandstones of the Carpathian basin represent very fine to medium-grained subarkosic and sublithic arenites and wackes. Their detrital framework is dominated by quartz, feldspar and subordinate rock fragments, micas, glauconite and bioclasts. The dominant recognized cement types are: Fe-bearing calcite, quartz overgrowths, dolomite and ankerite, and kaolinite. K-feldspar overgrowths, chlorite/chlorite-smectite rims, illite, pyrite, siderite, anhydrite and rhodochrosite are minor cements of the sandstones. Siderite and rhodochrosite have been recognized only in the west, and anhydrite in the east.

2. The $\delta^{18}O_{VPDB}$ data ($-8.8$ to $-1.7\%$) of the dolomite and the coarsely crystalline calcite indicate that the carbonate cements precipitated from the porewater with the $\delta^{18}O_{VSMOW}$ values between $-3.5$ to $0.0\%$ which points to a mixture of marine and meteoric waters. The $\delta^{13}C_{VPDB}$ values of carbonates ($-7.8$ to $2.1\%$), suggest derivation of carbon from microbial methanogenesis of organic matter. The $^{87}Sr/^{86}Sr$ values (0.7087 to 0.7093) in coarsely crystalline calcite, higher than in Badenian seawater, suggest that pore-fluid had interacted with continental silicates.

3. Fluid inclusions give in general temperatures <60°C (at maximum 80°C) for the calcite cements, and pressures of about 375 bars. The fluid was CO$_2$-bearing, of moderate salinity (of ~10% and ~13wt.% NaCl eq.), of moderate isotopic composition and with a density of ~1.1 g/cm$^3$. Petrographic and isotopic studies of cements in the sandstones suggest that the Middle Miocene deposits underwent diagenetic processes at temperatures not higher than 100°C.

4. Most Middle Miocene sandstones show a good and a very good porosity of about 20% and permeability >100 mD. The porosity reduction appears to be depth-controlled; the porosity data show a general decrease with an increase in depth. Both primary intergranular and secondary intragranular and intercrystalline pore types are present in the sandstones. Primary pores are abundant and are affected by compaction and cementation by about 26 and 35% in the west, as well as by approximately 36 and 43% in the east, respectively. Some increase in porosity was caused by the dissolution of detrital grains (mainly feldspars) and by the decay of soft parts of organisms. Comparing the sandstones from the western and eastern parts of the Carpathian Foredeep, the first ones show better filtration abilities.

5. The history of diagenesis of the Middle Miocene sandstones in the basin studied includes two stages: eo- and mesodiagenesis. Mechanical compaction (crystallisation of chlorite/chlorite-smectite, microcrystalline calcite, pyrite, siderite, kaolinite and quartz cements), as well as the dissolution of feldspars and micas correspond to eodiagenesis. The cementation of the following minerals: K-feldspar, dolomite and ankerite, coarsely crystalline calcite and illite as well as albisation, and the dissolution of feldspar grains and carbonate cements correspond to mesodiagenesis.

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