Temperature and isotopic relations in carbonate minerals in the Middle Jurassic sideritic rocks of central and southern Poland

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The present study assesses the physico-chemical character of the fluids responsible for the genesis of carbonate minerals in the Middle Jurassic sideritic rocks at the northeastern margin of the Holy Cross Mts. and in the Częstochowa region. These rocks occur at present at depths between 30 and 600 m. Fluid inclusion and isotopic analyses have been performed in the carbonate minerals from sideritic sandstones, clayey siderites and sideritic coquinas. Siderite is the main carbonate mineral of the sideritic rocks. Calcite and ankerite are also present. The siderite is represented by two varieties, Mg-rich siderite (sideroplesite, less commonly – pistomesite) and siderite. Two generations of siderite have been distinguished – an early and a late one. The early siderite was formed at temperatures of about 20°C in the zone of microbiological methanogenesis from marine waters with some influence of meteoric waters (δ¹⁸O from −7.84 to −1.92‰ VSMOW). The late siderite crystallized at temperatures of about 62–110°C from pore waters enriched in δ¹³C (δ¹³C >0‰ VSMOW) as compared with the isotopic composition of the waters responsible for the early siderite generation. The conducted fluid inclusion analyses point to formation of the cements from complex fluids of brine and carbon dioxide character, with densities slightly exceeding 1 g/cm³ and salinities varying from 10.5 to 16.9 wt.% NaCl eq. and from 6.4 to 14.0 wt.% NaCl eq. in the Holy Cross Mts. and in the Częstochowa region, respectively. The homogenization temperatures lie in the intervals of 62–110°C and 60–97°C, respectively and represent elevated values compared with data from the Polish Lowlands. Apart from burial, other heat sources must have been important for the lithogenesis of the Middle Jurassic deposits.

Key words: fluid inclusions, isotopes, carbonate minerals, sideritic rocks, Middle Jurassic.

INTRODUCTION

The term “siderite” encompasses minerals of the solid solution series between sidereite and magnesite, most frequently, sideroplesite and pistomesite (Bolewski, 1982). Most hitherto published papers present temperature conditions responsible for vein sidereites or magnesites of hydrothermal origin (e.g., Hein, 1993; Hurai et al., 2002; Lugli et al., 2002; Schmidt Mumm and Wollgang, 2002; Fernández-Nieto et al., 2003; Strmić Palinkaš et al., 2009; Palinkaš et al., 2016). Few papers provide data on fluid inclusions in sidereites from sedimentary rocks (Rezaee and Schulz-Rojahn, 1998).

A basis for fluid inclusion studies is an assumption that during the crystallisation of pore-filling minerals in sedimentary rocks, small amounts of basin fluids are trapped (Roedder, 1984). Generally, the fluid inclusions are relict portions of the solutions that no longer exist. Therefore, thermal and isotopic studies may serve to reconstruct the primary conditions of mineral formation and of the composition and density of palaeofluids (Jarmolowicz-Szulc, 1999). Information on the primary volume and composition should remain preserved. This is very difficult to constrain in the sedimentary rocks, which may be deeply buried and subsequently uplifted. Fluid inclusion bearers show variable resistance towards external conditions, which is why temperature results obtained for them may vary in significance (Jarmolowicz-Szulc, 2015).

In diagenetic studies, thermometric interpretation has to take into account a number of factors (Goldstein, 2001). First, the character of fluid inclusions (primary or secondary) needs to be considered. Next, the measured values may reflect a wide range of salinity, because the crystals have grown from mixed fluids. Then, deep burial of deposits may cause stretching and leakage of inclusions, so the temperature values obtained may not correspond to primary conditions of mineral formation (Goldstein, 1986).

The present research demonstrates the significance of fluid inclusions in relation to carbonate cements, mainly sidereite, locally ankerite and calcite. The inclusion and stable isotope data served as a geological thermometer. Additionally, carbon and oxygen isotope ratios in carbonate minerals have been used for calculation of the isotopic composition of the fluid from which these minerals have crystallized. Thus, fluid inclusion analysis accompanied by isotopic studies of the carbonate minerals in the sideritic rocks from two areas of Poland – the northeastern margin of the Holy Cross Mts. and the Częstochowa region (Fig. 1) contributed to better understanding of the origin of these sidereite deposits.

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GEOLOGICAL SETTING AND STUDY AREA

The study area (Fig. 1) represents a southern part of the Polish Basin that during the Jurassic was the eastern arm of the Central European Basin System (Pierkowskii et al., 2008). The thickness of the Middle Jurassic strata at the northeastern margin of the Holy Cross Mts. varies from 180 m (south-east) to about 800 m (north) (Daniec, 1970). The deposits are represented by sandstones and mudstones with interbeds of claystones and sideritic iron ores, mainly of Aalenian, Bajocian and Bathonian age (Kozłowska and Maliszewska, 2015). The thickness of the Middle Jurassic strata in the Częstochowa region changes from 85 m (south) to about 184 m (north) (Kopik, 1998). The deposits are composed of Bajocian and Bathonian sandy claystones and mudstones, which locally contain dark claystones with siderite (known as ore-bearing clays; Kopik, 1998). The difference in the thickness of the Middle Jurassic deposits between the two areas under discussion results from their palaeogeographic position within the epicontinental basin. It is presumed that the northeastern margin of the Holy Cross Mts. occupied the central part of the basin, whereas the Częstochowa region a marginal part (Feldman-Olszewska, 1998).

The sideritic rocks were collected from two boreholes at the northeastern margin of the Holy Cross Mts. (Gutwin and Wąglany k/Opoczna) and from four boreholes in the Częstochowa region (Biskupice 25BN, Łutowiec 135Ż, Parkoszowice 58BN and Zrbice 33BN) (Fig. 1 and Table 1). The deposits occur at depths varying from 30 to 600 m. The samples studied in the Częstochowa area are from moderate depths between ~100 m to at maximum ~380 m (Parkoszowice 58BN – depth from 101.3 to 104.2 m; Biskupice 25BN – depth 134.7 m; Łutowiec 135Ż – depth 178.9 m; Zrbice 33BN – depth 372.7 m), while the sandstones studied at the northeastern margin of the Holy Cross Mts. lie much deeper, up to about 650 m (Gutwin – depth 201.6 m; Wąglany k/Opoczna – depth from 267.7 to 643.8 m).

Lithological sections of the Gutwin and Łutowiec 135Ż boreholes by Kozłowska and Maliszewska (2015) are shown in Figure 2. A simplified section of the Zrbice 33BN borehole may be found in Leonowicz (2015). According to Feldman-Olszewska (pers. comm., 2013), the rocks represent various Middle Jurassic sedimentary environments, such as the offshore, transition zone, shoreface, deltaic and estuarine regimes. Siderite layers and concretions, and sideritic sandstones, are observed mainly in the Aalenian, Bajocian and Bathonian rocks, at the northeastern margin of the Holy Cross Mts. and in the Bajocian and
Bathonian rocks of the Częstochowa region (Kozłowska and Maliszewska, 2015).

There are a number of recent papers on the stratigraphy, sedimentology, geochemistry and palaeoenvironments of the Middle Jurassic strata of the Częstochowa region (e.g., Majewski, 2000; Marynowski et al., 2007; Szczepanik et al., 2007; Wierzbowski and Joachimski, 2007; Zator et al., 2009; Gedl and Ziaja, 2012; Witkowska, 2012; Leonowicz, 2012, 2013, 2015). The Middle Jurassic deposits at the northeastern margin of the Holy Cross Mts. were studied by Kozłowska and Maliszewska (2015). Their research was focused on the mineralogy and petrography of the sideritic rocks. The mineralogy of the Middle Jurassic sideritic concretions in the Silesian-Cracow Monocline was studied by Krzykawski (2012) and Witkowska (2015). Siderites in the Carboniferous sandstones from the Lublin Graben close to the study areas were described by Kozłowska (1997, 2001, 2004).

METHODOLOGY

GENERAL ANALYTICAL PROCEDURES

The analytical procedures comprised sampling and preparation, microscopy of the minerals and inclusions, geochemical analyses, and auxiliary studies.

Based on observations of 276 thin sections using a Nikon Eclipse LV 100 Pol polarizing microscope, 13 samples were selected for further study (Table 1). Thin-sections were stained with Evanny’s solution to identify the carbonate minerals. Four samples were subjected to cathodoluminescence analysis using the so-called “cold cathode”, CITL MK5 type from Cambridge Image Technology Ltd. (voltage 16kV, current 600 µA). The chemical composition of the carbonate minerals was determined on 12 samples (Appendix 1). Microchemical studies were performed using an electron scanning microscope LEO 1430, combined with EDS ISIS. Uncovered carbon-coated thin-sections were analysed. Back-scattered electron images (BSE) were also made. The studies were conducted in the Polish Geological Institute – National Research Institute in Warsaw.

PREPARATION AND ANALYTICAL TECHNIQUES FOR FLUID INCLUSION STUDIES

13 samples for fluid inclusion studies were prepared using standard preparation techniques (Shephard et al., 1985; Jarmołowicz-Szulc, 2001). Double-sided-polished thin sections, 0.1–0.2 mm thick, were obtained for low temperature mounting. Microscopic observations were conducted using a polarizing microscope in transmitted and reflected (UV) light. The analytical steps corresponded to a microscopic analysis of fluid inclusions (Leitz Orthoplan), fluorescence studies and microphotography (Nikon microscope and UV device) as well as microthermometric analyses. The latter included heating and freezing using a Fluid Inc. System, mounted on a Leitz Orthoplan microscope and the Linkam equipment with digital microphotography. The Fluid Inc. System and the Linkam stage were calibrated against melting temperatures of the pure chemicals and phase transitions in synthetic fluid inclusions (SYNFLINC standards; Reynolds 1993). The uncertainty limits are 0.2°C below –100°C, 0.1°C between –100 and +100°C, and 0.2°C above 100°C. Fluid inclusions in the cement were studied by freezing in order to avoid volume changes of the inclusions. The measurements embraced homogenization temperatures and determinations of eutectic and ice melting temperatures of the brine inclusions (Appendix 2).

* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1323

**Table 1**

<table>
<thead>
<tr>
<th>Area</th>
<th>Borehole</th>
<th>Depth [m]</th>
<th>Age</th>
<th>Type of rocks</th>
<th>Vol.% of siderite</th>
<th>Type of siderite</th>
<th>Vol.% of other carbonate minerals</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northeastern margin of the Holy Cross Mts.</td>
<td>Gutwin</td>
<td>201.6</td>
<td>Bj2</td>
<td>sst</td>
<td>28.0</td>
<td>Sdp Pt</td>
<td>12.7 Ak</td>
<td>PL EDS FI</td>
</tr>
<tr>
<td></td>
<td>Wąglany</td>
<td>267.7</td>
<td>Bt3</td>
<td>scq</td>
<td>16.0</td>
<td>Sdp</td>
<td>36.3 Ak</td>
<td>PL EDS FI</td>
</tr>
<tr>
<td></td>
<td>k/Opoczna</td>
<td>395.2</td>
<td>Bt1-2</td>
<td>cls</td>
<td>57.7</td>
<td>Sdp</td>
<td>0.0</td>
<td>PL EDS FI IS</td>
</tr>
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<td></td>
<td>406.0</td>
<td>Bt1-2</td>
<td>cls</td>
<td>59.7</td>
<td>Sdp Pt</td>
<td>0.0</td>
<td>PL FI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>597.2</td>
<td>Aa1</td>
<td>cls</td>
<td>67.4</td>
<td>Sd Sdp Pt</td>
<td>0.0</td>
<td>PL EDS FI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600.2</td>
<td>Aa1</td>
<td>sst</td>
<td>32.7</td>
<td>Sdp Pt</td>
<td>0.0</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>643.8</td>
<td>Aa1</td>
<td>sst</td>
<td>43.7</td>
<td>Sdp</td>
<td>0.0</td>
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</tr>
<tr>
<td>Częstochowa region</td>
<td>Biskupice 25BN</td>
<td>134.7</td>
<td>Bt1</td>
<td>sst</td>
<td>40.0</td>
<td>Sdp Pt</td>
<td>18.0 Ca</td>
<td>PL CL EDS FI IS</td>
</tr>
<tr>
<td></td>
<td>Łotowicze 1352</td>
<td>178.9</td>
<td>Bt1</td>
<td>cls</td>
<td>50.3</td>
<td>Sdp</td>
<td>0.0</td>
<td>PL EDS FI IS</td>
</tr>
<tr>
<td></td>
<td>Parkoszowice 58BN</td>
<td>101.2</td>
<td>Bt2</td>
<td>cls</td>
<td>65.0</td>
<td>Sdp</td>
<td>5.0 Ca</td>
<td>PL FI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>102.3</td>
<td>Bt2</td>
<td>cls</td>
<td>72.0</td>
<td>Sdp</td>
<td>0.0</td>
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<td></td>
<td></td>
<td>104.1</td>
<td>Bt2</td>
<td>cls</td>
<td>76.0</td>
<td>Sdp</td>
<td>3.0 Ca</td>
<td>PL CL EDS FI</td>
</tr>
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<td></td>
<td>Zrębiec 33BN</td>
<td>372.7</td>
<td>Bt2</td>
<td>sst</td>
<td>30.0</td>
<td>Sd Sdp</td>
<td>0.0</td>
<td>PL CL EDS FI IS</td>
</tr>
</tbody>
</table>
Temperature of homogenization was approximated as the temperature of trapping due to small pressure correction in fluid inclusions which homogenize into liquid phase (Roedder, 1984). Isochores were calculated with the Flincor program (Brown, 1989) and FLUIDS package (Bakker, 2003). Different varieties of the FLUIDS package, mainly AqSo1e (Bakker and Brown, 2003), were applied.

Analyses of the isotopic composition of oxygen and carbon in seven siderite and one calcite samples were conducted in the Isotope Laboratory of the Maria Curie-Skłodowska University at Lublin (Table 2). The method was described by Durakiewicz and Halas (1994) and Durakiewicz (1996). Gaseous carbon dioxide...
was released from carbonates during reaction with phosphoric acid (Mc Crea, 1950; Al-Aasm et al., 1990). Isotope measurements of carbon and oxygen were conducted in the modified mass spectrometer MI 1305 with a measurement precision of ±0.08‰ (one sigma). Measurements were conducted with reference to international standards (Durakiewicz, 1996). The values of δ¹³C were expressed at the scale of the VPDB, while δ¹⁸O results were obtained in the VPDB and VSMOW scales.

### CHARACTERISTICS OF THE SIDERITIC ROCKS

The material studied comes mainly from clayey siderites and sideritic sandstones (Fig. 3), locally from sideritic coquinas. Siderite is the main component of the sideritic rocks. This mineral represents Mg-rich siderite (sideroplesite, less frequently pistomesite), and locally siderite.

The clayey siderites contain micritic, microsparic and spar siderite and clay minerals. Sideroplesite is the main siderite mineral (micrite, microspar, spar), while pistomesite (microspar, spar) and the siderite (micrite, spar) appear locally. The sideroplesites show the following chemical composition (in mol. %): 71.4–85.8 – FeCO₃, 6.5–9.3 – MgCO₃, 6.6–13.3 – CaCO₃ and 0.0–1.5 – MnCO₃ (Appendix 1). Clay minerals are represented by kaolinite, berthierine and illite (Kozłowska and Maliszewska, 2015). Calcite and ankerite are the other carbonate minerals present in the rock. Quartz sands of sill- and sand-size occur in varying amounts. Feldspar grains, mica flakes, zircon, pyrite, hematite and the organic matter are accessory components. Calcite, locally pyritized, faunal fragments are common. Clay and carbonate ooids were observed in a few samples. The carbonate ooids are composed mainly of sparpy sideroplesite or pistomesite, rarely of calcite and ankerite. Locally, clayey siderites are cut by calcite, ankerite and/or pyrite veins.

The sideritic sandstones are represented by fine- to medium-grained quartz arenites. Quartz is the main detrital material andfeldspars, micas and zircon are subordinate. Shell fragments and ooids are observed in variable amounts. Fragments of bivalves, echinoderm, gastropods and foraminifers are composed of carbonates (commonly calcite, occasionally ankerite and siderite) and clay minerals (kaolinite and berthierine). Ooids consist mainly of berthierine, sparc sideroplesite or calcite and locally of kaolinite and pyrite. The main minerals in the sandstones are carbonates, as sideroplesite (micritic, microsparitic, sparitic) and pistomesite (sparitic), siderite (micritic, sparitic), ankerite and calcite. The most common sideroplesites show the following chemical composition (in mol. %): 75.3–86.3 – FeCO₃, 5.9–21.4 – MgCO₃, 1.9–16.2 – CaCO₃ and 0.0–4.2 – MnCO₃ (Table 2). Clay minerals such as berthierine, kaolinite, illite and locally chlorite also occur (Kozłowska and Maliszewska, 2015). Locally, the sideritic sandstones are cut by calcite, ankerite, sideroplesite and/or pistomesite veins.

The sideritic coquina (biodrasts 20% of rock volume) from the Wagłany k/Opoczna borehole is composed mainly of ooids and bioclast fragments, such as echinoderms, bivalves, brachiopods, gastropods and bryozoans. The berthierine ooids have been replaced to a variable degree by ankerite and sideroplesite. The cement is composed of microsparry and sparry sideroplesite and ankerite (Appendix 1).

### CHARACTERISTICS OF THE CARBONATE MINERALS STUDIED

Siderite is the main carbonate mineral studied in the sideritic rocks, while calcite and ankerite are less frequent. The Mg-rich siderite represents sideroplesite and pistomesite of microspar and spar crystal size (Fig. 3), very often in the form of rhombohedra. Two siderite generations – early and late ones – may be distinguished based on the microscopic observations. The early generation is represented by micritic and microsparitic sideroplesite, locally by siderite, whereas the late one has sparitic (partly rhombohedric) sideroplesite (Fig. 4A) and rare pistomesite. The rhombohedra are more frequent in the sideritic rocks at the northeastern margin of the Holy Cross Mts. than in the Częstochowa region (Appendix 1). Rhombohedric crystals of sideroplesite and pistomesite often display zonal structure, related to the varying contents of iron and magnesium, as well as

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### Table 2

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Age</th>
<th>Depth [m]</th>
<th>Type of carbonate</th>
<th>Content [%]</th>
<th>δ¹³C VPDB [‰]</th>
<th>δ¹⁸O VPDB [‰]</th>
<th>δ¹⁸O VSMOW [%]</th>
<th>δ¹⁸O VSMOW H₂O [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wagłany k/Opoczna</td>
<td></td>
<td></td>
<td></td>
<td>Sdp, sp ooid</td>
<td>70  30</td>
<td>−17.68</td>
<td>−3.86</td>
<td>26.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sdp</td>
<td>100 0</td>
<td>−8.63</td>
<td>−7.84</td>
<td>22.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pt sp rb cement</td>
<td>0 100</td>
<td>−9.58</td>
<td>−10.45</td>
<td>20.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sdp</td>
<td>0 100</td>
<td>−10.83</td>
<td>−8.52</td>
<td>21.77</td>
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<tr>
<td>Częstochowa region</td>
<td></td>
<td></td>
<td></td>
<td>Bebrick</td>
<td>66 50</td>
<td>−13.19</td>
<td>−5.21</td>
<td>28.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sdp</td>
<td>69 60</td>
<td>−13.19</td>
<td>−5.21</td>
<td>28.56</td>
</tr>
</tbody>
</table>

*δ¹⁸O VSMOW water of sideroplesite which crystallized at a temperature of 20°C; S1 – early generation of siderite; S2 – late generation of siderite; for explanations see Table 1
Fig. 3. Photographs in polarizing microscope (PL)

A – siderite represented by pistomesite rhombohedra (arrow) and ankerite cement (Ak) in sideritic sandstone (Gutwin borehole, depth 201.6 m, crossed polars); B – part of photo A; two-phase inclusions (arrows) in pistomesite rhombohedron (Pt) and ankerite (Ak); plane polarized light; C – pistomesite ooids (Pt) in clayey siderite composed of sideroplesite micrite (Sdp); pistomesite in the form of rhombohedra (Waglany k/Opoczna borehole, depth 597.2 m, plane polarized light); D – part of photo C; single two-phase inclusion (arrows) in pistomesite rhombohedron (Pt); plane polarized light; E – siderite cement; sparry sideroplesite (arrow) and micrite sideroplesite (Sdp) in sideritic sandstone (Biskupice 25BN borehole, depth 134.7 m, crossed polars); F – part of photo E; one-phase inclusions (arrows) in sparry sideroplesite (Sdp); plane polarized light; G – sideroplesite ooid (arrow) and micrite sideroplesite (Sdp) in clayey siderite (Parkoszowice 58BN borehole, depth 101.2 m, plane polarized light); H – part of photo G; two-phase inclusions (arrows) in sparry sideroplesite in ooid (Sdp); plane polarized light
seen in BSE images (Fig. 4B). The siderite minerals can occur as a mass of clayey siderites, a cement filling the pore space in the sideritic sandstones (Fig. 4B) and a mineral replacing berthierine in ooids (Fig. 4C). Some varieties of sideritic minerals contain fluid inclusions. This is why sparry individuals, often rhombohedra, of the sideroplesite and the pistomesite have been micro-thermometrically analysed (Fig. 3 and Appendix 2). The micritic siderite and siderooplesite, however, do not contain fluid inclusions. Inclusions in the micritic sparic crystals are too small to be measured. The calcite and ankerite either form cements in the sideritic rocks, or fill veins (Fig. 4D). These minerals also contain fluid inclusions. However, due to the low abundance and size of the inclusions, only some samples could have been selected for temperature measurements (Appendix 2). The isotopic analyses were conducted both in siderooplesite and pistomesite, as well as on calcite in the same samples (Table 2).

### GENERAL CHARACTERISTICS OF THE FLUID INCLUSIONS

The liquid-vapour inclusions are small in size and not abundant. Their average size falls into the interval of 1–3 \( \mu m \) that is difficult to observe in heating and freezing experimental modes. The inclusion shapes vary, but no form dominates. Some inclusions are oval, others are more or less regular in shape, or are shapeless. The rare occurrence and small sizes of inclusions are significant, occasional stretching symptoms may be noticed. The character of inclusions in general is primary. The inclusions are mostly one phase, locally with two phases. The fluid to vapour ratio varies, but generally the fluid volume prevails. Occasionally, the two-phase character of the inclusions corresponds to a co-presence of two liquid phases (L1 and L2). The fluid inclusions are randomly positioned, meaningful relations with crystallographic planes are hard to determine as is classification of distinct F1As (Fluid Inclusion Association, sensu: Goldstein and Reynolds, 1994; Goldstein, 2003), which is not possible in practice due to the low abundance of two-phase fluid inclusions. In some cases, only one-phase inclusions were observed (e.g., in the Parkoszowice 58BN borehole).

### TEMPERATURE RESULTS OF FLUID INCLUSION STUDIES

The carbonates in the sideritic rocks contain rare fluid inclusions. They exhibit a primary character, small size, and either one or two phases.

Temperature results are shown in Appendix 2. Microphotographs show inclusions in siderooplesite and pistomesite of selected rock samples (Fig. 3). As shown in the table, the following

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**Fig. 4. Photographs by polarizing microscope (PL) and scanning electron microscope (BSE)**

A – two generations of siderite – the early generation (S1 – microsparitic siderooplesite) and the late generation (S2 – sparitic siderooplesite) in clayey siderite (Lutowiec 135Z borehole, depth 178.9 m, crossed polars); B – zonal structure in rhombohedral crystals of siderooplesite (Sdp) and pistomesite (Pt) which form cement in siderite sandstone; 1, 2 – numbers of points of analysis (Appendix 1) (Gutwin borehole, depth 201.6 m, BSE image); C – pistomesite (Pt) ooids with berthierine (Be) relics in sideritic sandstone cemented by micritic siderooplesie (Sdp); quartz (Q) (Waglany k/Opoczna borehole, depth 597.2 m, crossed polars); D – calcite (Ca) veins in clayey siderite with micritic siderooplesie (Sdp) (Parkoszowice 58BN borehole, depth 101.2 m, crossed polars)
values have been measured for two-phase inclusions: temperature of homogenization ($T_h$), ice melting temperatures ($T_m$). For one-phase inclusions only $T_m$ values were determined, since no metastable contraction bubble was created during the experiment.

Temperature values are grouped in columns in Appendix 2, showing characteristic features such as eutectic temperature, ice melting, clathrate melting and homogenization values. The "Fluid" column gives a suggestion as to the possible type of the individual inclusion-fill, based on the individual temperature data. Fluid salinities and densities in the inclusions in simplified two-component systems are shown in Appendix 2.

Summing up the results, the number of measurements of homogenization temperatures ($T_h$) in the sandstones is not large. The values of homogenization temperatures for the siderite fall into the interval between 60 and 100°C. Temperatures of ice melting are relatively low and vary between −10.0 to −3.4°C. The salinity of fluids is moderately high and varies with respect to the type of cement and borehole location. The salinity corresponds to intervals from 7.8 to 13.9 wt.% NaCl eq. and from 9.2 to 12.9 wt.% NaCl eq. for siderite and calcite, respectively. The density of fluids is close to 1 g/cm³. The eutectic temperatures are also variable and between −40 and −30°C. This suggests the presence of two valent cations in the brines, e.g., containing calcium and/or magnesium ions (Shephard et al., 1985; Schmidt Mumm and Wolfgramm, 2002).

ISOTOPIC RESULTS

Isotopic carbon and oxygen results are shown in Table 2 and in Figure 5, restricted to the samples studied by the fluid inclusion method. They are mostly for sideropelites, with only some for pistomesite and calcite. Two siderite generations are often observed coexisting in the rocks, while only a few samples contain just one siderite generation (the early or the late one). Some isotopic results represent the cumulative products of varying proportions of two siderite generations (Table 2). The samples do not co-vary with the depth and age of the rocks.

At the northeastern margin of the Holy Cross Mts. the δ13C VPDB values in the early sideropelites of the Aalenian age are −8.63‰ and in the Bathonian are −17.68‰. The corresponding δ18O VPDB values are −7.84 and −3.86‰. The δ13C VPDB values in the late sideropelites and pistomesite of the Aalenian age are equal to −10.83 and −9.58‰, respectively. The corresponding δ18O VPDB values are −8.82 and −10.45‰.

In the Częstochowa region the δ13C VPDB values change in the Bajocian early sideropelites from 22.85 to −8.87‰ and the Bathonian sideropelites are −7.48‰. The corresponding δ18O VPDB values are from −3.81 to −1.92‰ and −2.01‰. The δ13C VPDB value in the Bathonian calcite is −2.01 and δ18O VPDB value is −5.38‰.

INTERPRETATION AND DISCUSSION

TEMPERATURE MEASUREMENTS

The majority of carbonates occurring in the sideritic rocks show crypto- or fine crystalline crystal habits. This is why the inclusions were observed only in the sparry sideropelites and pistomesite crystals and in the ankeritic and calcitic cement in the sideritic sandstones or clayey siderites.

Determination of inclusion character resulted in primary and secondary individuals. We have used Roedder’s (1984) criterion: the primary inclusions are rare, randomly distributed and have no characteristic position in the cements of minerals. That makes the evaluation of inclusion character and genesis difficult. The size of inclusions of 1–3 µm, type and lack of clarity of samples also causes difficulties in temperature measurements and observations in the freezing and heating modes. The processes were sometimes seen only partly during measurement cycles on the Linkham stage (Appendix 2).

Temperature results obtained for inclusions are those eutectic, homogenization and ice melting values (Appendix 2). However, not all characteristic temperature values were obtained for all the samples.

At the northeastern margin of the Holy Cross Mts., most measurements were performed on the cement-forming rhombohedral crystals of pistomesite and sideropelites in sideritic rocks from the Wąglany k/Opoczna borehole (Appendix 2). The homogenization temperatures there vary from 62 to 110°C. In the rhombohedral of pistomesite cement in the sideritic sandstone from the Gutwin borehole homogenization temperatures lie in the interval between 107 and 139°C. In the Wąglany k/Opoczna borehole the homogenization temperatures in the rhombohedral crystals of pistomesite in ooid were ~137°C and the spar sideropelites crystal in ooid showed 94.7°C. Only one homogenization temperature value was obtained in ankerite cementing a sideritic coquina (168°C). Other temperature values obtained in the Holy Cross Mts. area correspond to the eutectic temperatures that point to brine and carbon dioxide presence in the fluids in the inclusions. In some cases also clathrate and ice melting values were measured. Based on these data, it seems that in case of sideropelites cement at a depth of ~643 m, the fluid is a brine of salinity between 10.5 and 12.9 wt.% NaCl eq.
and a density of 1.03–1.05 g/cm³. The pistomesite cement from much shallower depth displays a very low fluid salinity in contrast to the ankeritic cement in the same borehole which reveals higher salinity and fluid density.

The following features can be described for the sideritic samples from the Częstochowa region in the minerals from the Parkoszowice 58BN borehole, which occur in a relative narrow depth interval: one-phase inclusion associations in sideroplesite, which point to trapping at temperatures of 40–50°C (Goldstein, 2001); variation of ice melting temperatures in the interval from –5.3 to –9.7°C. The $T_m$ results for the rhombohedral sideroplesite are between –5.3 and –6.6°C, while those for the sideroplesite in ooids are from –5.3 to –9.7°C, that corresponds to salinity intervals of between 7.8 and 10.5 wt.% NaCl eq, and from 7.8 to 13.9 wt.% NaCl eq, respectively. The ooids display a large scatter in values that may be connected with a variation of the fluid character during crystallisation of the inner/outer parts of the ooid. However, such a differentiation cannot be estimated because of the low abundance of fluid inclusions. Homogenization temperatures have been measured for individual inclusions. For calcite they mostly fall into the interval between 60 and 70°C (depth 104.1 m). The salinity of fluids in calcite varies from 9.2 to 12.9 wt.% NaCl eq.

The following characteristics may be presented for the sample from the Biskupice 25BN borehole (depth 134.7 m): sidente character variability; one- and two-phase inclusion associations; variation of eutectic temperatures for brine inclusions from –52 to –28°C; variation of ice melting temperatures (from –3.4 to –10.0°C), whereas most of results for sideroplesite fall into the $T_m$ interval between –7.3 and –10.0°C (in cements). Homogenization temperatures vary and fall into the interval between 55 and 100°C (sideroplesite). The salinity of fluids varies from 10.5 to 13.9 wt.% NaCl eq.

In the sample from the Łutowiec 135Ż borehole (depth 178.9 m) one-phase inclusions have been observed and a single ice melting value measured (–4.4°C), that points to a low fluid salinity of about 6.37 wt.% NaCl eq, and a density of 1.05 g/cm³.

The following features have been recognized for the Zrębiec 33BN borehole (depth 372.7 m) in sideroplesite rhombohedra in cement: one-phase fluid inclusion associations; eutectic temperatures of –42°C (more complex system than the two-component brine); variation in ice melting temperatures (from –6.2 to –9.2°C), that implies salinity in the interval from 9.2 to 12.9 wt.% NaCl eq, and fluid density of 1.07 g/cm³; potential presence of carbonate dioxide in two-phase aqueous inclusions. That last feature is similar to the observations reported by Hauri et al. (2002) for siderites in the Carpathian veins.

Observations of fluid inclusions together with varying homogenization temperatures of two-phase inclusions, their variable L/V ratio, suggest that the temperature data obtained for them have a random character not constraining the primary conditions of cement formation.

The ice melting temperature results after freezing are very significant and valuable for interpretation. Based on these values obtained in fluid inclusion studies, a complex character of fluids in individual samples may be deduced. The most simple way to present these results is to express them as a wt.% NaCl eq. Using standard calculation programs for H₂O-NaCl system (FLUIDS package, AqSo1e program) fluid salinities and density have been obtained, in the interval from 8.2 to 14.0 mass% NaCl and of about 1 g/cm³, respectively.

The relationship between the homogenization temperatures and fluid salinity for the two-phase inclusions is shown in Figure 6.

The eutectic temperatures close to –30°C or even –40°C suggest (especially in calcite) a presence of more complex fluids than the simple system of NaCl-H₂O, as for example H₂O-NaCl-CaCl₂-MgCl₂ (Shephard et al., 1985; Bodnar, 2003). Based on the AqSo1e (system H₂O-NaCl-CaCl₂) and AqSo3e (system H₂O-NaCl-MgCl₂) programs such a trial of calculations for multi-component systems has been made, though with several assumptions introduced. Due to this fact (e.g., lack of exact mole ratios), the results obtained after the Oakes et al. equation (1990, fide Bakker and Brown, 2003) should be regarded as approximate.

**ISOTOPES**

The carbon and oxygen isotopic results in both regions studied are similar. Most determinations concern the samples where the early siderite predominates over the late one (Table 2). Two-isotope data have been obtained in the samples containing a late generation of siderite from the same depths as those studied for fluid inclusions. The results of δ¹⁸O determinations for early generation of siderite-sideroplesite fall within the range of –22.85 to –7.48‰ VPDB. They indicate that the sideroplesite was formed in the zone of microbiological methanogenesis, where a bacterial fermentation of the organic components was the CO₂ source (Irving et al., 1977; Morad, 1998). The δ¹⁸O values range between –7.84 and –1.92‰ VPDB. The formula after Carothers et al. (1988) has been used to estimate the δ¹⁸O of the pore water responsible for
crystallisation of the early siderite generation. The δ^18O values suggest that the early sideropelites precipitated from water of δ^18O VSMOW in the range of −11.11 to −5.01‰, assuming a crystallisation temperature of about 20°C (Baker et al., 1995; Rezaee and Schulz-Rojahn, 1998). Such values indicate a mixture of marine and meteoric waters.

The results of δ^13C and δ^18O determinations for the late generation of siderite were obtained only for the rocks from the northeastern margin of the Holy Cross Mts. The results of δ^13C determinations for late generation of siderite — sideroplesite and pistomesite are −10.83 and −9.58‰ VPDB. The late generation of siderite is characterized by a high magnesium content. According to Macaulay et al. (1992), altered minerals rich in Mg, e.g. micas, could have been a magnesium source. According to Desborough (1978) the magnesium could have been released from kerogen during sediment burial. It seems that in the rocks under study, carbon released from organic matter in the thermal decarboxylation zone might have been a source of this element for the late, Mg-rich siderite generation. The same source of carbon for Mg-rich siderites was suggested by Morad et al. (1994) and Rezaee and Schulz-Rojahn (1998). The δ^13C values are −8.82 and −10.45‰ VPDB. The homogenisation temperature for the late siderite generation were 90–110°C and 62–98.8°C, respectively (Appendix 2). The temperature data calculated with use of Carothers et al. (1988) formula point to precipitation of the late siderite from the pore waters displaying δ^18O in the interval from about −5 to 3.5‰ SMOW, most often >0‰ SMOW (Fig. 7). Such values of δ^18O for pore water suggested that the late siderite has precipitated from waters richer in the ^18O isotope in comparison with the water composition of the early siderite crystallisation. The enrichment in the oxygen isotope content in pore waters is already possible at several hundred metres of burial due to the water-sediment interaction (McKay et al., 1995).

The oxygen and carbon isotopic values in the calcite cement were obtained for one sample from the Częstochowa region. The δ^13C value points to organic matter as the carbon source (Baker, 1991). It was impossible to measure a homogenization temperature in this sample. Measurements were performed in the calcitic vein on another sideritic rock. The values of 59.8 and 67.8°C (Appendix 2) have been regarded as a probable temperature of calcite crystallisation. The isotopic and temperature values for calcite have been used in the Friedman and O’Neil (1977) formula. For the calcite crystallisation, they point to the δ^18O pore water equal to about 0‰ VSMOW.

CONCLUSIONS

1. The main carbonate minerals of the Middle Jurassic sideritic rocks at the northeastern margin of the Holy Cross Mts. and in the Częstochowa region are represented by sideroplesite, less frequent pistomesite, and siderite. They form cements and ooids. Early and late generations of siderite have been distinguished. Apart from this mineral, calcite and ankerite in the form of cements and veinlets are present as well.

2. One-phase inclusions and associations of two-phase inclusions with a different phase ratio are predominant. As compared with the Częstochowa region, two-phase inclusions are more abundant and the phase ratios are more homogeneous at the northeastern margin of the Holy Cross Mts.

3. The salinity of fluids in the inclusions varies in the range between 1.7 and 16.9 wt.% NaCl eq. for siderites in the rocks from the northern margin of the Holy Cross Mts. The fluid density is close to 1 g/cm³ in the Częstochowa region, and the salinity oscillates between 6.4 and 13.9 wt.% NaCl eq. It varies for siderites in form of the cements and those occurring as ooids. The fluid density is also close to 1 g/cm³. Complex chemical brine systems may occur as fluids, e.g., H₂O-NaCl-CaCl₂-MgCl₂ or H₂O-CaCl₂-MgCl₂ as well as mixed ones (H₂O-CO₂).

4. Studies of two-phase fluid inclusions present in the crystals of the late siderite generation — sideroplesite and pistomesite — in the Middle Jurassic sideritic sandstones and clayey siderites, display homogenization temperatures in the interval of 55.0–137.1°C. They suggest crystallisation in deep burial conditions. The calcite in the veinlet showed a temperature of ~60°C. Higher homogenization temperatures of ~168°C were determined in the ankeritic cement of a siderite coquina.

5. The temperature results vary with respect to the borehole and the type of cement in both regions. The character of inclusions and the homogenization temperature results are very different. The rocks occur at the depth of about 100 to >600 m, and no temperature tendency may be observed, either as regards depth or type of cement.

6. The homogenization temperatures in the carbonates, are slightly higher than the results obtained in the Middle Jurassic sandstones in sideritic rocks in the Polish Lowlands (Maliszewskia et al., 2007). These facts support the authors’ conclusion that, apart from burial, another heat source was a cause of increased temperatures characteristic for the lithogenesis of the Jurassic deposits.

7. The isotopic determinations of δ^13C VPDB (from −22.85 to −7.48‰ VPDB) in the early siderite generation point to formation of this mineral in the zone of microbiological methanogenesis. The isotopic oxygen composition δ^18O VPDB (from −7.84 to −1.92‰ VPDB) points to siderite precipitation from marine and also meteoric waters at temperatures of ~20°C.
8. The results of δ13C for the late generation of siderite (−10.83 and −9.58‰ VPDB) suggest that carbon could have been released from the organic matter in the thermal decarboxylation zone. Based on data compilation of δ18O values (−8.82 and −10.45‰ VPDB) and of homogenization temperatures (90–110°C and 62–98.8°C) the conclusion can be drawn that the late siderite generation crystallized from pore waters of δ18O >0‰ VSMOW. The calcite also precipitated from the pore waters with δ18O of about 0‰ VSMOW.

9. Values of δ18O VSMOW of pore water for the late siderite and calcite generations are higher when compared with those characteristic for the water responsible for the early siderite crystallisation. An enrichment in 18O isotope might have been caused either by a water-rock reaction during burial of the deposit or by an influx of the marine water to the sediment.

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