# INSTRUMENTAL METHODS APPLIED IN THE INVESTIGATIONS OF CARBONATE MINERALS IN THE MIDDLE JURASSIC SIDERITIC ROCKS WITH RESPECT TO DIAGENETIC PROCESSES

## METODY INSTRUMENTALNE STOSOWANE W BADANIU MINERAŁÓW WĘGLANOWYCH SKAŁ SYDERYTOWYCH JURY ŚRODKOWEJ W KONTEKŚCIE DIAGENEZY

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**Abstract.** Carbonate minerals in the Middle Jurassic sideritic rocks from the Polish Lowlands, north-eastern margin of the Holy Cross Mountains and the Częstochowa region have been studied applying accessible instrumental methods. The following techniques were applied: polarization microscope, staining with the Evamy's solution, cathodoluminescence, microprobe, fluid inclusions and isotopic analyses. Most of these methods were not available either in the 20ies of the past century when studies of sideritic iron ores in Poland had begun, or in 50ies and 60ies when they were in full progress.

The sideritic rocks are mainly represented by clayey siderites (they contain also muddy and sandy varieties), sideritic sandstones and sideritic coquina, less frequently by sideritic conglomerates and mudstones. Sideroplesite is the main carbonate mineral that builds the sideritic rocks, while pistomesite and siderite are less frequent. Fe-calcite and Fe-dolomite, ankerite, and sporadic dolomite occur in lesser amounts.

Sideroplesite and siderite have crystallized in the early diagenesis (eodiagenesis), in the zone of microbiologic methanogenesis, at temperatures of about 20°C, from the porous waters of marine origin, or from marine waters mixed with fresh waters. Sideroplesite enriched in magnesium, pistomesite, calcite and ankerite sequently have formed at the later diagenetic stage (mezodiagenesis). These minerals have crystallized at temperatures above 60°C, from the porous waters of marine origin, or from the fluid which interacted with the adjacent rocks. Fe-calcite was formed in the zone of microbiologic methanogenesis, while the ankerite – in the zone of thermal decarboxylation.

**Key words:** cathodoluminescence, microprobe, fluid inclusions, carbon and oxygen isotopes, sideritic rocks, carbonate minerals, Middle Jurassic.

**Abstrakt.** Na podstawie dostępnych obecnie metod instrumentalnych zbadano minerały węglanowe skał syderytowych jury środkowej z Niżu Polskiego, północno-wschodniego obrzeżenia Gór Świętokrzyskich i rejonu Częstochowy. Zastosowano: mikroskop polaryzacyjny, barwienie roztworem Evamy'ego, katodoluminescencję, mikrosondę energetyczną, analizę inkluzji fluidalnych i izotopową. Większość z tych metod nie była dostępna w latach dwudziestych, kiedy rozpoczęto badania syderytowych rud żelaza w Polsce, ani w latach pięćdziesiątych i sześćdziesiątych, kiedy były kontynuowane.

Skały syderytowe są reprezentowane głównie przez: syderyty ilaste (obejmują również odmiany mułkowe i piaszczyste), piaskowce syderytowe i muszlowce syderytowe, rzadziej przez zlepieńce syderytowe i mułowce syderytowe. Głównym minerałem węglanowym budującym skały syderytowe jest syderoplesyt, rzadziej pojawiają się pistomesyt i syderyt. W zmiennych ilościach występują Fe-kalcyt oraz Fe-dolomit i ankeryt, sporadycznie dolomit.

Syderoplesyt i syderyt krystalizowały we wczesnej diagenezie (eodiagenezie) w strefie mikrobiologicznej metanogenezy w temperaturze ok. 20°C z wód porowych pochodzenia morskiego lub wód morskich zmieszanych z wodami słodkimi. W późniejszym etapie diagenezy (mezodiagenezie) tworzyły się w kolejności: syderoplesyt z większą zawartością magnezu, pistomesyt, kalcyt i ankeryt. Minerały te krystalizowały w temperaturze powyżej 60°C z wody porowej pochodzenia morskiego lub wody, która weszła w reakcję z otaczającymi skałami. Fe-kalcyt tworzył się w strefie mikrobiologicznej metanogenezy, natomiast ankeryt w strefie termalnej dekarboksylacji.

**Słowa kluczowe:** katodoluminescencja, mikrosonda energetyczna, inkluzje fluidalne, izotopy węgla i tlenu, skały syderytowe, minerały węglanowe, jura środkowa.

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## INTRODUCTION

In the early twenties Kuźniar (1924, 1925) has initiated studies on the Middle Jurassic siderites in the area of the Holy Cross Mts. His major paper comprises results on the sideritic iron deposits in Parczew (Kuźniar, 1928). The important paper by Jaskólski (1928) that described the study results of the Doggerian ore-bearing clays in the Częstochowa region, was published in the same year. This research was continued by Jaskólski after the World War II together with Ekiert (Jaskólski, Sawicka-Ekiert, 1955). In 1966 Ekiert described the petrography of the Doggerian iron ores from eight boreholes in the Wieluń, Olsztyn and Zawiercie region. The paper published by Turnau-Morawska (1961) on the Łęczyca Upper Vesulian (now Upper Batonian) ore-bearing formations should be considered as the most important and most interesting petrographic description of the iron ore in Poland. The petrographic characteristics of the Middle Jurassic iron ores from the Kamień Pomorski region was presented by Dadlez (1963, 1964). Due to the then limited instrumental methodology, the petrographic studies were restricted mainly to the determination of the mineral composition and iron content in the rocks.

Owing to newer analytical possibilities, that allowed a better characterization of the mineral content and determinations of genesis of minerals in the sediments, the research on sideritic rocks has re-started at the Polish Geological Institute – NRI. It has been initiated by A. Maliszewska together with A. Kozłowska and M. Kuberska. Thus, over the years, the sideritic rocks from the Polish Lowlands (Maliszewska *et al.*, 2006; 2007a, b, 2018), and those from the NE margin of the Holy Cross Mts. (Kozłowska *et al.*, 2008, 2011, 2013; Kozłowska, 2014; Kozłowska, Maliszewska, 2015; Jarmołowicz-Szulc, Kozłowska, 2016) and from the Częstochowa region (Kozłowska *et al.*, 2012, 2013; Kozłowska, Maliszewska, 2015; Jarmołowicz-Szulc, Kozłowska, 2016) (Fig. 1) were subjected to comprehensive examinations.

The present paper shows the characteristics of the carbonate minerals that build sideritic rocks based on recently accessible instrumental methods. Its aim is to show the importance of methods applied in the interpretation of the genesis of rocks.

## METHODS OF STUDIES

### STUDIES USING THE POLARIZATION MICROSCOPE

The analysis of thin sections was conducted at PGI-NRI in the Nikon polarization microscope Optiphot 2. The mineral percentage (vol.%) of the sideritic rocks was either obtained from the point analysis of 300 grains counting by use of the integration stage produced by Prior, or by estimation.

To define the type of carbonate cements all thin sections were stained with the Evamy's solution (Migaszewski, Narkiewicz, 1983). Examinations have proved a presence of siderite and dolomite, that do not stain, and of Fe-dolomite and ankerite that are stained to light blue and blue colours, respectively, of pink-violet Fe-calcite and red calcite. The cathodoluminescence analysis (CL) was performed using the so called cold cathode, models CCL 8200 mk3 i CITL MK5 (equipped with EDX), both produced by Cambridge Image Technology Ltd, and mounted at PGI-NRI on the Nikon polarization microscope. Cathodoluminescence is a useful tool for differentiation of carbonate cements since different carbonates display different luminescence. The calcite luminesce in yellow-orange, orange-red or red-brownish colours, dolomite shows the red extinction, while Fe-dolomite, ankerite and siderite do not luminesce (black colour). The interpretation of the cathodoluminescence observations was based on the manual of Marshall (1988).

### EDS ISIS ANALYSES

Studies were performed at PGI-NRI using the electron scanning microscope (LEO 1430), equipped with EDS ISIS of Oxford Instruments production. Samples as uncovered thin sections, covered with the coal, were examined. The chemical composition of carbonates was determined. For the quantitative X-ray microscale analysis the SEM Quant program was applied. All quantitative results were calculated to the molecular composition.

### FLUID INCLUSIONS STUDIES

The fluid inclusion studies were conducted according to the earlier general research scheme (Jarmołowicz-Szulc, 1999), that comprises both the introductory studies and characteristics of inclusions, and the microthermometric analyses. Fluid inclusions were examined at PGI-NRI in special two-sided polished thin sections mostly by use of the Nikon Optiphot microscope equipped with the fluorescence device (ultraviolet and blue lights) and the freezing – heating Linkam stage. A standard procedure of cold preparation (Goldstein, Reynolds, 1994), recently verified, was applied. The interpretation of the fluid inclusion assemblages was based on the suggestions of Goldstein (2001).

Heating and freezing of samples occurred in the temperature intervals ranging from the room conditions (19–29°C) to +100°C and to −70°C, respectively. The precision of the measurements was calibrated using the SynFlinc standards and was found to equal 1.0°C and 0.1°C in the positive and negative intervals, respectively.

Isochores, salinity and other parameters were calculated using both the complex FLUIDS package (Bakker, Brown, 2003), and the FLINCOR program (Brown, 1989), which comprises less complex chemical systems.

**Fig. 1. Location of the studied boreholes; grey area – extent of the Middle Jurassic in Poland after Lott *et al.* (2010)**

Lokalizacja badanych otworów wiertniczych; szary obszar – zasięg jury środkowej w Polsce wg Lotta i in. (2010)

## ISOTOPIC STUDIES

The isotopic composition of carbon and oxygen in the carbonate minerals were carried out by professor S. Hałas with co-workers at the Mass Spectrometry Department of the Institute of Physics at Maria Curie-Skłodowska University in Lublin on $CO_2$ obtained from the carbonate samples in reaction with the phosphatic acid using standard procedures (McCrea, 1950; Al-Aasm *et al.*, 1990). Measurements were performed in the modified MI1305 spectrometer (Hałas, 1979; Hałas, Skorzyński, 1980; Durakiewicz, Hałas, 1994; Durakiewicz, 1996). The precision of measurements is ±0.1‰.

## RESULTS OF STUDIES

### SIDERITIC ROCKS

The Middle Jurassic sideritic rocks are represented by: predominating clayey siderites (they comprise also muddy and sandy varieties), sideritic sandstones, sideritic coquina and less frequent sideritic conglomerates and mudstones.

The sideritic rocks are usually accumulated as layers and concretions. The siderites in the Polish Lowlands have been mostly formed in the Lower and Upper Bajocian and the Lower Bathonian. The clayey siderites and sideritic coquina (the Łęczyca region), less frequently sideritic sandstones

have been distinguished (Maliszewska *et al*., 2007a, b, 2018). In the northern margin of the Holy Cross Mts., the siderites occur in the deposits of Lower Aalenian, Lower and Upper Bajocian, Lower and Middle Bathonian as well. Clayey siderites and sideritic sandstones are predominant there. The sideritic coquina, conglomerates and mudstones are present, too (Kozłowska *et al*., 2008; 2013). In the Częstochowa region the siderites are Upper Bajocian and Lower and Middle Bathonian in age. The clayey siderites dominate over the sideritic sandstones, while the sideritic coquina and mudstones are local (Kozłowska *et al*., 2013). The following papers present a compact description of the sideritic rocks: Kozłowska, Maliszewska (2015) and Maliszewska *et al*. (2018). The sideroplesite, that belongs to the siderite-magnesite isomorphic series ($FeCO_3$ 70–95%, $MgCO_3$ 5–30%, Bolewski, 1982) is the main component of the sideritic rocks. The pistomesite ($FeCO_3$ 50–70%, $MgCO_3$ 30–50%, Bolewski, 1982) is relatively frequent, while the mineral of the sideritic composition ($FeCO_3$ >95%, Bolewski, 1982) occurs rarely (Maliszewska *et al*., 2006, 2007a, b, 2018; Kozłowska *et al*., 2008, 2013; Kozłowska, Maliszewska, 2015; Jarmołowicz-Szulc, Kozłowska, 2016).

**Clayey siderites** are dark brown and compact. They are mostly built of sideroplesite (Fig. 2A–F), the content of which changes from 50 to 98% of the rock and of clay minerals (kaolinite, illite, berthierine) ranging from 0 to 35 vol.%. Quartz grains aleuritic and psammitic in size occur in variable amounts – about 40 vol.% at the maximum. The content of bioclasts and ooids does not exceed 4 vol.% (Fig. 2A, D, E). Accessory are the following components: feldspars, micas, zircon, pyrite, hematite and the organic matter. Locally, the clayey siderites are cut by veinlets filled with the calcite, ankerite (Fig. 2F) and pyrite.

**Sideritic sandstones** are mostly represented by fine- and medium-grained, greyish brown, compact quartz arenites (Fig. 2G, H; 3A–F). The quartz grains content varies from 16 to 80 vol.% of the rock, while feldspars, micas and the zircon are subordinate. Bioclasts and ooids (built mainly of berthierine and carbonate) occur in variable amounts, the maximum content of each component may reach up to 18 vol.% (Fig. 2H; 3C–E). The carbonatic minerals, such as: sideroplesite, pistomesite, ankerite, calcite (Fig. 2G, H; 3A–F) and clay minerals (kaolinite, illite, berthierine, chlorites) build the sandstone cements. Locally the rock is cut by veinlets filled with calcite, ankerite, sideroplesite (Fig. 3F) and pistomesite.

**Sideritic coquina** are mostly brown or greyish brown in colour. They display an organodetrital structure and a directional texture underlined by bioclasts. Bioclasts, mostly fragments of bivalves, echinoderms, brachiopods, foraminifers, gastropods and tubs of serpuls, are the main components (Fig. 3G, H). Their content in the rock varies from 20 to 80 vol.%. Also quartz grains, berthierine and carbonate ooids and feldspars and rock clasts occur in small amounts. The clasts are cemented by the sideroplesite (Fig. 3H), ankerite (Fig. 3G), calcite, pistomesite and clay minerals (berthierine illite, kaolinite). Veinlets filled with the calcite, dolomite, sideroplesite, pistomesite, kaolinite and by ores are observed in the coquina.

## CARBONATE MINERALS

Mg-siderite – sideroplesite is the main carbonate mineral in the sideritic rocks. Pistomesite occurs locally, while siderite is sporadic. They are accompanied by minor amounts of calcite and ankerite.

**Siderite, sideroplesite and pistomesite** were found in the sideritic rocks as the ground mass (Fig. 2A–F), the cement that fills the pore space (Fig. 2G, H, 3A–F), replacing the clay minerals in ooids (Fig. 2D, 3C), and locally, filling the voids in bioclasts and form veinlets (Fig. 3F). These minerals occur in form of the micrite (Fig. 2A, D–G), microspar

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**Fig. 2. A. Clayey siderite composed with micritic sideroplesite (Sdp) with gastropoda calcite shell. Goszczynno 4/III borehole, depth 66.4 m, crossed polars. B. Clay-mudstone siderite with sideroplesite microspar. Wyszmontów 1 borehole, depth 77.5–77.6 m, crossed polars. C. Clay-sandy siderite with sideroplesite spar. Omięcin XI/3 borehole, depth 184.4 m, one polar. D. Partly rhombohedric crystals of pistomesite (Pt) in ooid in clayey siderite composed with micritic sideroplesite (Sdp). Wąglany k. Opoczna borehole, depth 395.4 m, crossed polars. E. Calcite (Ca) and ankerite (Ak) ooids in clay siderite; orange and yellow luminescence of calcite, non-luminescence of ankertite and sideriplesite (Sdp), dark blue luminescence of kaolinite (arrow). Parkoszowice 58BN borehole, depth 101.0 m, CL image. F. Calcite (Ca) and ankerite (Ak) vein in clay siderite with micrite sideroplesite (Sdp). Jaworznik 144Ż borehole, depth 138.9 m, crossed polars. G. Micrite sideroplesite (Sdp) and ankerite (Ak) cements in sideritic sandstone. Mniszków IG 1 borehole, depth 972.0 m, crossed polars. H. Berthierine (Be) ooid and bivalve shell (arrow) in sideritic sandstone cemented by sideroplesite (Sdp) spar. Mołdawa borehole, depth 308.0 m, one polar**

**A.** Syderyt ilasty zbudowany z mikrytu syderoplesytowego (Sdp) z kalcytową skorupką ślimaka. Otwór Goszczynno 4/III, głęb. 66,4 m, nikole skrzyżowane. **B.** Syderyt ilasto-mułkowy z mikrosparem syderoplesytowym. Otwór Wyszmontów 1, głęb. 77,5–77,6 m, nikole skrzyżowane. **C.** Syderyt ilasto-piaszczysty ze sparem syderoplesytowym. Otwór Omięcin XI/3, głęb. 184,4 m, bez analizatora. **D.** Częściowo romboedryczne kryształy pistomesytu (Pt) w ooidzie w syderycie ilastym zbudowanym z mikrytu syderoplesytowego (Sdp). Otwór Wąglany k. Opoczna, głęb. 395,4 m, nikole skrzyżowane. **E.** Ooidy kalcytowe (Ca) i ankerytowe (Ak) w syderycie ilastym; kalcyt wykazuje żółtą i pomarańczową luminescencję, ankeryt i syderoplesyt (Sdp) nie świecą, kaolinit (strzałka) ma ciemnoniebieską luminescencję. Otwór Parkoszowice 58BN, głęb. 101,0 m, obraz CL. **F.** Żyłka wypełniona kalcytem (Ca) i ankerytem (Ak) w syderycie ilastym z mikrytem syderoplesytowym (Sdp). Otwór Jaworznik 144Ż, głęb. 138,9 m, nikole skrzyżowane. **G.** Piaskowiec syderytowy scementowany mikrytem syderoplesytowym (Sdp) i ankerytem (Ak). Otwór Mniszków IG 1, głęb. 972,0 m, nikole skrzyżowane. **H.** Ooid berthierynowy (Be) i muszla małża (strzałka) w piaskowcu syderytowym scementowanym sparem syderoplesytowym (Sdp). Otwór Mołdawa, głęb. 308,0 m, bez analizatora
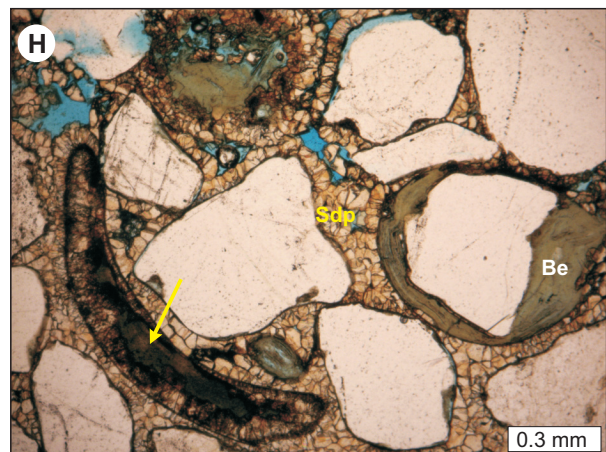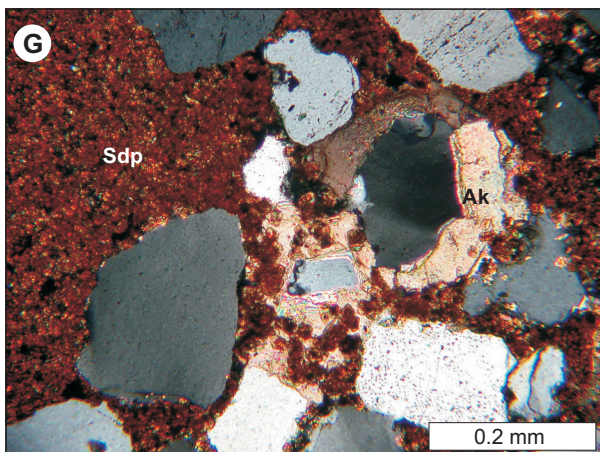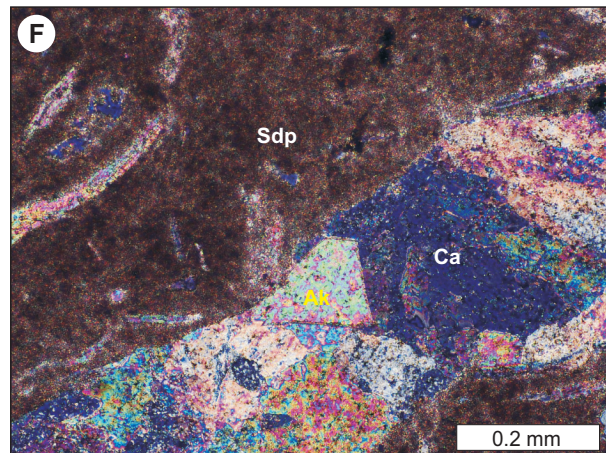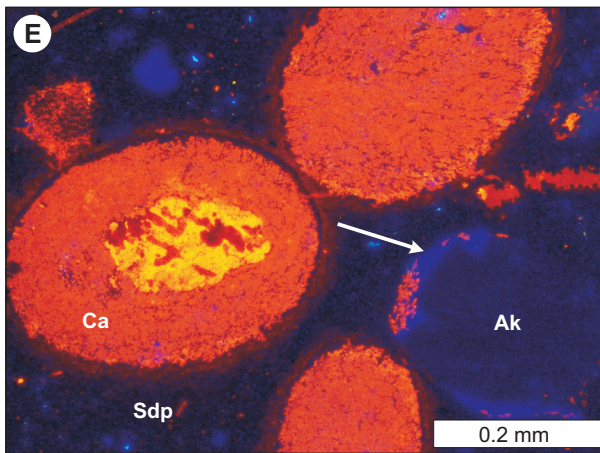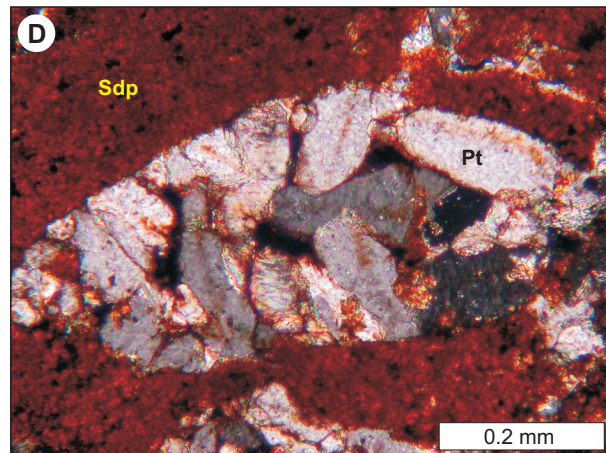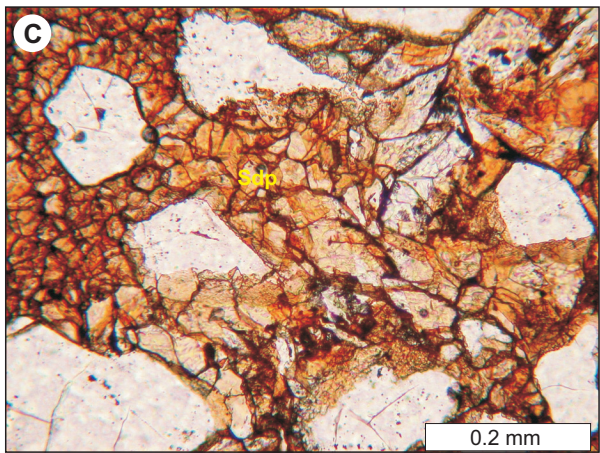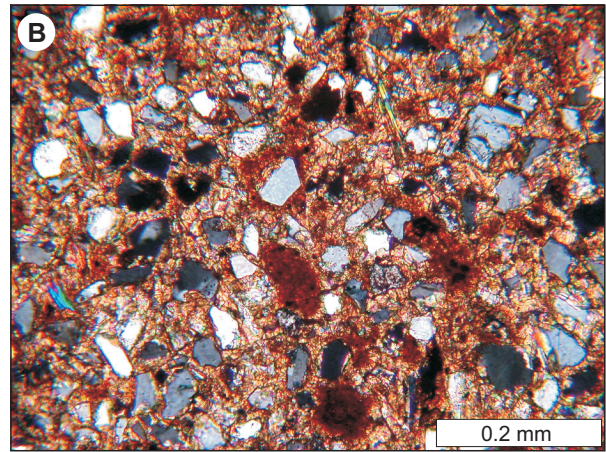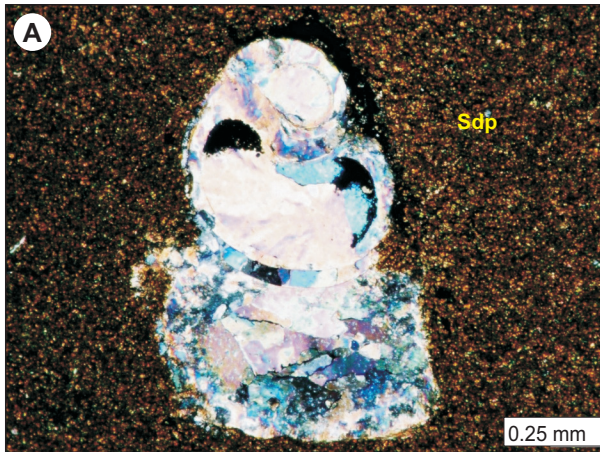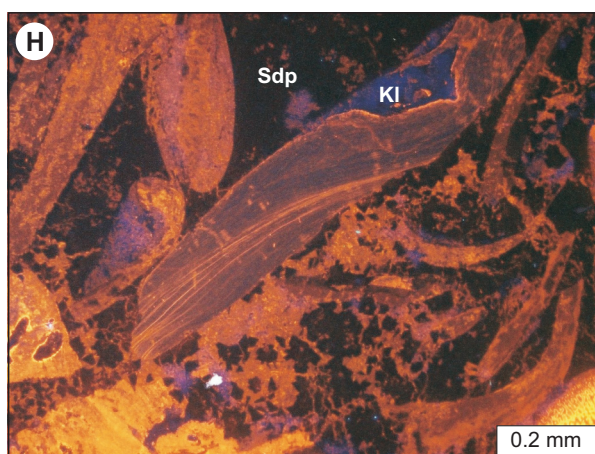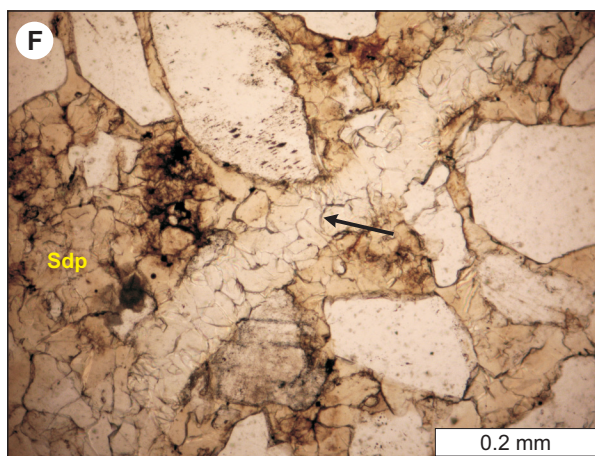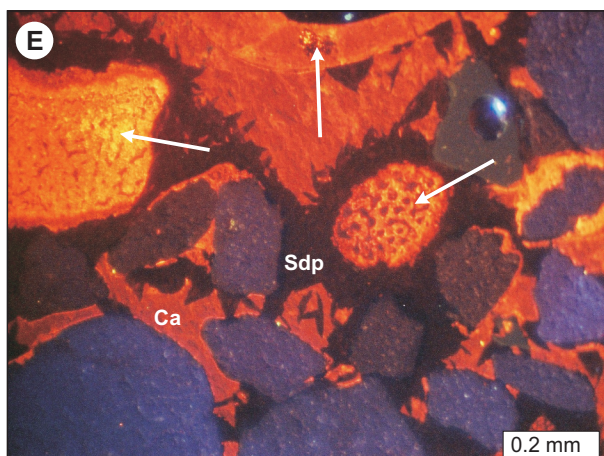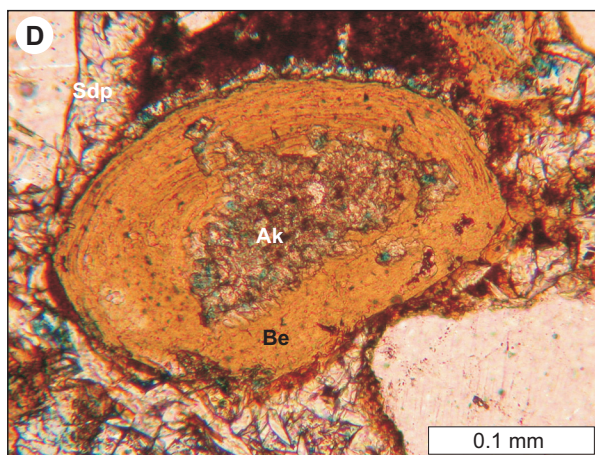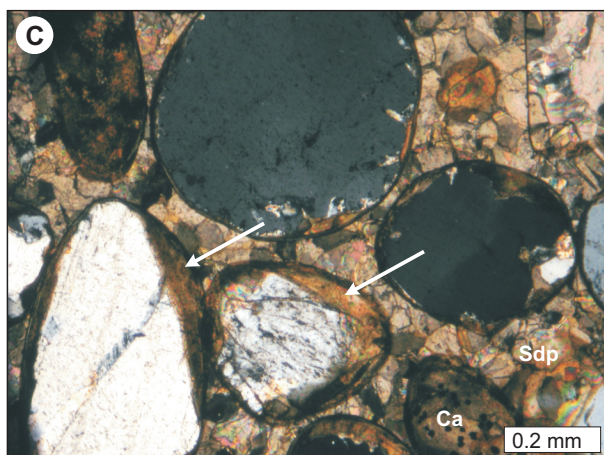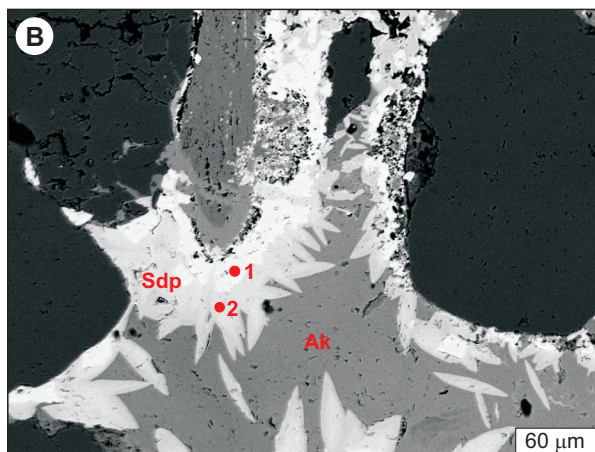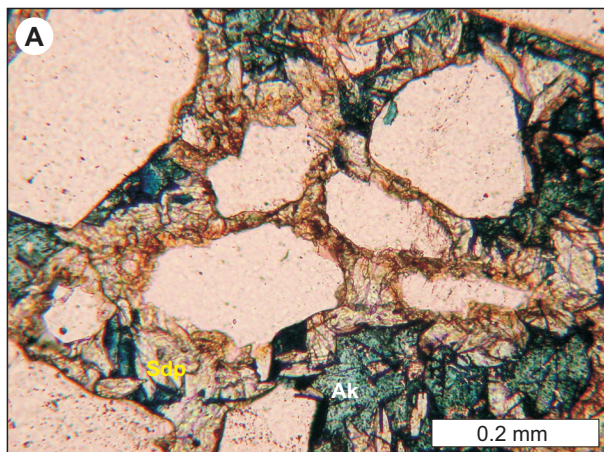
**Fig. 3. A. Rhombohedric crystals of sideroplesite (Sdp) and ankerite (Ak – blue colour by Evamy's solution) cement in sideritic sandstone. Gutwin borehole, depth 250.75 m, one polar. B. Sideroplesite (Sdp) rhombohedra with zonal structure and ankerite (Ak) in sideritic sandstone cements; point 1 – $Fe_{0.784}Mg_{0.082}Ca_{0.115}Mn_{0.019}CO_3$, point 2 – $Fe_{0.687}Mg_{0.180}Ca_{0.123}Mn_{0.010}CO_3$. Omięcin XI/3 borehole, depth 172.9 m, BSE image. C. Berthierine ooids replaced by calcite (Ca) and sideroplesite (arrows) in sideritic sandstone cemented by sideroplesite (Sdp) spar. Mołdawa borehole, depth 308.0 m, crossed polars. D. Berthierine (Be) ooids replaced by ankerite (Ak) in sideritic sandstone cemented by sideroplesite (Sdp) spar (rhombohedrons) and ankerite (blue colour by Evamy's solution). Omięcin XI/3 borehole, depth 172.8 m, one polar. E. Sideritic sandstone with bioclast fragments (arrows) cemented by sideroplesite (Sdp) and calcite (Ca); red and yellow luminescence of calcite, non-luminescence of sideroplesite. Władysław borehole, depth 200.5 m, CL image. F. Sideroplesite (arrow) vein in sideritic sandstone cemented by sideroplesite (Sdp) spar. Mołdawa borehole, depth 244.0 m, crossed polars. G. Dense packing of shell fragments in sideritic coquina; crystals of ankerite (Ak); Omięcin XI/3 borehole, depth 28.6 m, crossed polars. H. Calcite shell fragments with brown, orange and yellow luminescence what is related with content of iron and mangagium in sideritic coquina; non-luminescence of sideroplesite (Sdp) and dark blue of kaolinite (Kl). Gąsiorów 1 borehole, depth 233.0 m, CL image**

**A.** Romboedryczne kryształy syderoplesytu (Sdp) i ankerytu (Ak – barwa niebieska wywołana roztworem Evamy'ego) tworzą cement w piaskowcu syderytowym. Otwór Gutwin, głęb. 250,75 m, bez analizatora. **B.** Romboedry syderoplesytu (Sdp) z widoczną budową zonalną i ankeryt (Ak) tworzące cement w piaskowcu syderytowy; punkt 1 – $Fe_{0.784}Mg_{0.082}Ca_{0.115}Mn_{0.019}CO_3$, punkt 2 – $Fe_{0.687}Mg_{0.180}Ca_{0.123}Mn_{0.010}CO_3$. Otwór Omięcin XI/3, głęb. 172,9 m, obraz BSE. **C.** Ooidy berthierynowe zastępowane przez kalcyt (Ca) i syderoplesyt (strzałki) w piaskowcu syderytowym scementowanym sparem syderoplesytowym (Sdp). Otwór Mołdawa, głęb. 308,0 m, nikole skrzyżowane. **D.** Ooid berthierynowy zastępowany przez ankeryt (Ak) w piaskowcu syderytowym scementowanym sparem syderoplesytowym (Sdp) (romboedry) i ankerytem (barwa niebieska wywołana roztworem Evamy'ego). Otwór Omięcin XI/3, głęb. 172,8 m, bez analizatora. **E.** Piaskowiec syderytowy z fragmentami bioklastów (strzałki) scementowany syderoplesytem (Sdp) i kalcytem (Ca); kalcyt wykazuje czerwoną i żółtą luminescencję, syderoplesyt nie świeci. Otwór Władysław, głęb. 200,5 m, obraz CL. **F.** Żyłka syderoplesytowa (strzałka) w piaskowcu syderytowym scementowanym sparem syderoplesytowym (Sdp). Otwór Mołdawa, głęb. 244,0 m, nikole skrzyżowane. **G.** Gęsto upakowane fragment muszli w muszlowcu syderytowym; kryształy ankerytu (Ak); Otwór Omięcin XI/3, głęb. 28,6 m, nikole skrzyżowane. **H.** Fragmenty muszli kalcytowych o brązowej, pomarańczowej i żółtej luminescencji związanej z zawartością żelaza i manganu w muszlowcu syderytowym; syderoplesyt (Sdp) nie wykazuje luminescencji, kaolinit (Kl) ma luminescencję ciemnoniebieską. Otwór Gąsiorów 1, głęb. 233,0 m, obraz CL

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(Fig. 2B) and spar (Fig. 2C, H, 3A–D, F), often as rhombohedra. The iron carbonates that were treated with the Evamy's solution do not stain and do not show luminescence. Microscopic studies (Jarmołowicz-Szulc, Kozłowska, 2016), permitted to distinguish two generations of sideroplesite – the early and the late one similarly to the Carbonifereous sandstones in the Lublin Though (Kozłowska, 1997, 2001, 2004). On the other hand, siderite represents only the early generation, while pistomesite – only the late generation. The micritic and microsparitic sideroplesite, locally siderite, have been identified in the late generation. When compared with the early one, the late generation is characterized by a larger crystal size and a higher magnesium content. It is represented by the sparitic sideroplesite, rarely by pistomesite. The chemical composition of sideroplesite and pistomesite, based on the EDS ISIS analyses, is as follows: 63.9–91.4% mol $FeCO_3$, 5.2–32.1% mol $MgCO_3$, 1.9–18.7% mol $CaCO_3$ and 0.0–4.2% mol $MnCO_3$ (Kozłowska et al., 2008, 2013; Jarmołowicz-Szulc, Kozłowska, 2016; Maliszewska et al., 2018). The zonal structure dependent on the variable content of iron and magnesium is often observed in the rhombohedral crystals of sideroplesite and pistomesite. That is well observed in the BSE images (Fig. 3B) (Jarmołowicz-Szulc, Kozłowska, 2016). As compared with the Częstochowa–Wieluń region and the Polish Lowlands, the rhombohedral forms of crystals are more frequent in the sideritic rocks in the northern margin of the Holy Cross Mts. On some sideroplesite and pistomesite crystals of spar size (sometimes of rhombohedral crystal habit), with fluid inclusions of appropriate size, microthermometric examinations have been completed. The homogenization temperatures obtained lie in the interval from 48.5 to 139.0°C, while the ice melting values correspond to the interval from –10.0 to 3.4°C, and the eutectic temperatures oscillate from –40 to –30°C (Jarmołowicz-Szulc, Kozłowska, 2016; Maliszewska et al., 2018). Most of isotopic carbon and oxygen determinations were carried out for the early generation of sideroplesite. The $\delta^{13}C$ PDB values change from –29.76 to 1.60‰, while the $\delta^{18}O$ PDB values from –7.84 to 1.86‰ (Maliszewska et al., 2007a, b, 2018; Kozłowska et al., 2008, 2013; Jarmołowicz-Szulc, Kozłowska, 2016). Isotopic examinations have been performed on two samples of the late generation of sideroplesite and pistomesite. The $\delta^{13}C$ PDB values are equal to –10.3 and 9.58‰, while $\delta^{18}O$ PDB are –8.82 and –10.45‰, respectively (Kozłowska et al., 2008, 2013; Jarmołowicz-Szulc, Kozłowska, 2016).

**Calcite** occurs in bioclasts (Fig. 2A), and it forms the cement in the sideritic rocks (Fig. 3E). It fills the veinlets (Fig. 2F) and replaces minerals that build ooids (berthierine, phosphates, Fig. 2E, 3C) and forms micritic and spar crystals. When treated with the Evamy's solution, calcite stains to red or to pink – violet (Fe-calcite). In cathodoluminescence it either displays yellow, yellow-orange (Fig. 2E, 3E), red, or brownish orange colours, or shows no luminescence. Its luminescence is connected with the presence of iron and manganese in the mineral. The chemical analyses in electron microprobe revealed the following composition of calcite: 0.0–5.7 mole % $FeCO_3$, 0.1–4.2 mole % $MgCO_3$, 90.0–99.6 mole % $CaCO_3$ and 0.0–4.1 mole % $MnCO_3$ (Maliszewska et al., 2007a; Kozłowska et al., 2008, 2013). The above data indicate that calcite is most often represented by Fe-calcite or Fe/Mn-calcite. The mineral contains abundant fluid inclu-

sions. Temperature measurements have been attempted but proved successful only in one case (Jarmołowicz-Szulc, Kozłowska, 2016). The homogenization temperatures for the calcite in the veinlet vary from 59.8 to 67.8°C. The $\delta^{13}$C PDB values change from –19.48 to –2.01‰, while the $\delta^{18}$O PDB values range from –8.11 to –1.22‰ (Kozłowska et al., 2008, 2013; Jarmołowicz-Szulc, Kozłowska, 2016).

**Ankerite and Fe-dolomite** in the sideritic rocks form cements (Fig. 2G, 3A, B, G), and veinlets (Fig. 2F), occur in the bioclasts and replace berthierine that builds the ooids (Fig. 2E, 3D). The dolomite, is present only locally, in veinlets. Ankerite and Fe-dolomite crystallize as microspar and spar. Dolomite does not stain when treated with the Evamy's solution, while Fe-dolomite and the ankerite stain to light blue and blue colours, respectively (Fig. 3A, D). In CL – dolomite luminesce in red, while Fe-dolomite and ankerite show no luminescence due to the high iron content (Fig. 2E). The chemical composition of Fe-dolomite and ankerite obtained from EDS ISIS analyses is as follows: 11.0–24.9 mole % $FeCO_3$, 14.6–27.5 mole % $MgCO_3$, 50.5–71.2 mole % $CaCO_3$ and 0.0–2.7 mole % $MnCO_3$ (Maliszewska et al., 2007a; Kozłowska et al., 2008; 2013). Numerous fluid inclusions have been observed in the Fe-dolomite and ankerite, and some of them were analyzed by means of the microthermometry (Jarmołowicz-Szulc, Kozłowska, 2016; Maliszewska et al., 2018). The homogenization temperatures vary from 75.9 to 185.3°C. The isotopic analyses were copleted for two samples containing ankerite. The $\delta^{13}$C PDB values are equal to –7.04 and –6.54‰, while those of $\delta^{18}$O PDB are –10.63 and –10.01‰ (Kozłowska et al., 2008, 2013).

## INTERPRETATION AND DISCUSSION OF RESULTS

### GENESIS OF CARBONATES

The occurrence of the siderites as layers and concretions impelled some researchers to considered them as syngenetic with the sediments in which they occur (Berg, 1944; Taylor, 1949). However, for a long time the majority of scientists launched the opinion that these rocks were formed due to diagenesis (e.g., Correns, 1942, 1952; Taupitz, 1954; Krajewski et al., 2001; Mücke, 2006; Stel, 2009). The studies on the siderites from the fossil sediments point to siderite crystallization in different environments – marine, brackish or fresh water (among others: Weber et al., 1964; Matsumoto, Iijima, 1981; Krajewski et al., 2001). Per analogy, the present formation of siderites may be also referred to different environments such as: the marine (Gautier, Claypool, 1984; Hałas, Chlebowski, 2004), brackish (Pye, 1981) or fresh water (Postma, 1969).

According to the sedimentological analysis carried out by A. Feldman-Olszewska (Feldman-Olszewska, 2005; Kozłowska et al., 2008, 2013), most of the siderites have formed in the marine environment, weakly oxidized, mainly in the transition zone between the normal and the storm waving

basis, and in the coast area, which is corroborated by numerous petrographic-mineralogical-geochemical data.

Three stages – the eo-, meso- and telodiagenesis (according to the division of Choquette and Pray, 1970) have been distinguished in the diagenetic history of the siderite deposits. The cementation was the most important diagenetic process for the formation of the carbonate minerals in the sideritic rocks. Significant was also the replacement of the primary calcite in the bioclasts and of the berthierine in ooids. The effects of other processes are less visible. The mechanical compaction has resulted in the denser packing of the detrital material, especially in the sandstones and the coquina, diminishing the pore space for the carbonate minerals. The dissolution is indistinct in the crystallization of the carbonates. In addition, the process of the vein filling by carbonate minerals can be observed.

At the **eodiagenetic stage** crystallized the sideroplesite (locally siderite) – the main mineral of the sideritic rocks. Continental waters delivered to the sediment could have been an iron source (Woodland, Stenstrom, 1979 fide Zymela, 1996; Blatt et al., 1980 fide Zymela, 1996) as well as the clayey and sulphide minerals brought from the land to the sedimentary basins (Pearson, 1979; Price, Sellwood, 1997). The activity of microorganisms that dissolved the organic matter in the sediment have played an important role in the precipitation of sideroplesite and siderite. It can be assumed that both minerals have formed at relatively low temperatures (<75°C, Morad, 1998) and at low depth.

The sideroplesites occur in the crystals of different size, which is connected with the rock type and the diameter of small channels and pores present in the intercrystalline space that enables the fluid circulation. In the clayey siderites, the sideroplesite most frequently occurs as very fine-grained crystals (micrite, microspar), with a predominance of anhedral or subhedral crystals; whereas in the sideritic sandstones and in the clayey-sandy siderites, the sideroplesite forms larger and better crystallized crystals (microspar, spar), locally euhedral.

In addition to the high $FeCO_3$ percentage the sideroplesites which occur in the Middle Jurassic sideritic rocks are characterized by a high content of $MgCO_3$ and $CaCO_3$ and a low $MnCO_3$. According to Mozley (1989) the high percentages of $MgCO_3$ (up to 41 mole %) and of $CaCO_3$ (up to 15 mole %) as well as below mole 1% of $MnCO_3$ point to the siderite precipitation from marine waters.

The results of the carbon isotopic $\delta^{13}C_{PDB}$ examinations of the Middle Jurassic sideroplesite suggest that theses minerals were formed in anoxic and/or suboxic conditions, in the zone of microbiological methanogenesis (Irvin et al., 1977; Morad, 1998). The oxygen isotopic composition $\delta^{18}O_{PDB}$ in the sideroplesite, assuming its crystallization temperature at 20°C (Baker et al., 1995; Rezaee, Schulz-Rojahn, 1998), points to $\delta^{18}O_{SMOW}$ of the pore waters most frequently in the interval between –6.00 and –1.00 ‰$_{SMOW}$. This is indicative of the presence porous waters of marine origin and the contribution of marine waters mixed with the fresh ones. As in-

dicated by fluid inclusion examinations based on the ice melting temperatures, that the salinity of the fluid varies from 1.7 to 16.9 weight % NaCl eq., while its density is about 1g/cm³ (Jarmołowicz-Szulc, Kozłowska, 2016). The values of the eutectic temperatures point to the presence of calcium and magnesium ions in the brines (Jarmołowicz-Szulc, Kozłowska, 2016).

In the **mesodiagenesis**, the development of the sideroplesite continued, while the pistomesite crystallized. These minerals form crystals of the microspar and spar size, often rhombohedral. In such rhombohedral sideroplesites and pistomesites, a zonal structure is often observed resulting from a distinct enrichment in magnesium in the marginal zones compared with the central part rich in iron. The zonality points to changes in the chemical composition of pore waters during crystallization. An increase in the magnesium content may be referred to the high Mg concentration in the formation waters (Morad et al., 1994). The sideroplesite and pistomesite rhombohedra have been observed mainly in the sideritic sandstones and clayey-sandy siderites, where these minerals have crystallized from the solution. They also fill the voids in bioclasts. Moreover, they occur in ooids in the sideritic rocks as the result of substitution of primary minerals. The isotopic determination of the late generation of sideroplesite and pistomesite, suming their cristallization over 60°C (based on fluid inclusion studies), indicate that the minerals have been formed from pore waters enriched in $^{18}O$ in comparison with waters responsible for the early siderolplesite and siderite precipitation. (Kozłowska et al., 2008; Jarmołowicz-Szulc, Kozłowska, 2016).

The calcite cements were next in the crystallization sequence, filling voids between the siderite and sideroplesite crystals, as well as the voids in a fabric and veinlets. Calcite occurs also as a secondary mineral in ooids. It represents an iron variety, with magnesium, and locally with manganese, which is characteristic of the late generation of this mineral (e.g., Mozley, Hoernle, 1990). The Fe-calcite crystallization that postdated sideroplesite is most probably caused either by a decrease in Fe/Ca ratio in the pore waters, or its depletion in iron resulting from the pyrite and siderite precipitation, or the iron depletion from migrating waters (Zymela, 1996). The biogenic carbonates could have been the calcium source for the calcite. The results of isotopic carbon $\delta^{13}C_{PDB}$ determinations for the Fe-calcites correspond to those obtained for siderites and sideroplesites, characteristic for the microbiological methanogenesis zone (Morad, 1998). The $\delta^{18}O_{PDB}$ values, assuming its crystallization temperature to be about 60°C (from fluid inclusions), indicate that Fe-calcite precipitated from waters of positive values of $\delta^{18}O_{SMOW}$ that corresponds to marine waters or the pore waters in reaction with the host rocks.

The Fe-dolomite and the ankerite have formed as the last carbonate cements in the Middle Jurassic sediments. Most probably the dolomite crystallized first. Both minerals here discussed either fill in the empty space in the pores after the sideroplesite and pistomesite crystallization or they replace berthierine in ooids, or calcite in bioclasts. The dolomite also fills the veinlets. The isotopic values for ankerite correspond to those obtained for the Middle Jurassic ankerites in Spitsbergen (Krajewski et al., 2001). According to the authors quoted, the ankerite cementation was a late diagenetic process under the conditions of the deep burial and at increased temperatures (80–100°C) of the environment dominated by the abiotic processes of the kerogen's decarboxylation. The fluid inclusions data of ankerite point to the crystallization interval of about 70–160°C. These results, together with $\delta^{18}O$ values, suggest that the ankerite has precipitated either from pore waters of marine composition, or waters that reacted with the host rock. Minerals altered and dissolved during burial could have been a source of calcium, magnesium and iron. The high temperature of ankerite formation may point either to a significant burial of the deposits, or to a contact with hydrothermal waters.

At the **telodiagenetic stage,** numerous fissures could have been formed in the Middle Jurassic sediments, among others as a result of the tectonic inversion of the Middle Polish Trough in the late Cretaceous (Dadlez, Marek, 1969). That could have caused an increased activity of the pore solutions of a chemistry of the meteoric waters, or an inflow of hydrothermal origin. Then veinlets filled, among others, with carbonatic minerals, as: calcite, ankerite and sideroplesite may have been formed.

## CONCLUSIONS

1. The sideritic rocks are mainly represented by clayey siderites, that contain also muddy and sandy varieties, sideritic sandstones and sideritic coquina. The sideritic conglomerates and mudstones are local.
2. The following methods are useful in the identification of the carbonate minerals:
 – the staining with the Evamy's solution, due to the differentiated colorization of carbonates;
 – the cathodoluminescence analysis, thanks to different luminescence colors or no luminescence of the carbonates;
 – EDS ISIS analyses, that determinates the chemical composition of the carbonate minerals.
3. The sideroplesite is the main carbonate mineral that builds the sideritic rocks, the pistomesite and the siderite are less frequent. The Fe-calcite and Fe-dolomite, ankerite, and sporadic dolomite occur in variable amounts.
4. The Fe-carbonates are in form of the micrite, microspar and spar. The Mg-siderites (sideroplesite and pistomesite) occurring locally in the rhombohedral forms, display a zonal structure, with a distinct enrichment in magnesium of the outer parts in comparison to the inner part rich in iron. That results from variable iron and magnesium contents in the solution from which the carbonates crystalized.
5. The sideroplesite and the siderite crystallized in the early diagenesis (eodiagenesis), while at the later stage of diagenesis (mezodiagenesis) sideroplesite with an increased

magnesium content, the pistomesite, the calcite and the ankerite crystallized successively.

6. The early generation of iron carbonates – sideroplesite and siderite, has been formed under anoxic and/or sub-oxic conditions, in the zone of microbiological methano-genesis, most probably at temperatures of about 20°C, from pore waters of the marine origin or marine waters mixed with the fresh waters. The late generation of the Fe-carbonates (sideroplesite and pistomesite), crystallized at temperatures over 60°C from the pore waters enriched in the $^{18}O$ isotope as compared with waters responsible for the early sideroplesite and siderite precipitation.

7. Fe-calcite, Fe-dolomite and ankerite crystallized at tem-peratures of about 60°C and 70–160°C from pore waters of marine origin, or from waters which have reacted with the host rocks. The carbon isotopic composition of Fe-calcites is characteristic for the zone of microbiological metanogenesis, whereas ankerite was most probably for-med in the zone of thermal decarboxilation.

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## STRESZCZENIE

Badania syderytowych rud żelaza jury środkowej rozpoczęto w latach dwudziestych XX w., na terenie obrzeżenia Gór Świętokrzyskich i w rejonie Częstochowy. Badania te były kontynuowane po II wojnie światowej. W latach sześćdziesiątych rozszerzono obszar badań na Kujawy i rejon Kamienia Pomorskiego. Ze względu na ograniczone wówczas metody instrumentalne, badania petrograficzne sprowadzały się głównie do określenia składu mineralnego. Wraz z pojawieniem się nowych możliwości analitycznych, pozwalających lepiej scharakteryzować skład mineralny i określić genezę mineralizacji osadów, powrócono do badań skał syderytowych, w Państwowym Instytucie Geologicznym – PIB. Zainicjowała je prof. Maliszewska wraz z Kozłowską i Kuberską.

Na podstawie dostępnych obecnie metod instrumentalnych zbadano minerały węglanowe skał syderytowych jury środkowej, z Niżu Polskiego, północno-wschodniego obrzeżenia Gór Świętokrzyskich i rejonu Częstochowy (fig. 1). Wykorzystano następujące metody badawcze: mikroskop polaryzacyjny, barwienie roztworem Evamy'ego, katodoluminescencję, mikrosondę energetyczną, analizę inkluzji fluidalnych i izotopową.

Skały syderytowe reprezentują głównie syderyty ilaste, obejmujące również odmiany mułkowe i piaszczyste, piaskowce syderytowe oraz muszlowce syderytowe. Zlepieńce i mułowce syderytowe występują lokalnie. (fig. 2A–H; 3A–H).

Głównym minerałem węglanowym budującym skały syderytowe jest Mg-syderyt – syderoplesyt, miejscami pistomesyt. Sporadycznie stwierdzono syderyt. Mg-syderyt i syderyt w skałach syderytowych występują jako: masa podstawowa skały (fig. 2A–F), cement wypełniający przestrzenie porowe w skale (fig. 2G, H, 3A–F), minerał zastępujący minerały ilaste w ooidach (fig. 2D, 3C), miejscami wypełnia pustki w bioklastach oraz tworzy żyłki (fig. 3F). Mg-syderyt i syderyt występują w formie mikrytu (fig. 2A, D–G), mikrosparu (fig. 2B) i sparu (fig. 2C, H, 3A–D, F). Mg-syderyt często tworzy kryształy romboedryczne. W obrębie kryształów romboedrycznych syderoplesytu i pistomesytu często obserwuje się budowę pasową, związaną ze zmienną zawartością żelaza i magnezu. Wyróżniono dwie generacje Mg-syderytu – wczesną i późną. Natomiast syderyt reprezentuje tylko wczesną generację.

Fe-kalcyt oraz Fe-dolomit i ankeryt występują w zmiennych ilościach, natomiast dolomit sporadycznie. Kalcyt występuje w bioklastach (fig. 2A), a ponadto tworzy cement w skałach syderytowych (fig. 3E), wypełnia żyłki (fig. 2F) oraz zastępuje minerały (berthieryn, fosforany) budujące ooidy (fig. 2E, 3C). Tworzy kryształy wielkości mikrytu i sparu. W katodoluminescencji świeci w barwach żółtych, żółto-pomarańczowych (fig. 2E, 3E), czerwonych, brunatno-pomarańczowych lub wykazuje brak luminescencji. Efekt świecenia jest związany z zawartością żelaza i manganu w kalcycie.

Ankeryt i Fe-dolomit tworzą cement w skałach syderytowych (fig. 2G, 3A, B, G), wypełniają żyłki (fig. 2F), występują w bioklastach i zastępują bertieryn budujący ooidy (fig. 2E, 3D). Dolomit, stwierdzono lokalnie, tylko w żyłkach. Ankeryt i Fe-dolomit krystalizują w postaci mikrosparu i sparu. W katodoluminescencji dolomit świeci na czerwono, natomiast Fe-dolomit i ankeryt nie wykazują luminescencji (fig. 2E), z powodu zawartości żelaza.

W historii diagenezy osadów syderytowych wyróżniono eo-, mezo- i telodiagenezę. Z procesów diagenetycznych mających wpływ na tworzenie się minerałów węglanowych w skałach syderytowych największe znaczenie odegrała cementacja. Ważnym procesem jest też zastępowanie przez minerały węglanowe, szczególnie pierwotnego kalcytu w bioklastach oraz berthierynu w ooidach. Efekty pozostałych procesów zaznaczają się w mniejszym stopniu. Kompakcja mechaniczna spowodowała ściślejsze upakowanie materiału detrytycznego, szczególnie w piaskowcach i muszlowcach, ograniczając przestrzeń porową do krystalizacji minerałów węglanowych. Efekty rozpuszczania są słabo widoczne w minerałach węglanowych. Ponadto, w skałach syderytowych zaznaczył się proces wypełnienia szczelin przez minerały węglanowe.

Syderoplesyt i syderyt krystalizowały we wczesnej diagenezie (eodiagenezie), natomiast w późniejszym etapie diagenezy (mezodiagenezie) tworzyły się w kolejności: syderoplesyt z większą zawartością magnezu, pistomesyt, kalcyt i ankeryt. Wczesna generacja węglanów żelaza – syderoplesyt i syderyt, tworzyły się w warunkach anoksycznych i/lub suboksycznych, w strefie mikrobiologicznej metanogenezy, prawdopodobnie w temperaturze ok. 20°C, z wód porowych pochodzenia morskiego lub wód morskich zmieszanych z wodami słodkimi. Późna generacja węglanów żelaza – syderoplesyt i pistomesyt – krystalizowała w temperaturze powyżej 60°C z wody porowej wzbogaconej w izotop $^{18}O$ w porównaniu z wodą, z której wytrącały się wczesny syderyt i syderoplesyt. Fe-kalcyt oraz Fe-dolomit i ankeryt krystalizowały w temperaturach odpowiednio: ok. 60°C i ok. 70–160°C, z wody porowej pochodzenia morskiego lub wody, która weszła w reakcję z otaczającymi skałami. Skład izotopowy węgla Fe-kalcytów jest charakterystyczny dla strefy mikrobiologicznej metanogenezy. Natomiast ankeryt tworzył się prawdopodobnie w strefie termalnej dekarboksylacji.