Origin of siderites from the Lower Jurassic Ciechocinek Formation from SW Poland

Paulina LEONOWICZ

Sideritic rocks, which are characteristic constituents of muddy-silty deposits of the Lower Jurassic Ciechocinek Formation, occur commonly as layers, lenses and small irregular concretions composed of siderite mudstone and siltstone as well as less common lenses of sideritic sandstones. Three types of siderite cement were observed in thin sections: fine-crystalline variety (S_F), coarse-crystalline rhombohedra (S_R) and fine-crystalline biogenic aggregates (S_A). In all these types BSE analysis revealed compositional zonation of crystals, with internal parts enriched in Mg, Mn and Ca and outer zones almost pure siderite. $\delta^{13}C$ values and chemical composition of siderites combined with the presence of early diagenetic pyrite indicate that siderite crystallized from brackish marine-derived solutions; only in the case of two samples from the lower part of the Ciechocinek Formation the freshwater origin cannot be excluded. Mn and Fe were supplied by rivers and released by Fe- and Mn-reduction in suboxic zone, whereas Mg and Ca were derived from sea water, which infiltrated into the sediment. Crystal zonation resulted from the diagenetic evolution of pore water as the sediment was buried. Similar composition and development of siderite crystals from different parts of one layer indicate that siderite precipitated simultaneously throughout the whole horizon. Precipitation began from the formation of numerous nuclei and continued by growth of crystals onto them. It could begin already in the iron reduction subzone and continued in the sulphate reduction and methanogenesis zones.

Paulina Leonowicz, Institute of Geology, University of Warsaw, Żwirki i Wigury 93, PL-02-089 Warszawa, Poland, e-mail: Paulina.Leonowicz@uw.edu.pl (February 9, 2006; accepted: February 10, 2007).
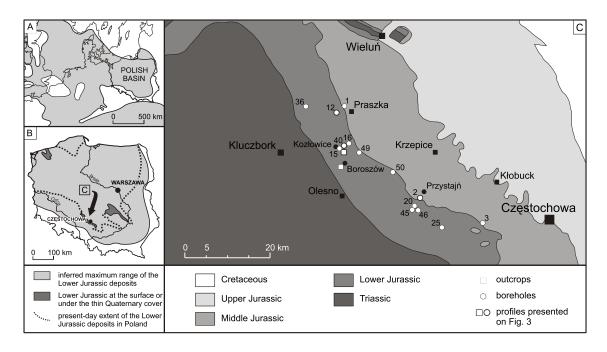
INTRODUCTION

Siderite is a common constituent of epicontinental Lower Jurassic deposits, originated in the extensive Central European Basin, which covered in Jurassic time a vast part of Europe. Sideritic mineralization, which takes form of concretions and layers in argillaceous rocks as well as cements and intercalations in oolitic ironstones, has been reported from many localities in Great Britain, NE France, Luxembourg and NW Germany (Schellmann, 1969; Raiswell, 1971; Sellwood, 1971; Siehl and Thein, 1989; Spears, 1989; Mücke and Farshad, 2005 and many others). Sideritic rocks are also common in the Polish Liassic occurring in both marine and freshwater deposits. These are mainly concretions and intercalations of siderite mudstones, in which some dispersed chamosite ooids were observed (Teofilak-Maliszewska, 1967, 1968). Some of the siderite occurrences, like those from the upper Hettangian Przysucha Ore-Bearing Formation in the Holy Cross Mts. region, were exploited for steel industry already in the 16th century and their petrology was recognized and described in many papers. Some others are of no economical importance and have

not yet been studied in detail. This is the case of the siderites from the Ciechocinek Formation, which until now have merely been mentioned in general petrographical studies on the Polish Liassic (Teofilak-Maliszewska, 1967, 1968; Krystkiewicz, 1999). In spite of their small economical importance, mineralogical and geochemical compositions of these siderites are worth studying, as they can be used in environmental interpretations and reconstruction of diagenetic sequences.

The main purpose of this paper is to outline the origin of siderites from the Ciechocinek Formation, which exposes in the Cracow-Silesian Upland, between Częstochowa and Wieluń (Fig. 1B, C) as well as verifying whether their chemical and isotopic composition reflects the chemistry of water in the sedimentary basin. In the Early Jurassic time Poland was situated in a marginal part of the Central-European Basin (Fig. 1A), in which displacements of shoreline, caused by sea level fluctuations, occurred quite frequently, resulting in a variability of sedimentary environments (Dadlez, 1969; Pieńkowski, 2004). Sediments deposited there are rather monotonous and consist of intercalating sands, silts and muds of both marine (mainly brackish-marine) and freshwater origin. Changes of sedimentary environment are not always distinctly marked in
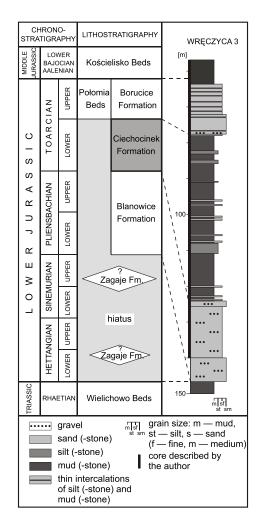
Fig. 1. Location of the study area

A — Polish Basin as a part of the Central-European Basin in the Early Jurassic (after Pieńkowski, 2004), **B** — epicontinental Lower Jurassic in Poland (after Dadlez, 1973 and Pieńkowski, 2004, simplified), **C** — location of studied profiles on a geological sketch-map of the Częstochowa-Wieluń region; boreholes: 1 — Praszka 1, 2 — Przystajń 2, 3 — Wręczyca 3, 12 — Nowa Wieś 12, 15 — Gorzów Śląski 15, 16 — Gorzów Śląski 16, 20 — Przystajń 20, 25 — Przystajń 25, 36 — Pogorzałki 36, 40 — Pawłowice 40, 45 — Bór Zajaciński 45, 46 — Dąbrowa 46, 49 — Skrońsko 49, 50 — Wichrów 50

the profiles and the lack of indicative fauna makes it sometimes difficult to distinguish fine-grained brackish and freshwater deposits. In such cases geochemical analysis of siderites, which record chemistry of pore water present during their precipitation, may be helpful.

CHARACTERISTICS OF THE CIECHOCINEK FORMATION

The Ciechocinek Formation is composed of grey, olive and willow-green, poorly consolidated mudstones and siltstones with lenses and subordinate intercalations of fine-grained sands and sandstones (Teofilak-Maliszewska, 1967, 1968; Leonowicz, 2005). The sediments often contain diagenetic siderite intercalations and concretions as well as pyrite concretions. Sedimentation of these deposits was linked with the marine transgression, which did not result in fully-marine conditions in the Polish Basin. Based on the presence of *Diplocraterion* burrows, fauna of *Estheria*, some agglutinating foraminifera and dinoflagellate cysts as well as the lack of typical marine fauna, the environment was defined as a brackish-marine (Pieńkowski, 2004). Pieńkowski (*op. cit.*) described the sedimentary basin as a large, shallow embayment with some deltaic facies in marginal parts. Dadlez (1969) and

Fig. 2. Lithostratigraphy of the Lower Jurassic in the Cracow-Silesian region (after Deczkowski and Daniec, 1981; Kopik, 1998; Pieńkowski, 2004) and the representative lithological profile of borehole Wręczyca 3; lacking part of core supplemented after Pieńkowski (2004)

Pieńkowski (*op. cit.*) link this transgression with the early Toarcian time, when the transgressional trend was pronounced throughout the whole Central-European Basin. The most precise dating of the Ciechocinek Formation, based on dinoflagellate cysts, pointed to the late Pliensbachian–early Toarcian age (*margaritatus–tenuicostatum* zones) (Barski and Leonowicz, 2002). However, taking into account sequence stratigraphy correlation and results of macrospore analysis (Marcinkiewicz 1957, 1960, 1964, 1971), Pieńkowski (2004) proposed to place it within the lower Toarcian.
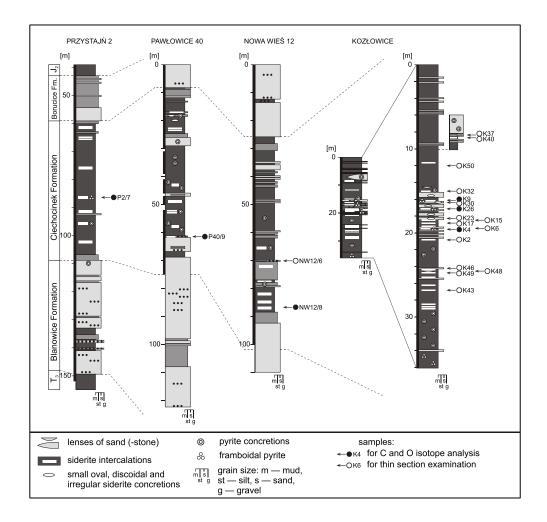
In the Cracow-Silesian Upland the Ciechocinek Formation overlies sandstones and subordinate mudstones of the Blanowice Formation and is overlain by the lithologically similar Borucice Formation (Fig. 2). Both of them were deposited mainly in alluvial and lacustrine environments (Pieńkowski *op. cit.*). The lower and upper boundaries of Ciechocinek Formation are distinct in these profiles where it is confined by erosional surfaces. Location of these boundaries is less precise and sometimes approximate when the change of depositional environment was gradual.

MATERIAL AND METHODS

Successions exposed in two clay-pits, belonging to the "Cerpol-Kozłowice" Enterprise and "Boroszów" Brickyard, as well as 14 boreholes, drilled by the Polish Geological Institute (Fig. 1C), were described and sampled. Sedimentological descriptions of the deposits as well as observations of lithology, dimension and shape of sideritic bodies were made. Samples of siderite mudstones, siltstones and sandstones were collected from different parts of the Ciechocinek Formation profile for petrological investigations.

Around 30 samples were selected for detailed examination under polarizing microscope, which included general description of the rock texture, analysis of development and volume of siderite cement as well as its relation to the grain framework and other cements. Selected samples of sandstones and siltstones were point-counted to estimate the cement volume and porosity.

From the set of samples examined under polarizing microscope, 6 were selected for carbon and oxygen isotope analysis (Fig. 3). Grain size of detrital framework, texture of siderite ce-

Fig. 3. Correlation of selected measured sections with location of studied samples

Simplified lithostratigraphic division, in which Ciechocinek Formation includes deposits marking transition between continental and marine environments, is marked; refer to Figure 3 for section locations; lacking parts of cores supplemented after Pieńkowski (2004) and Kieżel (1990, unpubl.); other explanations as in Figure 2

ment and position in the profile as well as the lack of other carbonate cements was taken into account. Additionally, 5 sub-samples were collected from the K-9 sample, representing siderite mudstone layer from Kozłowice outcrop, to determine whether there was any variation in isotopic composition of siderite cement in different parts of the layer. To identify the mineral composition of siderites chosen for isotopic analysis, bulk-rock XRD analyses were carried out. Samples were analysed in air-dried conditions, with a step size of 0.04° 2θ and 4 s counting time on a *DRON 2.0* diffractometer. Co-Kα radiation and a Fe-filter were used. Then, siderites were crushed to a fine dry powder and left to react with anhydrous phosphoric acid: samples K-4, K-9, K-26, P40/9 for 4 hours at 100°C and samples NW12/8, P2/7 for 72 hours at 50°C. The resultant CO_2 was purified by cryogenic distillation and analyzed on a *Finnigan MAT Delta^{plus}* spectrometer. Results are reported as $\delta^{13}C$ deviation relative to VPDB standard and $\delta^{18}O$ relative to SMOW standard.

Samples analyzed for isotopic composition were also studied by scanning electron microscope (SEM) in order to recognize the texture of siderite cement and to determine the presence of diagenetic pyrite crystals, undetectable using the optical microscope. Observations were carried out on a *Tesla BS 301* scanning electron microscope.

From the same 6 samples, 2 (K-4 and NW 12/8) were selected for back scattered electron (BSE) and wavelength dispersive system (WDS) analyses. Grain size of detrital particles and the texture of siderite cement were recorded. Samples were examined to determine the quantitative elemental composition of siderite crystals. Polished thin sections were analyzed using *Cameca SX 100* electron microprobe equipped with a back scattered electron detector, at 15 kV with a 10–40 nA beam current. Results of chemical analyses are expressed in mol percentages.

OBSERVATIONS AND RESULTS

DESCRIPTION OF SIDERITE BODIES

Sideritic mineralization occurs in all types of Ciechocinek Formation deposits. The most common are 1 to 20 cm thick layers and lenses of siderite mudstones and siltstones, which occur within muddy-silty successions (Fig. 4A). The grain size of detrital particles in these layers and lenses is usually the same as in the host rock. Sometimes mineralization occurs also in coarser-grained intercalations, however, these cases are less common. Moreover, where sand and mud intercalations appear, it is usually mud which underwent sideritization. Siderite layers usually show lateral persistence for several hundreds of metres, which is possible to observe in a single outcrop. Correlation of borehole profiles showed, however, that the layers were in fact extensive, flat lenses randomly distributed in the profile. In some parts of the succession, siderite is so abundant that it does not concentrate in separate layers but occurs throughout the whole sediment, which becomes heavy and grey-brown in colour. Such accumulations of sideritic mudstones, up to 16 m thick, were observed in the lower part of Nowa Wieś 12 and Wręczyca 3 cores.

In the case of sands, almost exclusively thin, up to 5 cm thick, lenses underwent sideritization. Most of them show well preserved cross-lamination, however, there are also load-type sandy lenses with strongly deformed lamination. Relatively thick and more extensive sandy

Fig. 4. Siderites from the Ciechocinek Formation

A — layer of siderite mudstone in muddy-silty deposits; **B** — sand layers with thin lenses and small oval and irregular concretions, composed of siderite mudstone; **C** — strongly deformed shrinkage crack and small, flattened burrow (black arrow) in cross-section; **D** — slightly flattened burrow of *Planolites* isp.; **E** — oval and discoidal concretions of siderite mudstone, collected from the sand layer, scale in cm; A, B, D, E — Kozłowice outcrop, C — Wręczyca 3 borehole, depth 111.5 m

units are usually poorly consolidated and siderite mineralization is poorly developed, taking the form of small aggregates growing on sand grains. However, in such deposits, intercalations and lenses as well as small oval, discoidal and irregular concretions, composed of siderite mudstones and siltstones, commonly occur (

. The latter structures, 1 to 10 cm long, are often arranged in horizons which laterally pass into the continuous siderite layers.
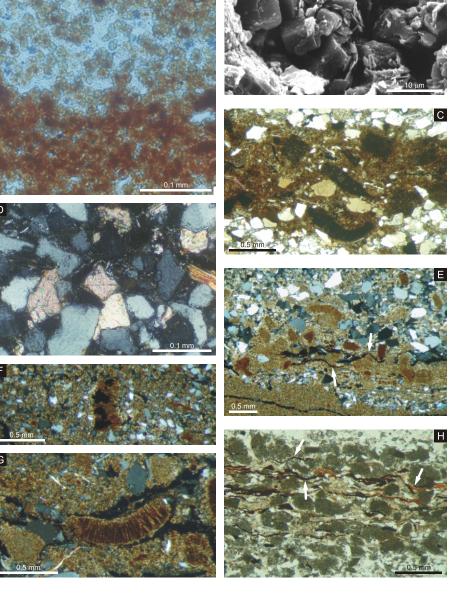
Sideritic rocks differ from surrounding deposits in their greater density and hardness as well as in the brown, rusty or cherry-red colour of weathered surfaces. Small burrows, mainly of the *Planolites* isp., occurring in these rocks are usually only slightly flattened (Fig. 4D), however, there are also burrows which show lenticular, strongly flattened cross-sections (Fig. 4C), resulting from the significant compaction. Also uncommon shrinkage cracks, which were observed in siderites from Wręczyca 3 and Wichrów 50 cores, show strong deformations visible in cross-section (Fig. 4C).

PETROLOGY OF SIDERITE

Examination of thin sections revealed three types of sideritic cement: fine-crystalline variety (S_F), coarse-crystalline rhombohedra (S_R) and fine-crystalline aggregates impregnated by mixture of undetermined Fe hydroxides (S_A).

Fine-crystalline siderite (S_F) occurs mainly as xenomorphic crystals, 1–15 μm in diameter, often combined in granular aggregates (Fig. 5A). They look like spherulites, however, this is only the impression resulting from the presence of concentric accumulations of ferric hydroxides to which siderite is partially altered. SEM and BSE image analyses revealed that siderite S_F could also appear as microcrystalline rhombohedra, up to 5 μm long (Fig. 5B). Intercalations consisting of S_F siderite type often contain some well-preserved plant debris (Fig. 5C). Coarse-crystalline siderite (S_R) is developed as euhedral or subhedral rhombohedra, the long axis of which varies from 0.01 to 0.1 mm (Fig. 5D). Xenomorphic forms are less common. The S_R variety occurs as pore-filling or basal cement as well as disseminated crystals

Fig. 5. Different varieties of siderite cement

A–C — fine-crystalline variety (S_F): **A** — granular aggregates of xenomorphic crystals, sample P40/9, one nicol; **B** — microcrystalline rhombohedra, sample NW12/8, SEM image; **C** — well-preserved, coalified plant debris in the thin intercalation of siderite mudstone, sample K-9, one nicol; **D** — euhedral rhombohedra and xenomorphic crystals of coarse-crystalline variety (S_R), sample K-4, crossed nicols; **E–H** — fine-crystalline aggregates (S_A) impregnated by Fe hydroxides: **E** — different shapes of aggregates; deformation of organic laminae around them (white arrows) as well as preserved structure of plant debris in some of them is visible, sample K-30, crossed nicols; **F** — structureless organic matter preserved inside siderite aggregate, sample K-40, crossed nicols; **G** — well-preserved structure of plant tissue within aggregate, sample K-30, crossed nicols; **H** — accumulation of ellipsoidal aggregates; deformation of organic laminae around them is well visible (white arrows), sample K-26, parallel nicols
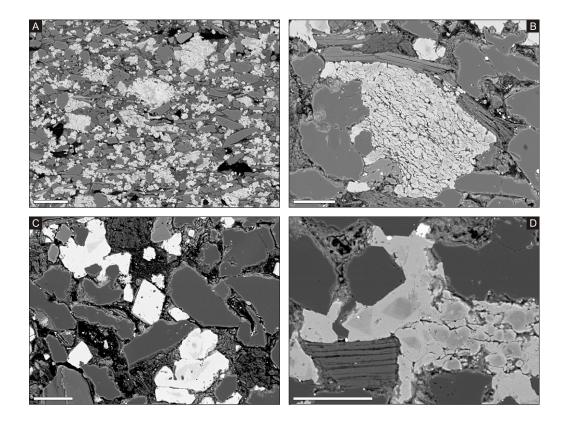
within other cements or clay matrix. This type of siderite is rarely altered. Clay minerals (mainly kaolinite) overgrew siderite crystals in a few samples, however, any signs of replacement by other authigenic minerals were not observed. The third type of siderite cement consists of fine-crystalline aggregates (S_A) of ellipsoidal, elongated, angular or irregular shape, the long axis of which reaches 0.5 mm (Fig. 5E–H). Aggregates occur usually in fine-crystalline background but sometimes they are also

present between grains of detrital framework. Mica flakes and organic laminae are usually deformed around them (Fig. 5E, H). In spite of the high concentration of Fe hydroxides, it is often possible to observe the well-preserved structure of plant tissue inside these aggregates (Fig. 5G). Some of them contain only structureless, unidentified organic matter (Fig. 5F); some others (usually these of elliptical shape) are completely devoid of organic remnants.

Siderite cement in mudstones and clayey siltstones is usually developed as the fine-crystalline variety (S_F) in which fine-crystalline aggregates (S_A) commonly occur. Cement volume is usually high and reaches up to 65–70% of the whole rock volume. BSE analysis of mudstone from NW12/8 sample revealed that aggregates of siderite crystals, filling the pore space between detrital grains, are usually larger that detrital constituents (Fig. 6A). Quartz siltstones and sandstones are mostly cemented with coarse-crystalline siderite (S_R); fine-crystalline aggregates (S_A) are less common. Detrital framework of sandstones and siltstones changes from grain-supported to this, in which individual grains are separated by cement, resulting in various volume of siderite. Cement crystals are usually smaller than detrital grains; their size changes depending on grain size of detrital constituents.

BSE IMAGE ANALYSIS

BSE analysis of two selected samples revealed details of siderite crystals from the different types of cement described above. Fine-crystalline siderite (S_F) was observed in the sample of siderite mudstone (NW12/8; Fig. 6A), fine-crystalline aggregates (S_A) and coarse-crystalline rhombohedra (S_R) — in the sample of siderite siltstone (K-4) (Fig. 6B–D). Noteworthy is the internal structure of aggregates (S_A), which are similar to S_F siderite but have grown preferentially in certain directions (Fig. 6B).

Crystals of all cement types are zoned, with one to four zones commonly developed (Fig. 6C, D). This zoning appears as bright-dark-bright sequences in BSE images, resulting from different chemical composition of particular zones. WDS analysis indicated that dark, usually internal parts of crystals are enriched in Mg and Mn (Fig. 7). Mg content reaches there 26% of all cations, thus they are classified as sideroplesite; they also contain up to 7% of Mn and up to 6% of Ca. Dark parts of crystals have usually regular, rhombohedric shape. Bright zones are almost pure siderite with small concentration of Mn and sometimes Mg (Fig. 7). Mg, Mn-poor siderite forms the external parts as well as single, homogenous crystals. Comparison of analyses of both

Fig. 6. BSE images of siderite cement

A — fine-crystalline siderite cement (S_F, light grey fields on a picture), sample NW12/8; **B** — fine-crystalline aggregate (S_A), sample K-4; **C, D** — rhombohedral and xenomorphic crystals of coarse-crystalline siderite (S_R); zonation of crystals is visible in both pictures, sample K-4; scale bar — 50 m
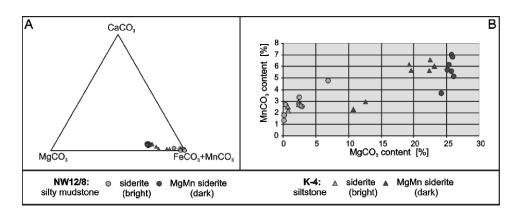
Fig. 7. A — ternary diagram illustrating elemental composition of zoned siderite crystals from siderite mudstone (NW12/8) and siderite siltstone (K-4), determined by WDS analysis; B — Mg and Mn content in dark and bright zones of siderite crystals from samples NW12/8 and K-4
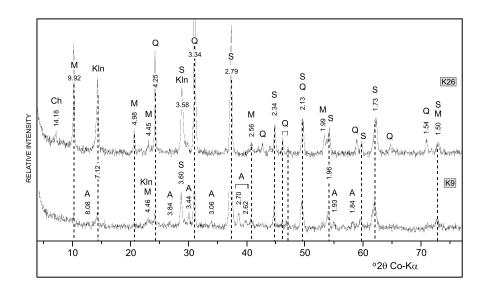

Fig. 8. Mineral composition of siderites from the Ciechocinek Formation exemplified by X-ray diffraction patterns of selected samples; air-dried whole-rock samples

S — siderite, Q — quartz, Kln — kaolinite, M — mica and illite, Ch — chlorite, A — apatite

T a b l e 1

Oxygen and carbon isotopic composition of siderites from the Ciechocinek Formation

Sample	$\delta^{13}C_{VPDB}$ [‰]	$\delta^{18}O_{SMOW}$ [‰]	Framboidal pyrite	Siderite type	Lithology
K-4	−13.47	24.89	++	S_R	siltstone
K-9$_{(1)}$	−8.83	27.31	+	S_F	mudstone
K-9$_{(2)}$	−8.61	27.04	+	S_F	mudstone
K-9$_{(3)}$	−8.59	27.29	+	S_F	mudstone
K-9$_{(4)}$	−8.77	27.42	+	S_F	mudstone
K-9$_{(5)}$	−8.54	27.24	+	S_F	mudstone
K-26	−10.91	27.59	+++	S_A	clayey siltstone
P2/7	−13.27	27.52	+	S_F	mudstone
NW12/8	−10.46	24.67	−	S_F	silty mudstone
P40/9	−10.11	27.92	−	S_F	sandstone

Framboidal pyrite: + occasional, ++ common, +++ abundant; siderite types: S_F — fine-crystalline, S_R — coarse-crystalline rhombohedra, S_A — fine-crystalline aggregates

samples (K-4 and NW12/8) revealed that they differ slightly in chemical composition of dark zones. Those from sample NW12/8 are richer in Mg and Mn than similar parts of crystal in sample K-4 (Fig. 7B). The composition of bright zones in crystals from both samples is similar. This comparison concerns mainly crystals of S_F and S_R types.

XRD ANALYSIS

Bulk-rock XRD analysis, carried out on samples selected for isotopic analysis, indicated that siderite is the only carbonate in the rocks analysed (Fig. 8). Other constituents include: quartz, kaolinite, illite and/or mica, small quantities of chlorite and — in sample K-9 — apatite. The latter is authigenic, possibly of biogenic origin, as no accumulations of detrital apatite were observed during thin section examination. It is worth mentioning that the presence of diagenetic phosphates in carbonate concretions was also reported by Pearson (1974, 1977) and Fisher *et al.* (1998) in siderites from Westphalian shales of Yorkshire in England, thus it may be more common phenomenon, worth further investigation.

CARBON AND OXYGEN ISOTOPIC COMPOSITION OF SIDERITE

Isotopic values for different types of siderite cement are only slightly variable (Table 1). $\delta^{13}C$ in all samples is negative and ranges from

–13.5 to –8.5 ‰ VPDB. The highest content of ^{13}C in carbon was noted in sample K-9, in other samples values of δ^{13}C are lower than –10‰. δ^{18}O values range from 24.7 to 27.9‰ SMOW. No significant differences in isotopic composition between subsamples K-9$_{(1-5)}$ were noted. It shall be remembered that the values obtained are averaged, because siderite crystals were too small for sampling particular zones of different chemical composition, which could differ also in isotopic composition. Thus, these results give only approximate characteristics of pore water.

As the interpretation of oxygen isotopes in siderites is generally problematic (Raiswell and Fisher, 2000) and, in this particular case, there are too many uncertainties, which would make conclusions untrustworthy, they will not be discussed further in this paper.

PYRITE

Pyrite is also a common constituent of Ciechocinek Formation deposits. It can be easy traced during outcrop examination, where it occurs as round, ellipsoidal and discoidal concretions, few millimetres to several centimetres in diameter. No deformations of laminae were observed around concretions, which points to their late, postcompactional origin. Pyrite was also observed in the vicinity of wood fragments as well as in the burrow fillings which are often pyritized. Beside this late, concretionary pyrite, SEM observations revealed also early diagenetic, framboidal and octahedral pyrite (Fig. 9), which occurred in siderites as well as in pure mudstones and siltstones. Diameter of framboids ranges from 2.5 to 8 μm. Octahedra reach 5.8–10 μm and occur as disseminated crystals or form irregular concentrations. From the set of siderite samples destined for isotopic analysis only samples NW12/8 and P40/9 were devoid of fine-crystalline pyrite.
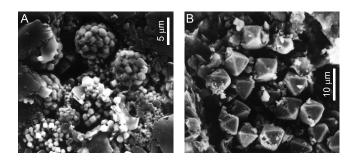

Fig. 9. Microcrystalline pyrite from the Ciechocinek Formation, SEM image

A — framboidal pyrite; **B** — octahedral pyrite crystals; Kozłowice outcrop

INTERPRETATION OF SIDERITE ORIGIN

MODE AND TIME OF SIDERITE CEMENTATION

Siderite mineralization from studied deposits occurs preferably in mudstones and siltstones, even in these cases where intercalations of sands and fine-grained deposits appear. Grain-size distribution in siderite beds is usually similar as in muddy-silty host rocks, which generally have low permeability. Thus, it appears most likely that precipitation of siderite began from pore fluids between detrital particles in some selected horizons, now cemented, rather than from solutions expelled from surrounding sediments. The presence of organic matter inside siderite concentrations, common in fine-crystalline variety (S$_F$) as well as in fine-crystalline aggregates (S$_A$), points to the close dependence of siderite crystallization on organic matter decay. This dependence is particularly evident in the case of siderite aggregates S$_A$, which probably formed as a result of sideritization of plant debris, fecal pellets and other organic remnants. Initial crystallization of siderite in some preferred layers could, thus, result from the higher concentration of organic matter in these horizons. The low permeability of muds prevented infiltration of the well-oxidized basin water into the sediment and oxidation of dispersed organic remnants. On the contrary, thicker layers of permeable sands enabled easy penetration of oxidized water and the siderite mineralization was poorly developed.

Initial crystallization of siderite in organic-rich horizons resulted in the formation of numerous nuclei dispersed in the sediment, which became preferential sites for the continued growth of zoned crystals. Further growth could proceed by utilization of alkalinity and carbonate ions, diffusing from the adjacent pore waters and was not limited by the amount and reactivity of organic matter in the layer, where siderite precipitated, as most of it could be consumed for the siderite nuclei formation. Similar isotopic composition as well as the same texture of siderite crystals in samples collected from different parts of one layer (samples K-9$_{(1-5)}$) point to the contemporaneous precipitation of the siderite crystallites in the whole horizon. The larger size of cement crystals compared with detrital constituents, observed in mudstone from sample NW12/8, as well as frequently observed texture of sideritic sandstones and siltstones, where individual detrital grains are separated by cement, point to the common displacive character of siderite precipitation. In some cases, siderite may also have precipitated passively, filling vacant pore space. This can be inferred from the grain-supported detrital framework, often observed in sideritic sandstones and siltstones, as well as from the size of siderite cement crystals in most of these rocks, which is usually smaller than the size of detrital grains.

The deformation of mica flakes and organic laminas around fine-crystalline aggregates (S$_A$) and slight flattening of some *Planolites* burrows suggest that cementation began quite early, while the sediment was soft with high porosity. Cementation of load-type sandy lenses with deformed lamination shows that crystallization of siderite continued after soft sediment deformation. It continued during deeper burial, post-dating significant compaction of deposits, which led to lithification of muds with strongly deformed shrinkage cracks and flattened burrows.

The origin of lenses and small oval, discoidal and irregular concretions, composed of siderite mudstones and siltstones, which occur in sandy layers is not certain. One possibility is that these are muddy intraclasts sideritized after erosion and redeposition, but this is not convincing in view of the prevalent oval, egg-like shape of concretions, differing from typical

shapes of intraclasts. The second possibility is that these concretions formed near the water-sediment interface in muddy sediment and were washed-out and transported by strong bottom currents along with the sands that now surround them. This explanation, however, is inconsistent with generally quiet depositional environment of the Ciechocinek Formation deposits (Leonowicz, 2002, unpubl.) and the lack of erosional structures in the flat siderite lenses that are associated with concretions as well as in continuous siderite layers, which laterally change into horizons with these concretions. Moreover, accumulations of siderite concretions occur only in sandy horizons; concretion levels were not observed in mud-silt deposits, thus, it is less probable that they ever existed. The third possibility is that these concretions are load-type structures, derived from one, originally continuous layer of mud, which overlaid the sands. The problem is that it is always sand that is loaded into a mud, not vice versa. Maybe, in this particular case, mud was already partly cemented and therefore heavier, but still plastic, what enabled loading into underlying sand. Explanation of these questions requires further studies.

COMPOSITIONAL ZONATION OF SIDERITE CRYSTALS

Zonation of siderite crystals records changes of pore-water chemistry during its precipitation. MnMg-rich siderite, which appears in the inner parts of crystals, had to crystallize first; this was followed by pure siderite, which now forms external zones and single, homogenous crystals. This regularity points to the decrease of Mg and Mn content in pore waters during ongoing diagenesis. Although composition of pore water was subject to short-lived fluctuations, resulting in formation of multiple zonation, general trends occur in all crystals.

The reasons of compositional zonation in carbonate crystals were extensively discussed in many mineralogical papers (Curtis *et al*., 1975; Pearson, 1979; Curtis *et al*., 1986; Mozley, 1989; Macaulay *et al*., 1993; Fisher *et al*., 1998; Hugget *et al*., 2000; Wilkinson *et al*., 2000 and many others). In general, chemistry of pore water can be influenced by two different processes: salinity of water in sedimentary basin and diagenetic alterations of unstable detrital constituents, leading to the release of chemical elements and consumption of others. Changes of sea level can modify pore water chemistry in more permeable sediments, resulting in the chemical zonation of continuously growing crystals (Curtis *et al*., 1986; Mozley, 1989; Macaulay *et al*., 1993; Hugget *et al*., 2000). As the sea water is enriched in Mg and Ca ions, and Fe and Mn ions are derived from the fresh water, transgression is marked by the increase of Mg and Ca content toward the margins of siderite crystallites. The same effect can be achieved by diagenetical alterations. If siderite begins to crystallize in suboxic zone, where the oxygenation of organic matter utilized Mn and Fe oxides, it would be enriched in these elements (e.g. Curtis *et al*., 1986; Fisher *et al*., 1998). At greater depths, Mn and Fe content declines as a result of siderite precipitation and decreased rate of Fe and Mn reduction. Simultaneously Mg and Ca concentrations remain constant with depth or even can increase, due to alterations of detrital particles, and as a result Mg/Fe + Mn and Ca/Fe + Mn ratios increase.

The low permeability of the Ciechocinek Formation makes it unlikely that fluctuations of sea level caused the compositional zonation of siderite crystals. More probable is that internal zonation of crystals resulted from diagenetic evolution of pore water chemistry linked with processes occurring below the sediment-water interface. Increased content of Mg cations in the internal zones of crystals points to the marine origin of pore waters (Mozley, 1989). However, the same parts of crystals contain also up to 6.9% of Mn, linked rather with freshwater environments. Such compositions could be caused by the mixing of marine and freshwater off the river mouths. Thus the starting composition of pore water, from which the internal parts of siderite crystals precipitated, resulted from the releasing of land-derived Mn and Fe ions in Mn- and Fe-reduction zones and the presence of Mg ions derived from brackish-marine basin water. Increased burial restricted infiltration of basin-derived water into the sediment, limiting supply of Mg. Simultaneously manganese reduction fell and the concentration of Mn ions declined. The only available cation was Fe^{+2}, which frequently reaches maximum concentration deeper than Mn^{+2} (see Curtis *et al*., 1986). Iron could be also derived to pore water during deeper diagenesis by the releasing from detrital Fe-bearing minerals, for example ferrous chlorites, which occur commonly in Ciechocinek Formation muds (Leonowicz, 2005).

CARBON ISOTOPIC COMPOSITION AND PYRITE DISTRIBUTION

Extensive geochemical studies of diagenetic processes indicate that along with progressive burial sediment passes through several geochemical zones, resulting from organic-inorganic interactions (Fig. 10). In freshwater deposits, precipitation of siderite begins in the iron reduction subzone and continues — if there is enough of Fe^{+2} ions — until reaching the thermal decarboxylation zone. The sulphate reduction zone is often

ZONE		CO_2 releasing reactions
oxic		$CH_2O + O_2 \rightarrow CO_2 + H_2O$
suboxic	nitrate reduction	$CH_2O + HNO_3 \rightarrow CO_2 + N_2 + H_2O$
suboxic	manganese reduction	$CH_2O + Mn^{+4} \rightarrow Mn^{+2}_{aq} + CO_2$
suboxic	iron reduction	$CH_2O + Fe^{+3} \rightarrow Fe^{+2}_{aq} + CO_2$
bacterial sulphate reduction		$CH_2O + SO_4^{-2} \rightarrow HS^- + CO_2$ $Fe^{+3} \rightarrow Fe^{+2}_{aq}$ [only in marine sediments]
microbial methanogenesis		$CH_2O \rightarrow CH_4 + CO_2$ $Fe^{+3} \rightarrow Fe^{+2}_{aq}$
thermal decarboxylation of organic matter		T ~ 75 °C Kerogen $\rightarrow CH_3COOHO + CO_2$

Fig. 10. The geochemical zonation of sediment, following progressive burial; generalized reactions, involving release of CO_2, are given for each zone (after Morad 1998, modified)

Zones of siderite precipitation are marked grey colour

poorly developed in such environments due to the lack of SO_4^{2-} in the overlying water column. In marine sediments, Fe^{+2} produced by iron reduction in suboxic and sulphate reduction zones, is mainly precipitated as sulphides, thus siderite cannot precipitate until the sulphate ions are consumed, i.e. in the methanogenesis and thermal decarboxylation zones. However, if there is excess of Fe^{+2} with respect to HS^-, siderite can also precipitate in the sulphate reduction or even suboxic zones.

Carbon isotope composition of early diagenetic carbonates is controlled by the $\delta^{13}C$ of carbon dioxide dissolved in pore water, which depends in turn on its origin (from atmosphere, sea water or generated by processes of organic matter degradation) as well as on whether diagenesis took place in a closed or open system. Each source mentioned above supplies CO_2 of a different carbon isotope composition. CO_2 released during oxidation of organic matter and bacterial sulphate reduction generally inherits isotopic composition from source organic matter and is characterized by $\delta^{13}C$ values about –25‰ PDB (Irwin *et al*., 1977). CO_2 originating as a result of bacterial fermentation can show variable values of $\delta^{13}C$ ranging from –30 to +20‰ PDB (Whiticar *et al*., 1986; see also Raiswell and Fisher, 2000), depending on the specific microbial processes involved. Thermally-induced reactions of decarboxylation supply CO_2 of a different isotopic composition with $\delta^{13}C$ values ranging from –10 to –25‰ PDB (Irwin *et al*., *op. cit*.). CO_2 from the sea water has $\delta^{13}C$ values about 0‰. River water is often slightly depleted in ^{13}C comparing with sea water. Values of $\delta^{13}C$ in carbonates precipitated in particular geochemical zones can differ from these mentioned above due to the mixing of CO_2 derived by different processes of organic matter decay as well as the infiltration of marine and meteoric waters into the upper part of deposits (Irwin *et al*., *op. cit*.; McKay *et al*., 1995; Morad, 1998).

Negative values of $\delta^{13}C$ obtained for siderites from the Ciechocinek Formation (Table 1) indicate that CO_2 was generated either by oxidation of organic matter or by bacterial fermentation. Slight increase of $\delta^{13}C$ values by mixing with CO_2 of marine and/or meteoric origin is also probable. As the depth of burial of Lower Jurassic deposits, estimated from the original thickness of younger rocks in the Cracow-Silesian Upland did not exceed 1 km (Sokołowski, 1973; Deczkowski and Franczyk, 1988; Dayczak-Calikowska and Moryc, 1988; Niemczycka and Brochwicz-Lewiński, 1988; Marek, 1988; Jaskowiak-Schoeneichowa and Krassowska, 1988), CO_2 originating as a result of abiotic decarboxylation reactions, which occur at temperatures higher than 75°C, can be excluded (McKay *et al*., 1995, Morad, 1998).

As in most samples analyzed, excluding NW12/8 and P40/9, the early diagenetic, framboidal and octahedral pyrite occurs, so it can be inferred that the precipitation of siderite took place from brackish or marine-derived solutions. Only in the case of samples devoid of pyrite, freshwater origin cannot be excluded. However, microcrystalline pyrite is not abundant, thus its formation should not limit crystallization of siderite. Taking into account this fact as well as results of carbon isotope analysis, it can be inferred that precipitation of siderite could began in the iron reduction subzone and continued in the sulphate reduction and methanogenesis zones. The statement that the growth of crystals lasted for a longer time and proceeded in different geochemical conditions is supported by the compositional zonation of crystals. The increased of $\delta^{13}C$ values, when compared to those typical of organic matter oxidation, could result from mixing of CO_2 generated in the suboxic zone with CO_2 derived from basin water and, in later stages, from mixing of CO_2 released during sulphate reduction and bacterial fermentation. It should be stressed, however, that presented values of $\delta^{13}C$ are averaged, obtained from whole sample analyses, so they combine isotope composition of crystals formed at different stages.

CONCLUSIONS

Crystallization of siderite in Ciechocinek Formation deposits began quite early, before noticeable compaction of sediment, and continued during deeper burial, post-dating processes of soft sediment deformation and significant compaction. Analyses of carbon isotope and chemical composition indicate that precipitation of siderite began already in the iron reduction subzone and continued in the sulphate reduction and methanogenesis zones.

The reason that siderite mineralization is commonly concentrated in some preferred layers and lenses in monotonous mud-silt succession is that they probably had a higher content of organic matter. Decay of abundant organic matter resulted in local carbonate supersaturation and early precipitation of siderite nuclei, which became favoured sites for further growth of cement crystals. Thicker layers of sand are not sideritized due to their high permeability, which allowed organic matter to be completely oxidized soon after deposition. The origin of lenses and small siderite concretions, occurring in sandy layers is not certain. Most likely these are load-type structures, derived from a continuous layer of mud, which was partly sideritized. The higher weight and still plastic properties enabled its loading into underlying sand.

Initial crystallization of siderite resulted in formation of numerous MnMg-rich nuclei, which precipitated simultaneously throughout the whole layer volume. Further precipitation continued by growth of particular crystals, zonation of which reflects changes in pore water chemistry during progressive burial. Texture of siderite cement indicates that it precipitated mainly by displacing surrounding detrital grains, however, passive filling of vacant pore space in some sideritic sandstones and siltstones is also possible. Similar texture and chemical composition of crystals from three siderite types (S_F, S_R and S_A) point to their similar origin. Thus, morphological differences do not result from different diagenetic conditions but from different grain size of host sediment and accessible space.

Chemical composition of internal crystal parts, which are enriched in Mg and Mn, resulted from the mixed, marine and freshwater, source of pore solutions. Mg ions were derived from marine basin water, whereas Mn and Fe were released in suboxic zone from land-derived particles. Increasing depth of burial limited the process of manganese reduction and restricted access of Mg from basin water. As a result external parts of crystals are almost pure siderite.

Chemical and isotopic composition of siderites from the Ciechocinek Formation as well as the presence of early

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