

Palaeoenvironmental significance of iron carbonate concretions from the Bathonian (Middle Jurassic) ore-bearing clays at Gnaszyn, Kraków-Silesia Homocline, Poland

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ABSTRACT:

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Iron carbonate concretion horizons are characteristic features of the Bathonian (Middle Jurassic) claystone-mudstone succession at Gnaszyn. They occur in single horizons, which generally represent the same genetic type. The siderite concretions are the main type of iron carbonate concretions at Gnaszyn; a second type is represented by phosphate-siderite concretions. On the basis of the fieldwork, and their petrographical and mineralogical characteristics, the genesis of the concretions and their palaeoenvironmental significance is discussed. The results of this study (based on the localization, mode of occurrence, mineralogy of iron carbonate concretions and also the textural relationship between the concretions and host sediment layers) suggest an early diagenetic origin of the concretions. The preferential occurrence of the concretion horizons in single layers in the ambient sediments was associated with particular conditions of their deposition and early diagenesis, favored by a slower sedimentation rate and more intense bioturbation, and related primarily to the greater availability of reactive iron ions. From the viewpoint of physicochemical conditions the horizons with iron carbonate concretions in the study area reflect the redox boundary between oxic/bioturbated and anoxic/non-bioturbated zones. The conditions favoring the formation of such horizons was possibly due to longer periods of diminished sedimentation rate when the redox boundary remained in the same position within the sediment.

Key words: Siderite concretions; Phosphate-siderite concretions; Palaeoenvironment; Bioturbation; Early diagenesis; Redox boundary; Bathonian; Jurassic; Poland; Cracow-Silesia Homocline.

INTRODUCTION

The formation of carbonate concretions in fine-grained sediments rich in organic matter takes place usually during shallow burial of the concretion-hosting sediments and is fuelled mainly by microbial processes. The latter lead to an increase in alkalinity,

which favours the precipitation of authigenic carbonate minerals (e.g. Berner 1968; Raiswell 1976, 1988; Raiswell and Fisher 2000, 2004; Irwin *et al.* 1977; Pearson 1974; Coleman 1985, 1993; Gautier 1982; Scotchman 1991; Dong *et al.* 2008). Such concretions may appear in particular horizons, preferentially in some lithologies due to a high organic content or to

higher permeability of the sediment and/or can also be connected to physico-chemical conditions occurring synchronously in a broad area of the basin (Sellez-Martinez 1996). The mineral composition of the concretion occurring in mudstone may provide hints on the depositional environment and the processes taking place in the ambient strata during concretion growth (Irwin *et al.* 1977; Mozley 1989; Mozley and Wersin 1992; Middleton and Nelson 1996).

The carbonate concretions are a characteristic component of a rather monotonous succession of Middle Jurassic dark coloured claystone and mudstone beds known as the ore-bearing clays. They have been exploited as a source of iron since the Middle Ages until the early 1980s (Ratajczak 1998). Their mode of occurrence, i.e., grouping in particular horizons and their subsequent absence in the remaining parts of the ore-bearing clays, most likely reflects fluctuations of some palaeoenvironmental parameters that took place during deposition of the sediments in question. This paper, which forms part of multidisciplinary studies on the Middle Jurassic from Gnaszyn (see Gedl and Kaim 2012, this issue), is a mineralogical study of the iron carbonate concretions and the host sediments. It aims at characterizing these two different rock-types in order to reconstruct the palaeoenvironment in the Gnaszyn succession.

GEOLOGICAL SETTING

The Gnaszyn succession represents the upper part of the ore-bearing clays in the vicinity of Częstochowa. These Middle Jurassic (Upper Bajocian–Bathonian) strata represent fine-grained dark-coloured clastic facies formed in the southern marginal part of the epicontinental Polish Basin, an eastern arm of the Mid-European Basin (Dadlez 1989). The stratigraphy of the Gnaszyn section is based on ammonites and the major part of the section encompasses the Garantiana–Retrocostatum ammonite zones (Różycki 1953; Matyja and Wierzbowski 2003). The upper part of the succession is exposed in the Gnaszyn clay-pit at Gnaszyn Dolny, and represents the Middle–lower Upper Bathonian Subcontractus–Retrocostatum ammonite zones (Matyja and Wierzbowski 2006; Gedl and Kaim 2012, this issue).

The carbonate concretions of the ore-bearing clays of the Cracow-Silesia Monocline have already been a subject of several previous studies. The basic mineralogical characteristics of the iron carbonate concretions were given by Ratajczak (1998) without determination of their genesis. Majewski (2000) provided

a sedimentological and palaeontological analysis of the Bajocian–Bathonian carbonate concretions from Częstochowa (Bugaj, Gnaszyn, and Grodzisko sections). He distinguished four main types of concretions in the ore-bearing clays: (1) early diagenetic calcite concretions with evidence of reworking, (2) early diagenetic fossiliferous calcite concretions, (3) early diagenetic siderite concretions with septaria, and (4) later early diagenetic massive siderite concretions. He concluded that formation of the concretions was related to a reduction in the sedimentation rate followed by early diagenetic processes. Zatoń and Marynowski (2004; 2006) studied the fossil content, organic geochemistry, and origin of the fossiliferous calcite concretions (Konzentrat-Lagerstätte-type concretions) that occur plentifully in the latest Bajocian part (Parkinsoni Zone, Bomfordi Subzone) of the succession. They suggested that the concretions precipitated diagenetically around organic remnants accumulated in minute depressions of the sea bottom due to the activity of bottom currents. Zatoń *et al.* (2006) studied hiatus calcite concretions from the younger part of the succession (Ogrodzieniec, Bugaj, Morsko and Krzyworzeka). They proposed a sequence of early-diagenetic (omission, erosion, and/or exhumation periods) and ecological (hardground colonization) processes as a mechanism leading to the formation of these concretions. Later, Zatoń *et al.* (2009) characterized some calcite concretions, including those from the Gnaszyn clay-pit, with respect to a framboid pyrite study. The origin of the siderite concretions has not yet been covered in any of the aforementioned contributions, apart from some investigations of Sitko *et al.* (2009), which focused on the chemical composition of the siderite in concretions occurring in the ore-bearing clays in the study area.

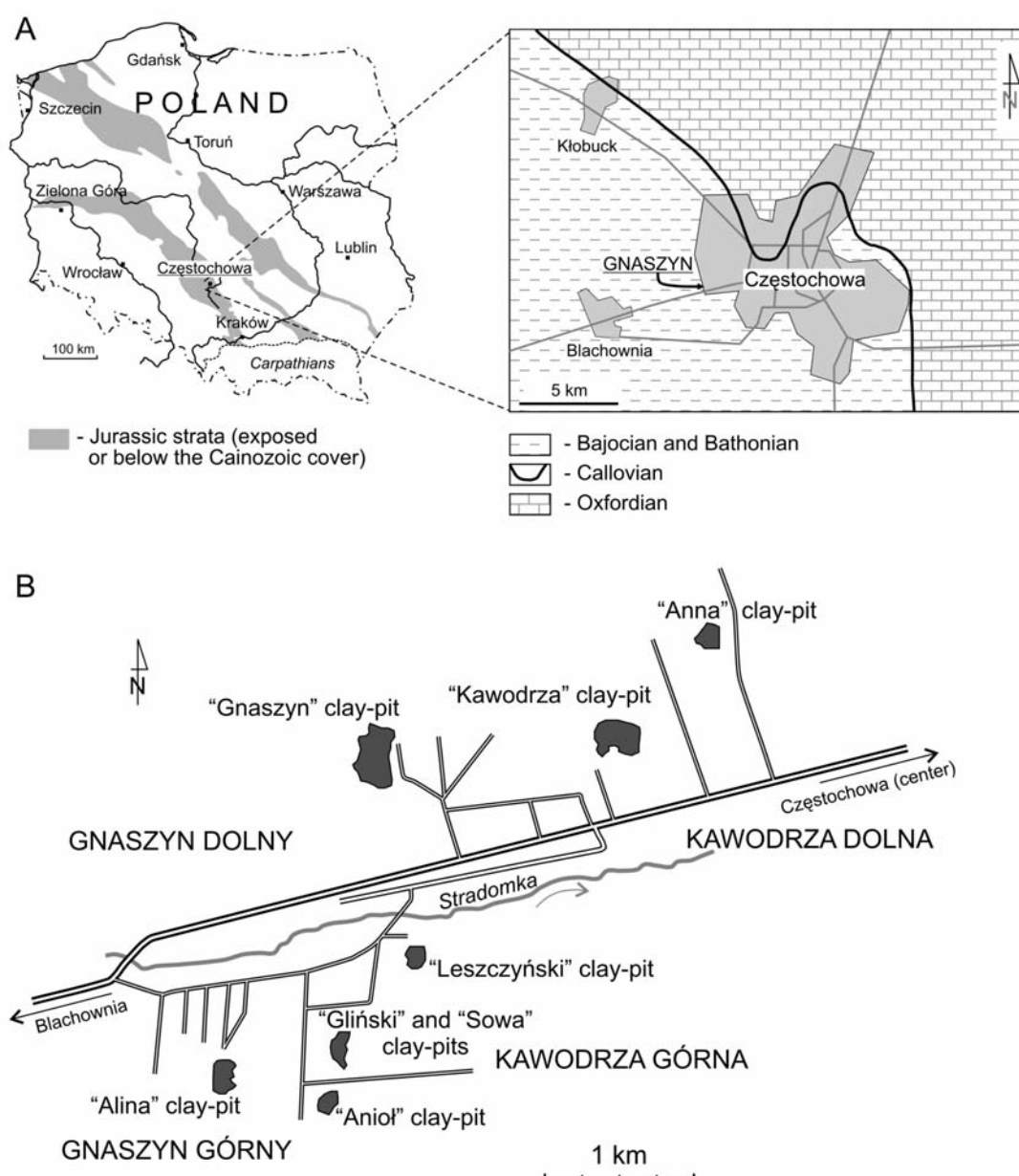
MATERIAL AND METHODS

Middle Jurassic iron carbonate rocks from ore-bearing clays of the Kraków–Częstochowa Homocline occur as concretion horizons, which show great lateral extent and limited thickness, from a few to a few dozen centimetres. The material studied herein comes from the Gnaszyn clay-pit (south-western suburbs of Częstochowa; Text-fig. 1), where a c. 20-m thick succession, consisting of dark grey claystone and light gray mudstone, contains eight horizons of iron carbonate concretions (Text-fig. 2). The latter were sampled from three sections (A, B, and C; A and B represent approximately the same part of the succession): Forty-five concretions (four to six concretions from each horizon)

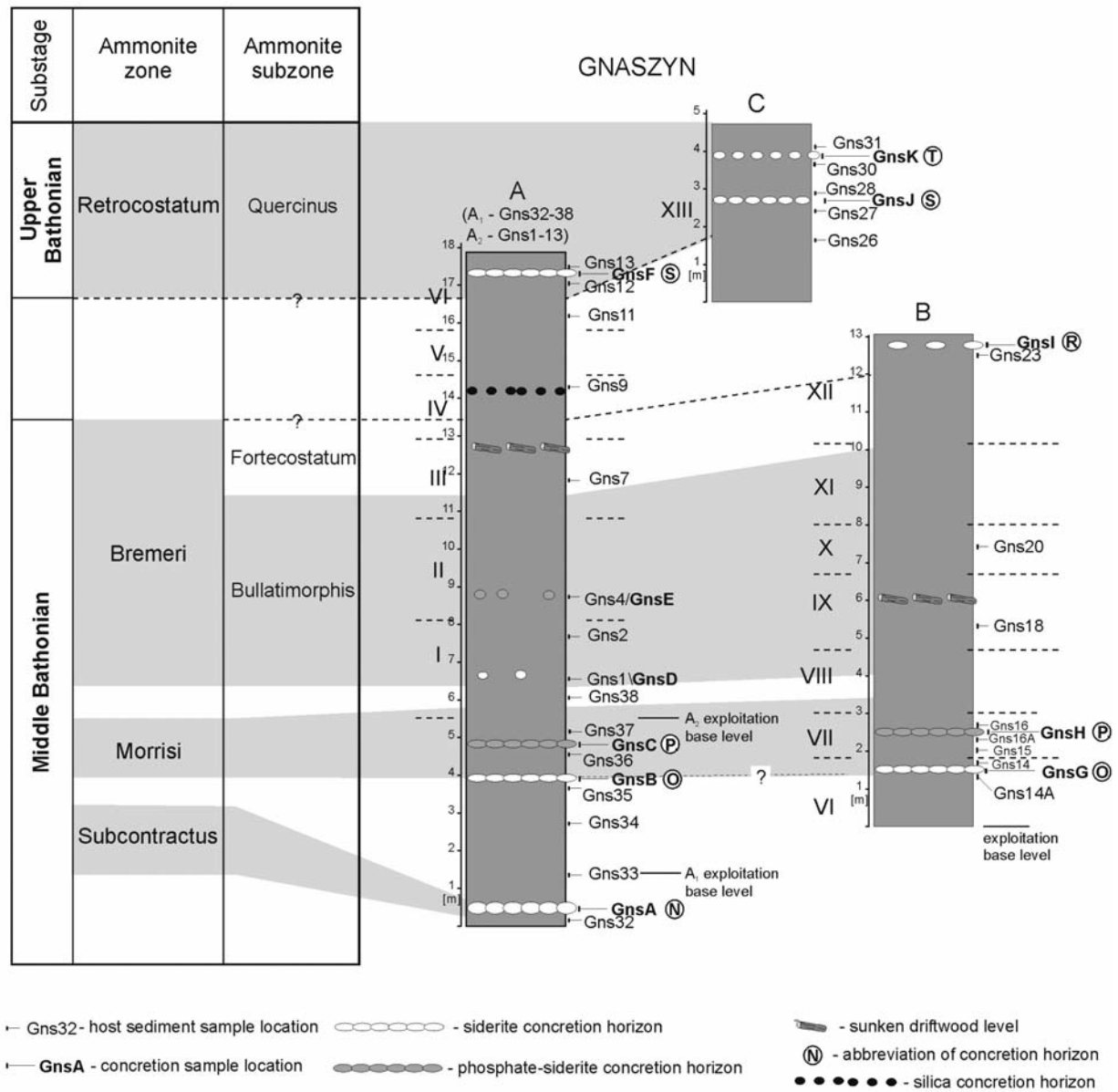
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were collected for morphological analysis. The length (A), width (B) and height (C) of each concretion were measured in three mutually perpendicular directions, from which A and B were marked as directions parallel to and C perpendicular to the bedding plane. The flattening and elongation ratio (C/A) were then calculated for each concretion. The measurements were followed by descriptive observations including colour, structure, estimated mineralogical composition, presence of septarian structures, and the preservation state of paper-thin shells. Twenty-seven samples of concretions and twenty-eight samples of host sediments were selected (Text-fig. 2) to determine the mineralogical character-

istics. Qualitative analysis of mineralogical composition was obtained using X-ray powder diffraction (XRD Philips X Pert ADP PW 1830). Microscopic analysis under polarized light (Nikon Eclipse 6000 POL, ING UJ) and under a scanning microscope with BSE detector YAG type (HITACHI S-4700 with NORAN Vantage system) enabled the recognition of mineral composition and textural relationship between concretions and surrounding rocks, and the determination of the degree and character of alteration, which led to concretion formation. Particular attention has been paid to the morphology of the siderite grains, their distribution within concretions and chemical composition.



Text-fig. 1. Simplified geological map of the Częstochowa region (A – after Majewski 2000) and location of the Gnaszyn clay-pit (B – after Matyja and Wierzbowski 2003)



Text-fig. 2. The succession of claystones and mudstones exposed in the Gnaszyn clay-pit and sample positions (based on original drawing by P. Gedl). Ammonite zones based on Matyja and Wierzbowski (2006).

RESULTS

The host sediment

The host rocks are dark-grey claystone and light-grey mudstone beds, with varying degrees of bioturbation and no clearly visible sedimentary structures (e.g., no primary lamination for the most part), containing abundant and diverse organic detritus (faunal and floral). The mineralogical composition is rather constant throughout the succession, displaying a predominance of quartz and clay minerals (illite/muscovite and kaolinite) with subordinate amounts of

feldspar, calcite and pyrite (Text-fig. 3). In microscopic view, the sediments look similar in colour, texture and structure, wherein delicate lamination is sometimes visible in the claystones though only in microscopic view (Text-fig. 4A and B). The matrix consists of a mixture of clay minerals, iron oxides and organic matter, with densely packed detrital (quartz, feldspar, calcite, muscovite) and biogenic material (calcareous paper-thin shells, chips of wood; Text-fig. 4). The paper-thin shells are generally poorly preserved and strongly deformed mechanically. The presence of pyrite in both the claystones and mudstones is limited to associations with biogenic material as in-

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Symbol of level	Type of concretions	Abundance	Distribution	Shape*	A (m)	B (m)	C (m)	C/A (m)	Size**	V (m ³ ·10 ⁻²)
GnsA	Siderite	Abundant	Regular	Oval, clearly flattened vertically	0.33	0.29	0.13	0.39	medium	0.65
GnsB	Siderite	Abundant	Regular	Oval, clearly flattened vertically	0.39	0.36	0.18	0.46	big	1.32
GnsC	Phosphate-siderite	Abundant	Regular	Oval, clearly flattened vertically	0.48	0.43	0.18	0.38	big	1.95
GnsD	Siderite	Rare	Irregular	Oval, slightly flattened vertically	0.14	0.12	0.09	0.64	small	0.08
GnsE	Phosphate-siderite	Rate	Irregular	Oval, slightly flattened vertically	0.11	0.11	0.07	0.61	small	0.04
GnsF	Siderite	Abundant	Regular	Oval, clearly flattened vertically	0.49	0.48	0.18	0.37	big	2.22
GnsG	Siderite	Abundant	Regular	Oval, clearly flattened vertically	0.40	0.38	0.17	0.43	big	1.35
GnsH	Phosphate-siderite	Abundant	Regular	Oval, clearly flattened vertically	0.47	0.44	0.17	0.36	big	1.84
GnsI	Siderite	Abundant	Regular	Oval, clearly flattened vertically	0.36	0.27	0.15	0.42	medium	0.76
GnsJ	Siderite	Abundant	Regular	oval, slightly flattened vertically	0.14	0.12	0.08	0.57	small	0.07
GnsK	Siderite	Abundant	Regular	Oval, slightly flattened vertically	0.12	0.11	0.07	0.58	small	0.05

fillings (framboids, framboidal aggregates and/or euhedral grains) inside calcareous shells, bioturbation marks and fragments of wood. Sporadic pyrite occurrences are observed as dispersed euhedral grains between other mineral components of the sediment.

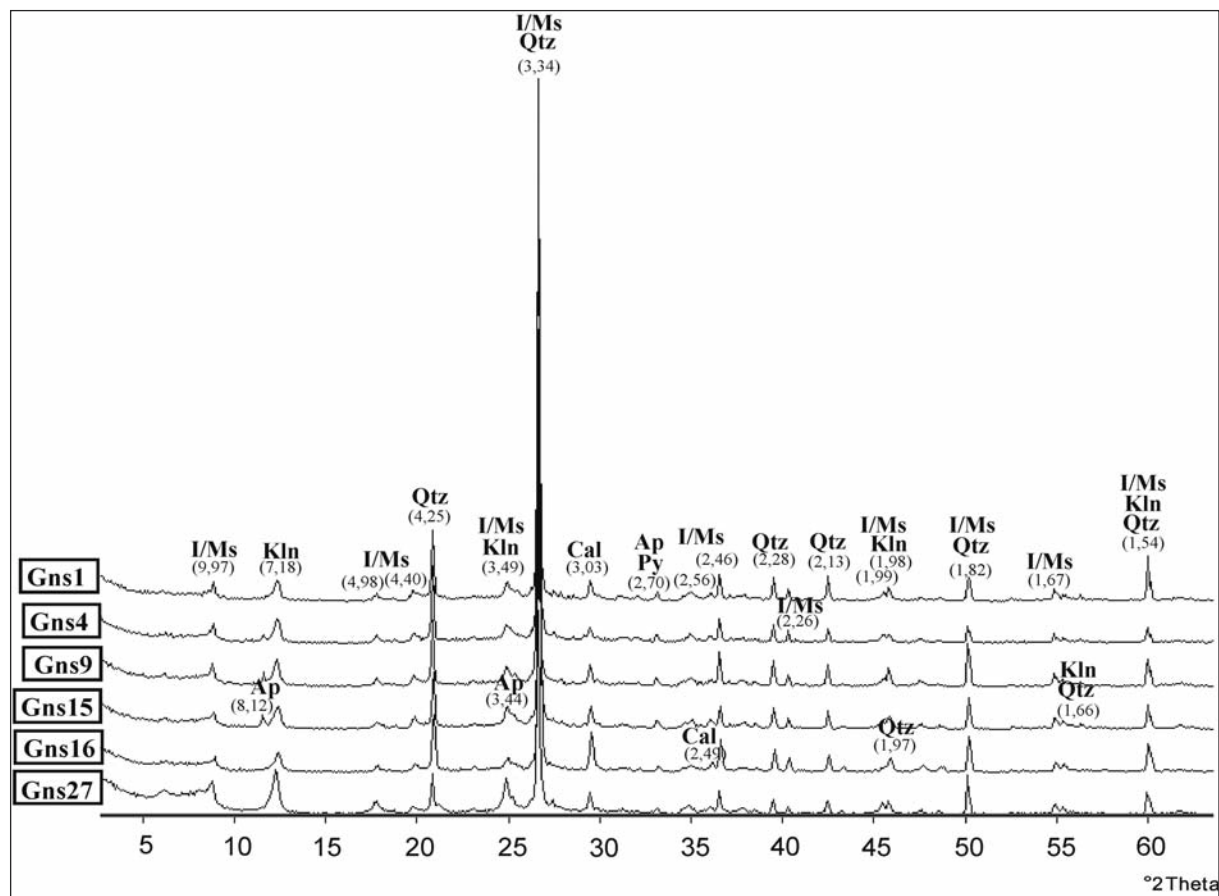
Iron carbonate concretions

The iron-carbonate rocks in the parts of the Cracow-Silesia Monocline investigated occur exclusively as concretions forming layers within claystone and mudstone beds of the ore-bearing clays. The horizons are irregularly vertically spaced within the succession. The shortest observed distance between two consecutive concretion layers is about one meter while the longest distance ranges up to several meters. The concretion horizons differ in concretion number, size and distribution within the layer. Generally the concretion levels have a wide lateral extent concordant with the bedding planes of the ambient strata. There are no other expressions of sideritic mineralization in the study area (e.g., continuous sideritic layers); however, there are irregular forms resulting from a coalescence of two or three concretions. The border between concretions and ambient rocks is sharp in all the levels examined and are easily distinguishable due to their distinctive light color, consistency, hardness and morphology. In some cases, bending of the claystone/mudstone laminae around a concretion is observed, especially in horizons where the concretions are distributed in spaces wider than 10 cm.

The external surface is similar in all of the concretions investigated; it is usually smooth and grey in colour. No bioturbation marks have been observed both on their external surface and inside the sideritic body. Each horizon is usually composed of concretions of similar shape and size. Based on measurements and shape, two main groups of concretions have been distinguished: (1) small and medium-sized, slightly flattened vertically, spheroidal and ellipsoidal, occurring mainly in the mudstone beds; and (2) medium to large-sized, clearly flattened vertically, ellipsoidal, typical of the claystone beds. The irregular bodies that occur at some levels result from the coalescence of two or three adjacent concretions.

The inner structure of some of the concretions is homogeneous and these are usually brownish-grey in

Table 1. Results of morphological and mineralogical study of iron carbonate concretions from Gnaszyn clay-pit. Concretion types determined on the basis of mineralogical characteristics; abundance and distribution on the basis of field observations, shape and size classified on the results of measurements of concretions (average for every concretionary horizons). Marks for: length-A; width-B, height-C and volume-V of the concretions (determination of the volume of the concretions based on the formula used by Dutton *et al.* 2000)



Text-fig. 3. Mineralogical composition of claystones and mudstones from Gnaszyn clay-pit. Exemplary X ray diffraction patterns of some selected samples. Markers for: Kln – kaolinite; I/Ms – illite/muscovite; Qtz – quartz; Cal – calcite; Ap – apatite, Py – pyrite

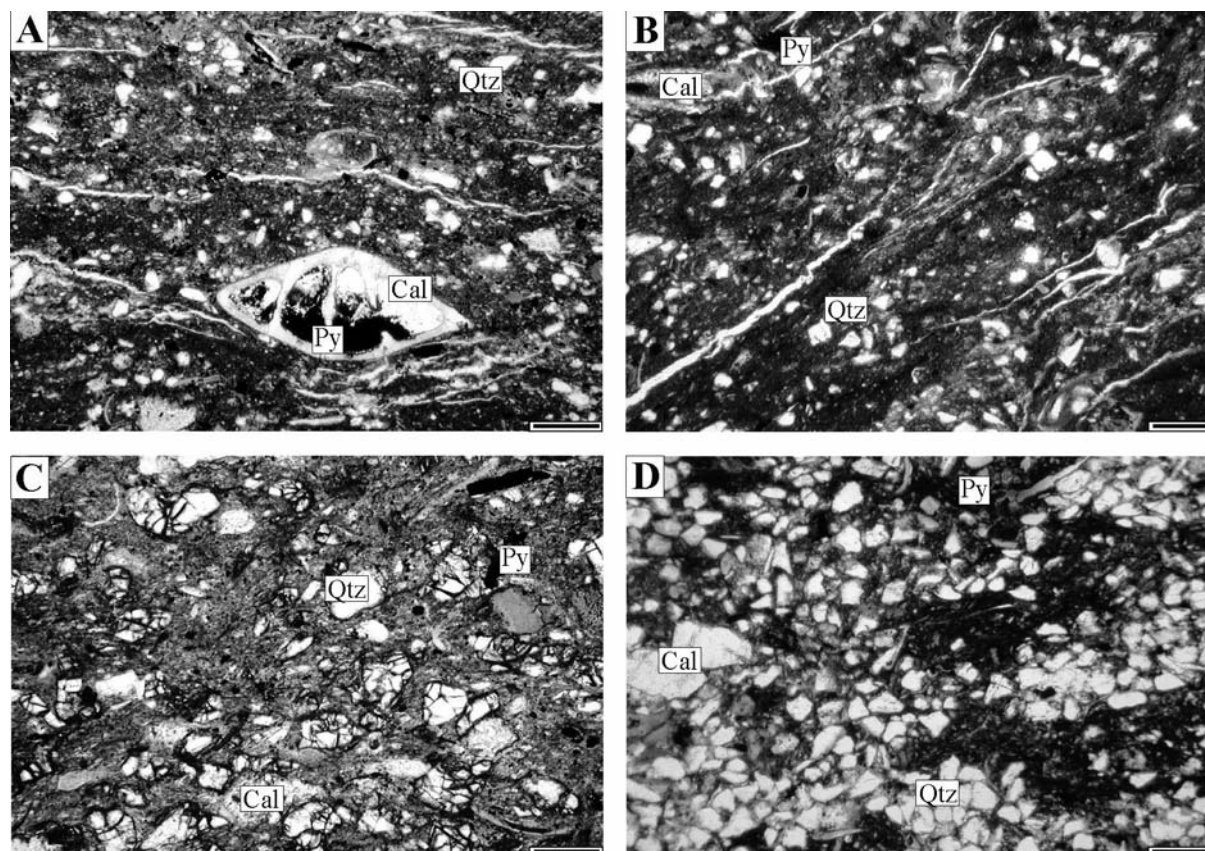
colour. Sometimes the concretions display two concentric layers varying in colour intensity. However, this does not reflect any significant difference in mineralogical composition (Text-fig. 5C). Some other concretions show an internal concentric zonation expressed by different colours, structure and mineral composition. The majority of the concretions have septarian structures developed inside their bodies that are invisible on their outer surfaces. As a rule, the concretions from the same horizon have septarian structures with cracks of similar morphology and fills of similar mineral composition. The cracks may occupy a variable volume within concretions (5 to 15%); similar proportions are usually observed in concretions from the same level but these may differ from those in concretions from other levels.

The majority of the concretions are composed predominantly of siderite (type I) and at three horizons of phosphate-siderite (type II). Detrital (quartz, feldspar, muscovite) and biogenic (calcareous) material and authigenic pyrite occur in the concretions as minor components. Examples of X-ray diffraction patterns of selected samples of siderite and phosphate-siderite

concretions are shown in Text-fig. 5C₁ and D₁ respectively. Concretions from the same level have a similar mineralogy and microstructure. In microscopic view, (polarized light) all the concretions have a similar yellow-brownish colour. Siderite concretions (type I) consist predominantly of siderite grains densely packed between sparse detrital grains of quartz, feldspar, muscovite, and calcareous shells (Text-fig. 6A–C). In the outer parts of some concretions, a slightly higher content of detrital quartz is observed.

The dominant morphological type of siderite is predominantly composed of xenomorphic grains – Sd₁ (5–10 µm in diameter); less common are fringes – Sd₂ (1–2 µm thickness) and idiomorphic grains – Sd₃ (1–10 µm in diameter), some of them elongated in one direction (Text-fig. 7). The idiomorphic grains occur very occasionally in the concretions, and commonly in association with calcite grains. Generally, the xenomorphic grains are well-preserved, with no traces of dissolution or replacement by other minerals. Individual grains are generally densely packed. The results of chemical analysis of different morphological forms

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Text-fig. 4. Microscopic view of dark grey claystones (A – sample Gns9; B – sample Gns15) and light grey mudstones (C – sample Gns27; D – sample Gns30) from Gnaszyn clay-pit. In claystones (Fig.4A and B) delicate lamination visible only in microscopic view. The background matrix of the claystones and mudstones consists of a mixture of clay minerals, iron oxides and organic matter. Between them occur grains of calcite (also calcareous shell), quartz, feldspars and micas. Markers for: Cal – calcite; Py – pyrite, Qtz – quartz. Scale bar for all photos – 50 μm

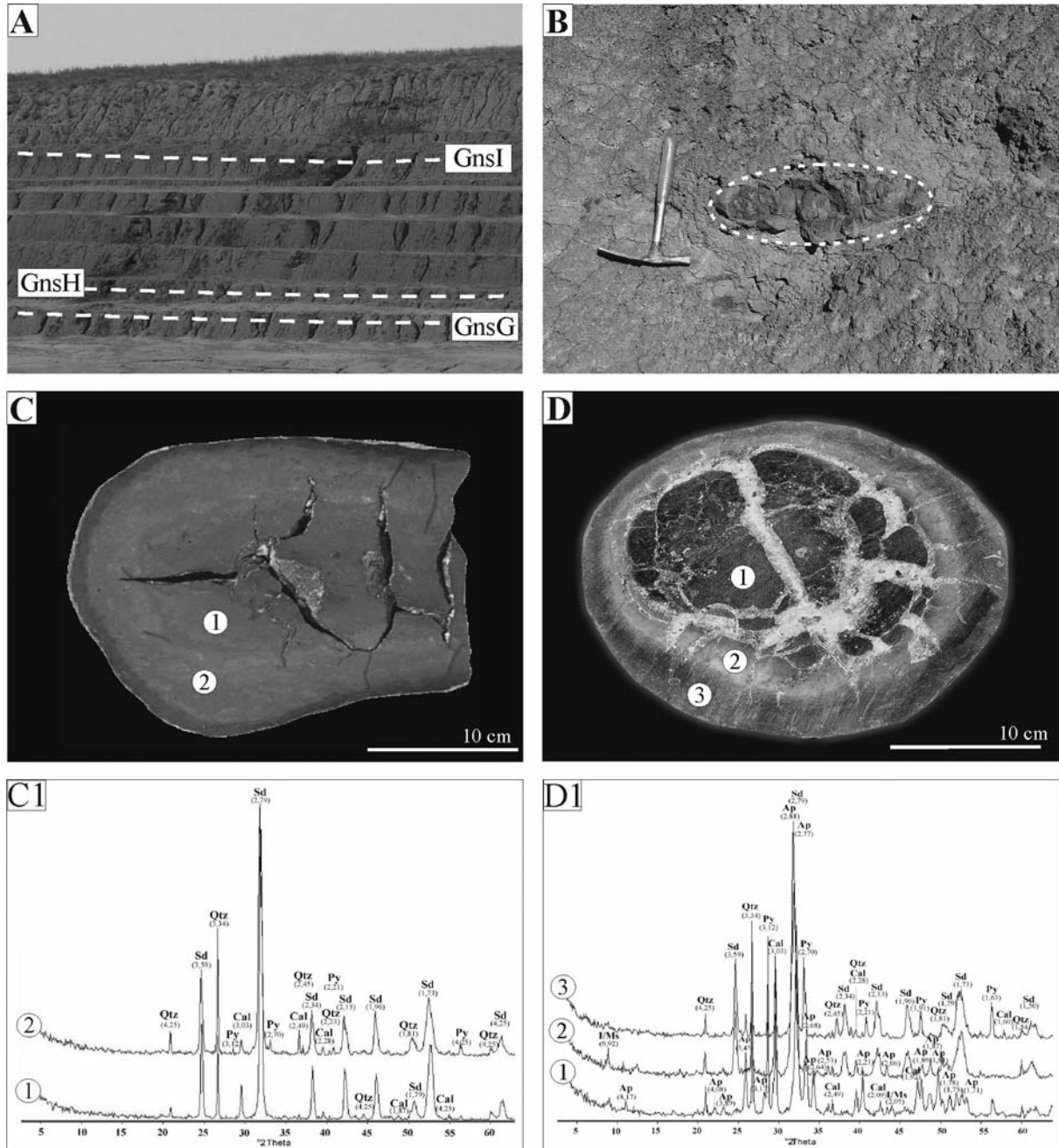
of siderite are presented in Table 2. Detrital quartz occurs as irregular and individual xenomorphic grains. Its content increases slightly from the inner to the outer parts of the concretions. The quartz grains are 20–150 μm in diameter and are rather weakly rounded. The grains are well preserved, with smooth surfaces, and are neither cracked nor do they show any signs of replacement or dissolution by siderite and other minerals. Single grains of feldspar (orthoclase) occur sporadically as rather small grains, 10–60 μm in diameter. They vary from well-preserved grains to highly weathered and cracked ones. The composition of the detrital components is similar to that in the surrounding rocks but they differ in both their quantities and state of preservation. Calcite is a main component of invertebrate skeletons and also occurs less commonly in the form of xenomorphic grains, 10–90 μm in diameter. Calcareous shells are not very abundant in the concretions. The size of the shells may vary from 15 to 200 μm in diameter. Delicate paper-thin shells are intact and generally well preserved, with no significant

compactional deformation. Pyrite occurs only in small amounts in the concretions, being much less abundant here than in the host sediment. In concretions, it typically fills and, in some cases, envelopes calcareous shells of microfossils. Three morphological types of pyrite have been observed: 1) framboids (5–25 μm in diameter); 2) framboidal aggregates (<1–2 μm in diameter); and 3) euhedral grains (5–10 μm in diameter). In general, there is no clear relationship between siderite and pyrite in the concretions (neither replacements nor dissolutions). Additionally, very small amounts of pyrite were found among the siderite grains predominantly in the form of euhedral grains (3–15 μm in diameter).

The dominant component of the inner part of the phosphate-siderite concretions (type II) is a cryptocrystalline mineral close to apatite (Text-fig. 6D). Within this part, numerous calcareous shells (40–200 μm in diameter) with associated idiomorphic pyrite are loosely distributed. Calcareous shells are generally replaced by apatite. Besides calcite, some detrital

grains of quartz, feldspar, and muscovite occur within these zones. The boundary between the inner and intermediate zones of these concretions is clearly defined by different structures and mineral composition. Septarian structures occur exclusively in the inner part. The intermediate zone is characterized by rather micritic structure and consists of xenomorphic apatite grains (1–5 μm in diameter), rounded by siderite

fringes (1–2 μm in thickness). Calcareous shells are occasionally replaced by apatite. The shells are not so abundant as in the inner zone. Detrital components (quartz, feldspar, and muscovite) are present as accessories. The outer zone has microsparitic structure, with xenomorphic siderite as the dominant mineral. Such xenomorphic grains most probably occupy voids after apatite grains (Text-fig. 6F). The siderite grains are 3–



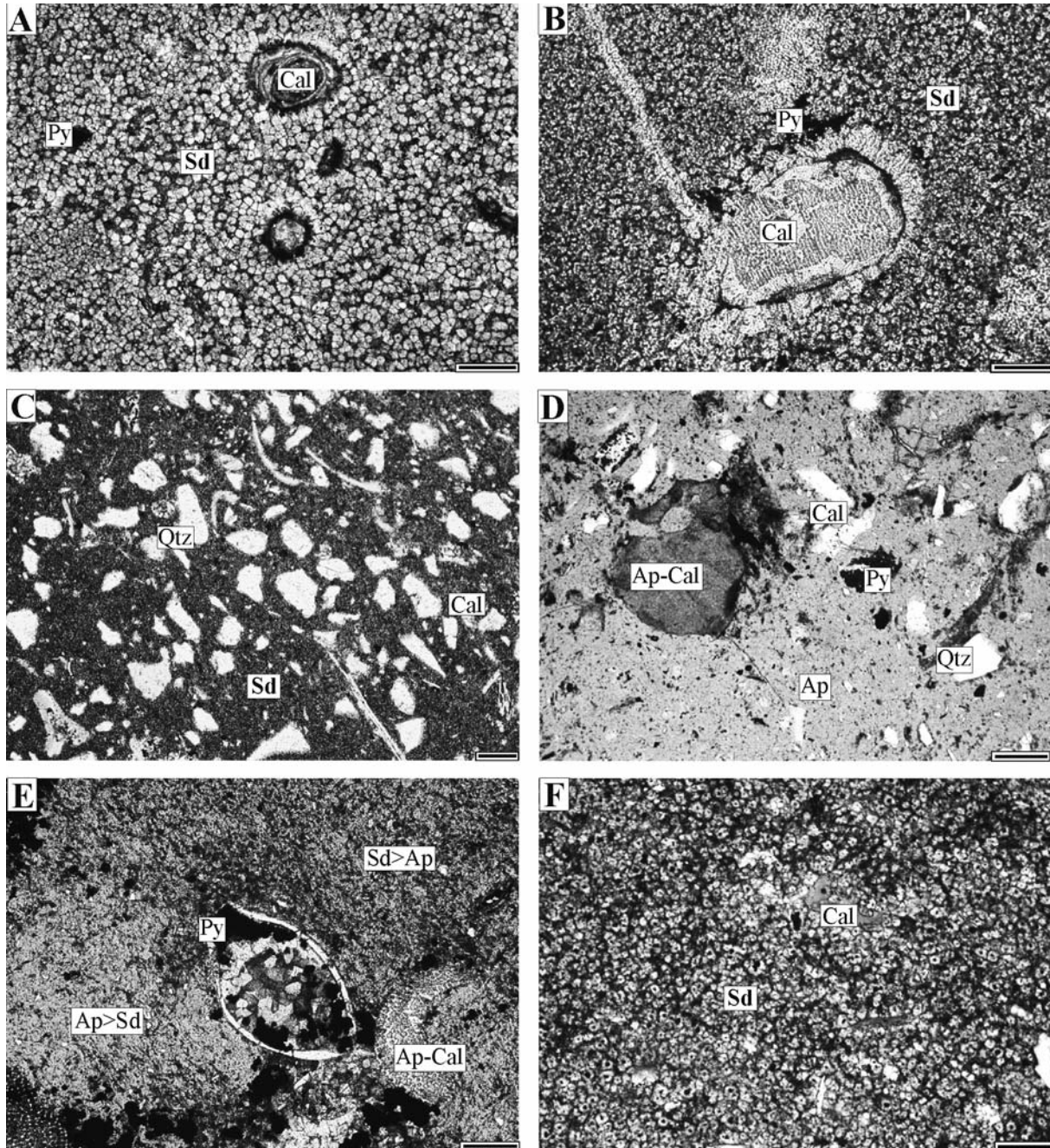
Text-fig. 5. Iron carbonate concretions from Gnaszyn clay-pit. **A** – lower part of Gnaszyn I section with three levels with iron carbonate concretions indicated (photo by P. Gedl); **B** – siderite concretion from the GnsG horizon (Gnaszyn B section); **C** – macroscopic view of fragment of siderite concretion derived from the GnsF horizon (Gnaszyn A section) and **C1** – X ray diffraction patterns of two selected samples from this concretion **D** – macroscopic view of phosphate-siderite concretion from GnsH horizon (Gnaszyn B section) and **D1** – X ray diffraction patterns of three selected samples from this concretion

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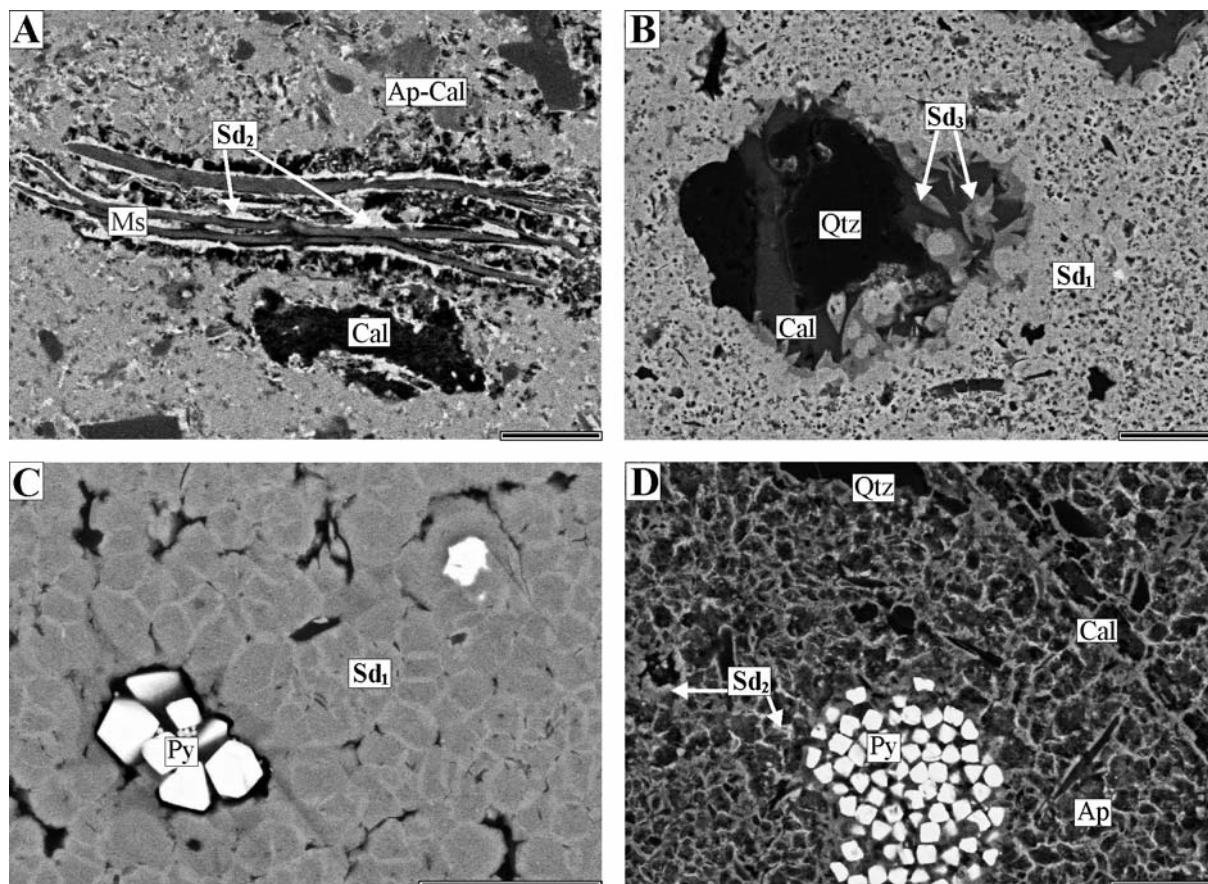
8 μm in diameter. No siderite fringes were observed here, whereas idiomorphic siderite grains, 1–7 μm in diameter, occur sporadically. The outer zone is similar to that of the siderite concretions in respect of its internal structure.

Generally, the apatite content within the phosphate-siderite concretions decreases with increasing amounts

of siderite. The former dominates in the inner part, being less common towards the outer zone. An opposite trend is observed for the biogenic material (i.e., calcareous shells). Also observed are changes in the state of preservation of this material: calcareous shells replaced by apatite predominate in the inner part of the concretions and also occur sporadically in the inter-



Text-fig. 6. Characteristic microstructure (polarized light) of siderite (A–C) and phosphate-siderite (D–F) concretions. The matrix of the siderite concretions consists of fine-grained siderite. Between the siderite grains occur single calcareous shells, quartz, feldspars and micas. The background of the phosphate-siderite concretions consists mainly of apatite (the inner zone-D), predominantly of siderite with apatite (the intermediate zone-E) and mainly of siderite (the outer zone-F). Markers for: Sd – siderite; Qtz – quartz; Cal – calcite; Py – pyrite, Ap-apatite, Ap-Cal – phosphatized calcite (shell), Sd>Ap – more siderite than apatite. Scale bar – 20 μm



Text-fig. 7. BSEM image of different morphological forms of siderite: xenomorphic grains – Sd₁ (from phosphate-siderite concretions-B and from siderite concretions- C); fringes – Sd₂ (from phosphate-siderite concretions-A, D) and idiomorphic grains - Sd₃ (from phosphate-siderite concretions-B). Other markers for: Ap-apatite, Cal – calcite, Ap-Cal – phosphatized calcite (shell), Ms-muscovite, Py – pyrite, Qtz – quartz; Scale bar – 20 μm

mediate zone; in the outer zone, the shells are well preserved, with no apatite replacement. The pyrite content is insignificant and shows a rather equal distribution in all three zones of the phosphate-siderite concretions. The content of detrital grains does not increase from the inner to the outer part of the concretions.

The predominant morphological type of siderite in the inner and intermediate parts of the phosphate-siderite concretions are fringes (Sd₂ on Text-fig. 7A,

D), 1–2 μm thick, occurring between other minerals. In the outer zone, both xenomorphic (Sd₁) and idiomorphic grains (Sd₃ on Text-fig. 7B) are observed, similar to those in the siderite concretions (type I). Generally, neither dissolution nor replacement traces of detrital or calcareous shells by siderite have been observed. The relationships between the morphological types of siderite cements and chemical composition are presented in Table 2.

Type of concretions		Characteristic morphological forms of siderite	Chemical composition			
			FeCO ₃	CaCO ₃	MgCO ₃	MnCO ₃
Siderite concretions		xenomorphic grains- Sd ₁	0,80-0,86	0,09-0,12	0,05-0,08	0,00-0,01
		idiomorphic grains- Sd ₂	0,72-0,75	0,12-0,15	0,11-0,12	0,01
		fringes- Sd ₃	0,85-0,90	0,07-0,09	0,03-0,06	0,00-0,01
Phosphate-siderite concretions	Inner zone	fringes- Sd ₃	0,78-0,82	0,09-0,16	0,05-0,09	0,00-0,01
	Intermediate zone	fringes- Sd ₃	0,81-0,84	0,12-0,09	0,60-0,70	0,00
	Outer zone	xenomorphic grains- Sd ₁	0,82-0,85	0,08-0,14	0,04-0,07	0,00-0,01
		idiomorphic grains- Sd ₂	0,65-0,69	0,15-0,21	0,12-0,15	0,01-0,02
		fringes- Sd ₃	0,81-0,84	0,08-0,12	0,07-0,08	0,01

Table 2. Relation between morphological type of siderite cements and their chemical composition in distinguished types of iron siderite concretions distinguished

DISCUSSION

The occurrence pattern of the iron carbonate concretions

The iron carbonate rocks in the Kraków-Silesia Monocline occur exclusively as single concretion horizons within ore-bearing clays. The concretions from different levels generally represent the same genetic type, with similar morphology, mineral composition, septarian crack system and crack infilling pattern. This suggests that concretions from the same horizon formed simultaneously and that the conditions of their formation were occurring repeatedly. It seems that similar physicochemical conditions obtained during the formation of the concretions. In the majority of horizons siderite concretions (type I) predominate and only at a few levels do phosphate-siderite concretions (type II) occur. The occurrence of concretionary horizons is not correlated with any lithological type of the host rock; similar concretions are present in both the dark grey claystones and the light grey mudstones. The concretionary horizons are not enriched in organic matter, organic detritus, neither do they show any increased accumulation of calcareous shells. Sedimentological and palaeontological data (Gedl *et al.* 2006) indicate that the concretionary horizons are more bioturbated and are characterized by a higher diversity of both planktonic and benthic organisms. The occurrence of iron carbonate concretions is correlated with lower sedimentation rate of the host sediments and much better oxygenation of the bottom waters.

Both the morphology of the concretions and their arrangement in laterally extensive horizons, concordant with the bedding planes of the surrounding strata suggest that the sideritic rocks formed under a cover of overlying sediment causing mechanical compaction. The preferential occurrence of concretionary horizons could be related to greater porosity and higher permeability of the host sediments than those of the sediments in which concretions do not occur. The formation of concretionary horizons is mostly related to the arresting of pore waters expelled from the underlying sediments by the mechanical compaction of overlying sediment (Raiswell 1971; Raiswell and White 1978, Sells-Martinez 1996, Lash and Blood 2004a). The concretionary horizons probably reflect the preferred pathways for pore waters, from which conditions of high availability of reduced iron (Fe^{2+}) and a high concentration of bicarbonates (HCO_3^-) caused supersaturation in respect to siderite.

The morphology of the concretions reflects the primary permeability pattern of the hosting rocks dur-

ing formation of the carbonate body (e.g. Raiswell 1971; de Craen *et al.* 1999; Hounslow 1998; Seilacher 2001). More rounded concretions show nearly identical (in horizontal and vertical direction) permeability of the host rocks. The formation of these concretions took place immediately before or at a very early stage of mechanical compaction and was initiated at a very shallow depth within the sediment column. On the other hand, the oval concretions, slightly or significantly flattened vertically, reflect more or less anisotropic permeability of the host rock. The concretions demonstrate this property of the host sediment by preferential growth in the bedding plane. The growth of oval concretions occurred slightly deeper in the sediment column (compared to that of the rounded concretions), but still at a very early stage of mechanical compaction of the sediment.

Evidences of early formation of the concretions

Enhancement of the textural difference between concretions and surrounding sediment resulted in the presence of bioturbation marks, porosity difference, state of preservation of calcareous shells, occurrence of pyrite, deformation of sediment laminae around concretions and occurrence of septarian structure inside concretions- allow to determine the relative time of concretion growth (Raiswell 1971, 1976, 1987; Oertel and Curtis 1972; Matsumoto and Iijama 1981; Gautier 1982; Coleman and Raiswell 1995; Raiswell and Fisher 2000; 2004). The lack of the indications of mechanical compaction in the concretions that are clearly visible in the hosting strata, suggests that the growth of the concretions started very early after burial of the sediment and preceded or was initiated at an early stage of mechanical compaction (Raiswell and Fisher 2000). Additionally, the occurrence of a card-house clay grain microfabric preserved within concretions is very good evidence of concretion growth prior to compaction (Lash and Blood 2004b).

The occurrence of concretionary horizons close to more intensively bioturbated layers of claystone and mudstone could indicate that concretion formation took place at a very shallow depth below the sea floor. However, the lack of the evidence of bioturbation, both on the external surface of the concretions and within the concretion matrix, that is common in the hosting sediments suggests that the formation of the concretions could have taken place just below the bioturbated zone. In oxic marine sediments this zone extends usually up to 10 cm below the sea floor (Wignall 1994). It is worth noting, however, that at some levels (e.g. A₂ and B) of the siliciclastic sediments at Gnaszyn Gedl *et al.*

(2006) reported vertical traces reaching 15–20 cm in length. The lack of primary structures (i.e., layering) preserved by the concretions may also suggest that the sediment had been bioturbated prior to concretion formation. The signs of bioturbation within the calcite concretions prevalent in the Gnaszyn clay-pit were noted by Majewski (2000) and Zatoń *et al.* (2009).

A high content of siderite in the concretions reflects a low amount of detrital grains and calcareous shells. Moreover, there are no signs of replacements of other minerals by siderite, which indicates high effective porosity of the host sediment during formation of the siderite concretions. This strongly suggests that growth of the concretions began during shallow burial of the host sediment, probably in the first meters of the sediment column. The primary porosity in freshly deposited fine-grained sediment is high (80–90% of the volume) and after shallow burial (to about ten meters in the sediment column) the porosity decreases significantly (to about 55%) due to compaction. In deeper buried rocks (a few hundred meters) further decrease in porosity is less pronounced (reaching about 30%) (Raiswell 1971). The mechanical compaction in the concretionary horizons is evidenced by dense packing of the detrital clasts and calcareous fossils, which are commonly cracked or crushed (especially the thin-shelled fauna). The detrital grains and calcareous shells in the iron carbonate concretions are weakly packed and they are usually siderite matrix supported. This also facilitates better preservation of fossils in the concretions than in the host sediment. The much better state of preservation of calcareous shells in the concretions compared to in the host sediment and the bending of laminae of host sediment layers around concretions suggest that concretionary growth preceded mechanical compaction of the host sediment layers. The bending of the laminae converging along the main concretion axis (which is visible in some concretion levels) proves that the concretions were already well cemented during mechanical compaction unlike the ambient siliciclastics (Raiswell 1971; Raiswell and Fisher 2000, 2004; Lash and Blood 2004a). It also strongly suggests that formation of the concretions took place before or at an early stage of compaction. The occurrence of septarian structures within the concretions could be evidence that the beginning of concretionary formation took place in a shallow burial environment (e.g. Raiswell 1971; Hasselbo and Palmer 1992; Wetzel 1992; Raiswell and Fisher 2000). The similar spatial distribution of pyrite, in the same morphological forms, both in the concretions and in the host sediment indicates that pyritization of the biogenic material in the host sediment formed in both types of rocks simultaneously. The study of Szczepanik *et al.*

(2006) suggests an early diagenetic origin of the pyrite in the host sediment. According to these authors, pyrite formation in the ore-bearing clays was independent from the geochemistry of the ambient sediments but relied solely on decomposing organic matter in fossil remains generating a local microenvironment. Therefore, it seems that pyritization of the organic remains in the surrounding sediment preceded the precipitation of siderite into iron carbonate concretions. The diminished amounts of pyrite in the concretions—when compared to the ambient rocks—correlates positively with lower amounts of fossil remains in the concretions. Nevertheless, it may also indicate conditions less favorable for pyrite formation in the concretion layers than in the other parts of the succession. The siderite is present only in the concretions and generally absent in the surrounding sediment.

Mechanisms of concretion formation

Siderite concretions (type I) are the predominant type of iron carbonate concretions in Gnaszyn. The uniform mineral composition reflects the homogeneous internal structure of these concretions and suggests that their formation took place under uniform physicochemical conditions. The pattern of siderite distribution in the concretion body, its morphological form and the lack of any evidence of siderite substituting other minerals, suggest that siderite precipitated in the spaces between the sediment grains and the calcareous fossil remains evenly throughout the entire concretion body.

The xenomorphic morphology and small size of the grains of the main siderite phase (Sd_1) indicates rather fast precipitation of the mineral from pore waters supersaturated by $FeCO_3$. In such condition the concretion formation was most probably initiated by simultaneous, rapid nucleation and growth of the nucleus. This process apparently consumed the majority of the available siderite resulting in the fine-grained appearance of the sideritic rock. Some idiomorphic grains of siderite (Sd_2) occur in the spaces between the xenomorphic grains (Sd_1), indicating their secondary origin. The textural evidence in the siderite concretions (manifested by the uniform distribution of siderite grains- Sd_1 , Sd_2 within the volume space of the concretion) can indicate their pervasive growth model. Pervasive growth of carbonate concretions starts with simultaneous nucleation and precipitation of isolated carbonate crystals within the host sediment (Raiswell and Fisher 2000).

The difference in the mineral composition of the phosphate-siderite concretions (type II) (characterized

by an increase in the amount of siderite along with a decreasing amount of apatite) and in the structure of the concretions (decreasing amount of calcareous material and its different state of preservation) towards the concretion edge indicate a distinct concentric growth model compared to the growth model of the siderite concretions. The concentric growth of the concretions suggests successive addition of different layers of cement to the outer part of the growing concretion (Mozley 1996; Raiswell and Fisher 2000). This indicates that growth of the phosphate-siderite concretions (type II) was gradual and had been initiated by phosphatization of the calcareous shells that frequently occur in the inner zone of concretions, followed by precipitation of apatite around other mineral particles in the inner and intermediate zone of concretions and then continued by precipitation of siderite. The textural relationships indicate that precipitation of siderite occurred in the outer zone of the concretions and had been preceded by formation of apatite in the inner and intermediate zones. A similar mode of occurrence and distribution of xenomorphic (Sd_1) and idiomorphic (Sd_2) siderite grains in the siderite concretions and in the outer zone of the phosphate-siderite concretions suggests an analogous cementation process.

The chemical composition of the same morphological form of siderite in the siderite concretions (type I) and phosphate-siderite concretions (type II) is similar. The differentiation of different morphological forms of siderite (xenomorphic grains - Sd_1 , idiomorphic grains - Sd_2 , fringes- Sd_3) is a reflection of their slightly different chemical composition. Each recognized morphology contains a slightly different but generally high contribution of $FeCO_3$ in comparison to $CaCO_3$ and $MgCO_3$. The concentration of $FeCO_3$ in all siderite types is invariably high but does not exceed 0.9 mol. The highest enrichment of $FeCO_3$ in relation to $CaCO_3$ and $MgCO_3$ are observed in the fringes (Sd_3), the intermediate values in the xenomorphic grains (Sd_1) and the lowest in the idiomorphic grains (Sd_2). All three siderite phases contain very little admixture of $MnCO_3$ (0.02 mol). The chemical composition of the sideritic rock reflects the condition of its precipitation and enables discussion of its origin (Matsumoto and Iijama 1981; Pye, 1984; Curtis and Coleman 1986; Mozley and Carothers 1992). Siderite occurring in marine sediments differs from fresh-water siderite in lesser (<0.9 mol.) enrichment in $FeCO_3$, slightly higher concentrations of $CaCO_3$ and $MgCO_3$ and rather small (less than 0.02 mol.) amounts of $MnCO_3$ (Mozley 1989; Mozley and Carothers 1992). The chemical composition of the siderite in iron carbonate concretions indicates its marine origin.

Palaeoenvironmental conditions of the concretion formation

The sedimentological, palaeontological (Gedl *et al.* 2006) and geochemical (Szczepanik *et al.* 2007; Marynowski *et al.* 2007; Wierzbowski and Joachimskiego 2007; Zatoń *et al.* 2009) data indicate that deposition of the siliciclastic sediments of the ore-bearing clays at Gnaszyn took place in marine conditions evoked by fluctuating conditions of deposition. The iron carbonate concretionary horizons are correlated with lower sedimentation rate of the surrounding sediments and much better oxygenation of the bottom waters. The concretion-hosting beds are more bioturbated and are characterized by a higher diversity in both plankton and benthos (Gedl *et al.* 2006).

The occurrence of siderite in the form of concretions, concentrated in single beds within the ore-bearing clays at Gnaszyn, and the fact that siderite is generally absent in the host sediments suggest that the formation of the iron carbonate concretions in the study area was related to specific physicochemical conditions during deposition and early diagenesis of the sediment. The presence of siderite indicates anoxic conditions (Gautier and Claypool 1984; Spears 1989) during their formation. The siderite concentrations in fine-grained rocks (e.g. claystone and mudstone) usually occur in early stages of diagenesis (Coleman 1985, 1993; Pye *et al.* 1990). In marine sediments (in comparison to fresh-water), the occurrence of siderite is restricted (because of the stronger affinity of Fe^{2+} for HS^- ions rather than HCO_3^- ions) and depends strictly on thermodynamic controls (Maynard, 1982). Generally, the stability of siderite under organic-rich, anaerobic conditions is characterized by a high concentration of dissolved iron (Fe^{2+}) and bicarbonates (HCO_3^-), with a low dissolved sulphide (HS^-) concentration (Curtis and Spears 1968; Coleman 1985; Curtis *et al.* 1986; Rajan *et al.* 1996). The precipitation of this mineral is generally possible in two diagenetic environments: in post-oxic (suboxic) conditions (through microbial reduction of organic matter); and in the zone of methanogenesis (through the combined effect of iron reduction with bacterial methanogenesis of organic matter (Maynard 1983; Curtis *et al.* 1986; Coleman 1985, 1994).

The chemical composition of the siderite in the iron carbonate concretions suggests a marine origin. The oxic conditions during deposition of the claystone and mudstone beds of the Gnaszyn succession, expressed by high concentrations of oxygen (positive Eh) and dissolved sulphates (SO_4^{2-}) in the water column and at the bottom, preclude direct precipitation of the siderite

from the sea water and indicate its formation from pore waters of the host sediment during early diagenesis. The occurrence of siderite in the concretions suggests a high availability of reduced iron (Fe^{2+}). The main source of this element and of the bicarbonates (HCO_3^-) was most probably microbial reduction of iron oxides (Fe^{3+}). These minerals are stable in oxic conditions but could be reduced to (Fe^{2+}) by microbial decomposition of organic matter in the iron reduction zone (Canfield 1989; Canfield *et al.* 1993; Coleman 1985; 1993). Moreover, the lower amount of pyrite in the siderite concretions compared to the surrounding sediment could indicate that iron reduction exceeded sulphate reduction. The precipitation of siderite is possible in conditions where iron reduction is more active than sulphate reduction (Coleman 1985; Pye *et al.* 1990). The results presented above support the earlier conclusions of Witkowska (2005) that the siderite in the concretions from the ore-bearing clays from the Cześćochowa vicinity is of organic origin.

Precipitation of apatite in organic-rich sediments is usually restricted to the uppermost part (few cm) of the sediment column. However, increasing concentration of bicarbonate (HCO_3^-) may reduce the depths of apatite precipitation, prohibiting further formation of this mineral (Jahnke *et al.* 1983; Jarvis *et al.* 1994; Krajewski *et al.* 1994). The stability field of apatite is generally independent of Eh and depends primarily upon pH conditions. The optimal conditions of apatite precipitation in marine sediments are in anaerobic environments with neutral to slightly alkaline pH values (Krambein and Garrels 1953; Froelich *et al.* 1988). The presence of apatite in the inner part of the phosphate-siderite concretions (type II) is related to the occurrence of calcareous shells in which apatite replaces calcite. Phosphatization of calcareous material is one of the earliest diagenetic processes in marine sediment rich in calcareous shells (Briggs and Kear 1994). Calcium carbonate surfaces favor apatite precipitation in marine sediments (de Kanel and Morse 1978). The mechanism of phosphatization is connected with microbial mineralization of organic matter. As a result of this process phosphates are released to the pore waters of the sediment. In consequence, pH decreases, causing dissolution of calcium carbonate and replacement of the carbonate ions by phosphates in the structure of the calcite. This mechanism leads to the preservation of the external shape of primarily calcite shells (Lucas and Prevost 1991). The lack of similar evidence of phosphatization in the outer parts of the phosphate-siderite concretions and the observed increase in siderite content associated with a decrease in apatite content in the phosphate-siderite concretions (type II)

seem to be caused by an increase in pH in anaerobic conditions. An increase in carbonate alkalinity as a result of microbial mineralization of organic matter in the sediment column promoted siderite precipitation after the formation of apatite.

From the viewpoint of physicochemical conditions, the spatially extensive levels with the iron carbonate concretions could reflect the position of the redox zone between the oxic, bioturbated surface zone and the deeper anoxic, non-bioturbated zone. The conditions favouring formation of the concretions in this zone could have remained stable at a time when the sedimentation rate had been significantly decreased. Typically, the redox zone in normal marine sediments is localized on or somewhat below the water/sediment interface. This zone is not fixed, and can migrate over time due to variable input of organic matter to the sea bottom or to variable oxygenation of the bottom waters (Katsev *et al.* 2006). The slower sedimentation rate during formation of the concretion-bearing layers contributed to more oxic conditions which immobilized the redox boundary deeper in the sediment column for a longer period of time. In addition, more intense bioturbation contributed to an increase in the concentration of reactive iron (Fe^{3+}) in the concretion-bearing layers of sediment. The occurrence of iron carbonate concretion horizons in the study area was most probably related to the greater supply of this component (reactive iron) during deposition and intense iron reduction during early diagenesis. Microbial iron reduction caused mobilization of reduced iron (Fe^{2+}) along the redox zone in the siliciclastics of the Cześćochowa ore-bearing clays and promoted formation of the iron carbonate concretions just below it.

The formation of such extensive concretion layers was certainly possible in the Gnaszyn succession due to a slow sedimentation rate during the periods of siderite precipitation. The rate of deposition in marine sediments has a strong influence on the rate of early diagenetic processes in that environment (Taylor and Macquarker 2000). At low rates of sediment burial, sediment residence time in early diagenetic zones is high, thereby resulting in greater intensity of early diagenetic reactions (e.g. enhanced production of bicarbonate resulting from microbial mineralization of organic matter), and consequently may lead to enhanced localized carbonate cementation in the form of concretions (e.g. Berner 1980; Raiswell 1987; Spears, 1989; Coleman 1985, 1993). Furthermore, the rate of deposition controls the availability of organic matter, reactive iron (Fe^{3+}) and sulphates (SO_4^{2-}). It affects in that way the presence or absence of early diagenetic

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minerals like siderite or pyrite (Goldhaber and Kaplan 1974; Coleman 1985, 1993; Maynard 1983). Slow deposition of the host sediment was responsible for its longer exposure to the oxygenated water column and favored more intense bioturbation and expansion of the oxygenated zone downward in the sediment column. It could have caused immobilization of the redox boundary deeper in the sediment column for a longer period of time. Additionally, intense bioturbation redistributed organic matter and reactive iron (Fe^{3+}) and favored their greater availability slightly deeper in the sediment column. Bioturbation may result in the redistribution of sediment components from deeper layers (for example, less reactive organic matter and iron sulphides) to shallower portions of the sediment column (for example, more reactive organic matter and iron Fe^{3+}), where they can be reduced (Aller 1994; Thamdrup *et al.* 2000). In this regard, the occurrence of iron carbonate concretion horizons in the study area could be related to a higher concentration of reactive iron (Fe^{3+}) created during the early diagenesis conditions favoring siderite precipitation as a result of sediment pore waters supersaturation, generated by microbial mineralization of organic matter with iron reduction below the zone of bioturbation.

CONCLUSIONS

- The iron carbonate rocks in the Częstochowa ore-bearing clays occur exclusively as siderite or apatite-siderite concretions distributed in distinctive horizons of wide geographical extent.
- Precipitation of concretionary cement in organic-rich layers took place simultaneously at certain levels on numerous nuclei dispersed in the host sediments.
- The localization, mode of occurrence, textural relationship between concretions and host sediments and the mineralogy of the iron carbonate concretions suggest an early diagenetic origin of the concretions.
- The concretions formed in anoxic conditions within the sediment, characterized by a high availability of reduced iron and a high concentration of bicarbonate ions, which probably originated from microbial reduction of iron and organic matter mineralization.
- The horizons with iron carbonate concretions are related to different physicochemical conditions during deposition and the early diagenesis of the ambient rocks.
- The concretionary horizons reflect localization of the redox zone between the bioturbated and oxygenated surface zone and the non-bioturbated deeper

anaerobic zone. Conditions favoring the formation of concretions in this zone remained in place because of a decreased sedimentation rate.

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