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SIDERITE CONCRETIONS IN PALEOCENE SERIES OF POLISH PART OF THE EASTERN FLYSCH CARPATHIANS

Abstract. The present paper deals with the results of studies of siderite concretions occurring in black Paleocene shales of the Dukla and Silesian Units. The samples were examined using optical and scanning microscopy, X-ray diffraction and chemical analysis (SEM-EDS, INNA, ICP and estimation of TOC). The main diagenetic minerals of these concretions are iron carbonates close to siderite. Less common are dolomite, ferrous dolomite and calcite. The first phases precipitated from pore solutions were carbonates enriched in manganese. The concretions studied contain up to 49.15 wt.% Fe_2O_3, at most 16.46 wt.% CaO and up to 8.49 wt.% MgO, whereas the content of organic carbon (TOC) is at most 1.42 wt.%. Sideritic concretions of Paleocene beds of the eastern part of the Flysch Carpathians represent, in fact, sideroplesites and manganospherites of early diagenetic origin. They are, in general, impoverished in all trace elements, except Sr, when compared with shales embedding them. The siderite-bearing series in question can be assigned to the siderite-pyrite and siderite geochemical facies.

Key-words: siderite concretions, Flysch Carpathians, diagenesis

INTRODUCTION

Siderite concretions are fairly common in the Flysch Carpathians and some their occurrences were reported already by Pusch (1836) in his Atlas. The formation of these concretions was related to specific conditions of sedimentation and diagenesis in geosynclinal basin as noticed by Narębski (1956, 1957), who examined in detail numerous occurrences of carbonate concretions and published pioneer papers on geochemical aspects of their origin in the Outer Carpathians. This problem was also studied by Gucwa and Wieser (1978), Muszyński et al. (1979), Rajchel and Szczepańska (1997) and Szczepańska (1998). These papers were referring mainly to carbonate concretions in the Skole Unit and other local occurrences. Narębski (1956) was the first to indicate ferrous dolomitic nature of concretions from Menilite (near Komańcza) and Transition Beds (near Wetlina) of the Dukla Unit. Thus, the current paper can be considered as supplementary to the mentioned publications.

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The present studies refer to the concretions occurring in Paleocene black shales of the Dukla and Silesian Units, called Majdan Beds and Upper Istebna Beds, respectively. These series were examined in detail by Ślączka (1958, 1971).

The concretions in black shales are lenticular in shape or occur as fairly continuous layers, 3–8 cm thick. Because of their hardness they often protrude from parent shales what facilitates their finding.

MATERIALS AND METHODS

The concretions examined show micritic texture and are dark grey with brownish tint on fresh surfaces but yellowish grey on weathered ones. For detailed mineralogical-geochemical studies six samples from three different cross-sections of the Dukla Unit were selected: the Jamista stream from Wisłok, the Roztoka stream from Maniów and the Solinka Górna stream from Wetlina, as well as (for comparison purposes) from one cross-section of southern part of the Silesian Unit: the Jabłonka stream from Bystre. The sampling sites are marked in Figure 1.

The samples selected were examined using optical and scanning microscopy, X-ray diffraction and chemical analyses (SEM-EDS, INNA, ICP and estimation of TOC).

Optical observations of universal thin sections were carried out using a polarizing ECLIPS E600 POL microscope produced by NICON. Morphology and chemical composition of individual grains were studied in the Laboratory of Electron Microscopy of the Jagiellonian University using a Japan JEOL JSM-5410 microscope and applying a NORAN VOYAGER 3100 EDS apparatus at the voltage 20 and 25 kV.

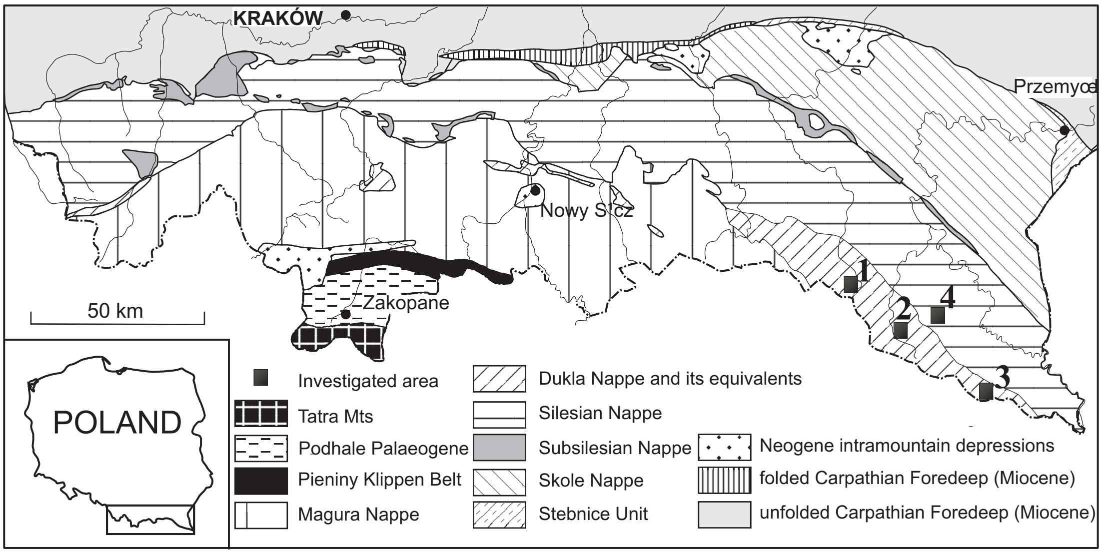

Fig. 1. Simplified geologic map of the Polish Outer Carpathians with marked location of sampling
1 — Wisłok, 2 — Maniów, 3 — Wetlina, 4 — Bystre

X-ray diffraction investigations of powdered samples were carried out using a Philips PW 1730 diffractometer, applying CuKα radiation at accelerating voltage 40 kV and anode current 30 mA.

Instrumental chemical analyses (INNA and ICP) were carried out in the Activation Laboratories Ltd., Ancester in Canada, using a 2MW Pool Type reactor, applying the Ge detectors ORTEC and CANBERRA and ICP spectrometers JARRELL ASH Enviro model and PERKIN ELMER model 6000.

The estimation of total organic carbon (TOC) was carried out using a LECO (USA) instrument after burning samples at 1250°C.

Detailed chemical data were obtained for three samples from the Dukla unit and one sample from the Silesian unit. In two samples (Wisłok and Maniów 2) the chemical data refer both to central and marginal parts of concretions.

RESULTS

Microscope observations have shown that the concretions consist of fine grains of carbonate minerals and clay material dispersed within the whole groundmass. Detrital quartz grains and framboidal pyrite occur in small amounts.

As follows from X-ray data, in three samples (Maniów 1, Maniów 2 and Bystre) siderite is the dominant mineral (Fig. 2a), whereas in two others (Wisłok and Wetlina) it

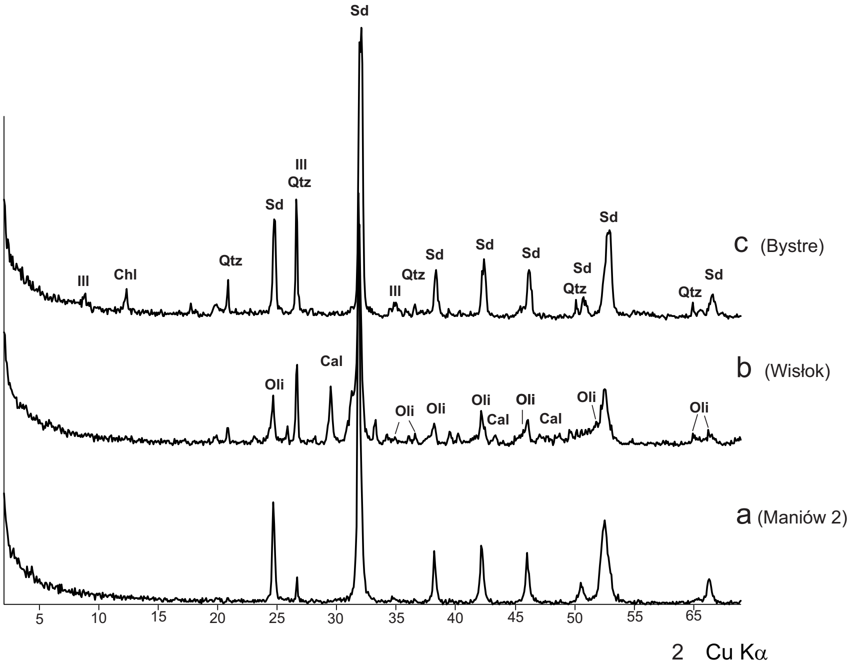

Fig. 2. X-ray powder diffraction patterns of siderite concretions studied
Cal — calcite, Chl — chlorite, Ill — illite, Oli — oligonite, Qtz — quartz, Sd — siderite

is accompanied by calcite. The latter carbonate dominates in the Wisłok sample, containing an oligonite admixture (Fig. 2b). X-ray data have also evidenced the presence of quartz, muscovite (illite) and chlorite admixtures, particularly abundant in the marginal part of the Maniów 2 sample (Fig. 2c).

Important data were obtained by means of observations with a scanning microscope, and particularly, point chemical analyses applying EDS countershaft. They have revealed that the idiomorphic, mainly Fe carbonates with an Mg, Ca and Mn admixture show the composition close to siderite (Phot. 1) and form pseudorhombohedral crystals, often rimming detrital, rounded quartz, calcite and, rarely, albitic feldspar grains (Phot. 2). Common are pyrite grains, forming both idiomorphic crystals and small framboids. Siderite crystals are of variable size (2–30 μm) and the smallest are often grouped in irregular aggregates (Phot. 3).

As follows from SEM-EDS analytical data, iron distinctly dominates among accompanying elements in the sideritic minerals:

$$\mathrm{Fe_{(1.08–1.6)}\,Mg_{(0.22–0.46)}\,Ca_{(0.1–0.27)}\,Mn_{(0.01–0.22)}\,(CO_3)_2} \quad (1)$$

$$\mathrm{Fe_{(0.8–1.3)}\,Mn_{(0.36–0.74)}\,Mg_{(0.17–0.28)}\,Ca_{(0.17–0.26)}\,(CO_3)_2} \quad (2)$$

It was noticed that the carbonates represented by formula (1) occur in outermost parts of individual crystals.

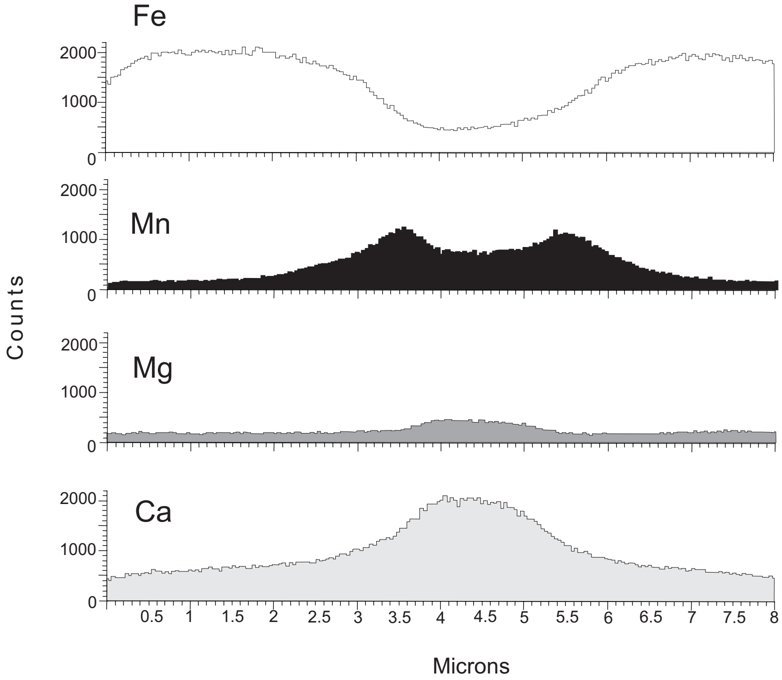

Fig. 3. Variations of Fe, Mn, Mg and Ca contents in a carbonate grain along the line marked in Phot. 4. (SEM-EDS analysis). Maniów 1 sample

In some of the concretions studied there also occur carbonates of different chemical composition, corresponding to dolomites and ferrous dolomites. Their general formula can be presented as follows:

$$Ca_{(0.81-1.11)}\,Mg_{(0.77-0.96)}\,Mn_{(0.02-0.70)}\,Fe_{(0.01-0.75)}\,(CO_3)_2$$

These minerals occur most commonly in the Wetlina sample and form crystallization centres of sideritic substance (Phot. 4).

A characteristic feature of all the samples is the enrichment in Mn of central parts of siderite crystals and at the contact with detrital grains, overgrown by siderite substance. These are the centres of crystallization of carbonates presented best in Figure 3. It was found that the Mn-enriched carbonates occur most abundantly in the Wisłok sample. These carbonates, close to rhodochrosite in composition, can be characterized by the following formula:

$$Mn_{(0.83-1.48)}\,Ca_{(0.31-0.53)}\,Fe_{(0.05-0.68)}\,Mg_{(0.1-0.43)}\,(CO_3)_2$$

Usually they form less regular grains (Phot. 3)

GEOCHEMISTRY

The chemical data of six samples of siderite concretions were correlated to those of the shales embedding them. It is comprehensible that their major elements considerably differ. The concretions are impoverished in SiO_2, Al_2O_3, Na_2O, K_2O and TiO_2 but enriched in Fe_2O_3, MnO, MgO, CaO and P_2O_5 (Table 1).

The content of SiO_2 varies within the limits 4.48–19.05 wt.% and the ranges of other elements are: 1.22–7.22 wt.% Al_2O_3, 012–0.84 wt.% Na_2O, 0.28–2.82 wt.%, K_2O and 0.07–0.35 wt.% TiO_2, whith the highest concentrations of these elements found in the Wetlina and Bystre samples, containing significant admixture of detrital material.

The contents of most abundant elements in the concretions studied vary within the below limits: 24.42–49.15 wt.% Fe_2O_3, 1.85–16.46 wt.% CaO, 0.34–8.49 wt.% MnO, 2.35–5.05 wt.% MgO and 0.08–5.41 wt.% P_2O_5. Some similarity of major element contents is noted between pairs of samples: Maniów 2 (middle part of the Dukla Unit) and Bystre (Silesian Unit) as well as Wetlina (eastern part of the Dukla Unit) and Wisłok (western part of the Dukla Unit). The highest contents of Mn (8.40 wt.% both in central and marginal part of the concretion) was found in the Wisłok sample, enriched in Mn carbonates.

The chemical data were recalculated into molecular percents in order to specify mineralogical character of the concretions studied. It was assumed that all Fe, Mg, Mn and Ca are bound with carbon dioxide in carbonates, although it cannot be quite correct as far as Fe and Mg are concerned, in view of the observed admixture of clay minerals. The results are presented in Table 2. For comparison purposes, the chemical composition and mineralogical character of siderite concretions from the Majdan Beds, analysed by W. Narębski, are detailed in Table 3.

TABLE 1

Chemical composition [wt.%] of siderite concretions and of shales embedding them

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	TOTAL	S	TOC
WESTERN PART OF DUKLA UNIT														
Wisłok shale	54.68	19.39	5.84	0.03	2.54	1.04	0.71	3.27	0.82	0.11	11.59	100.02	0.22	0.89
Wisłok-conc-marginal	11.71	3.13	31.18	8.40	3.70	9.85	0.16	0.62	0.14	2.23	28.98	100.09	0.03	0.97
Wisłok-conc-centre	11.94	2.46	24.42	8.49	2.95	16.46	0.19	0.41	0.12	5.41	26.86	99.72	0.04	1.42
MIDDLE PART OF DUKLA UNIT														
Maniów 2-conc-margin.	19.05	4.75	40.23	1.19	4.57	3.11	0.26	0.57	0.32	0.08	25.97	100.10	0.22	0.38
Maniów 2-conc-centre	4.48	1.72	49.15	3.56	4.58	3.86	0.12	0.28	0.07	0.21	32.37	100.40	0.03	1.22
EASTERN PART OF DUKLA UNIT														
Wetlina shale	nd	14.98	9.50	0.06	1.68	8.61	0.57	6.91	0.57	0.16	nd	43.04	0.07	0.73
Wetlina-conc	nd	6.76	29.46	1.28	2.35	15.50	0.84	2.82	0.35	4.30	nd	63.66	0.18	0.26
SILESIAN UNIT														
Bystre-conc	17.08	7.22	40.15	0.34	5.05	1.85	0.13	1.23	0.35	0.17	26.51	100.09	0.21	1.11

nd — not determined.
conc — concretion.

TABLE 2

Molecular contents of individual carbonates and mineralogical nomenclature of the concretions studied

Sample	Lithostratigraphic horizon	$FeCO_3$	$MnCO_3$	$MgCO_3$	$CaCO_3$	Mineralogical name
Wisłok	Majdan Beds	40.31	13.32	6.96	23.49	manganospherite and calcite
Maniów 2	Majdan Beds	64.80	3.75	9.57	6.22	sideroplesite
Wetlina	Majdan Beds	42.72	2.02	4.92	27.68	sideroplesite and calcite
Bystre	Upper Istebna Beds	58.22	0.53	10.56	3.30	sideroplesite

TABLE 3

Chemical composition and mineralogical character of sideritic concretions (analysed by W. Narębski)

Sample	FeO	MnO	MgO	CaO	$FeCO_3$	$MnCO_3$	$MgCO_3$	$CaCO_3$	Mineralogical name
Majdan 1	17.69	0.82	4.36	6.44	28.51	1.33	9.12	11.50	sideroplesite
Majdan 2	15.43	0.56	3.32	5.13	24.86	0.91	6.94	9.16	sideroplesite
Wetlina 1	27.71	0.93	4.85	nd	44.65	1.51	10.15	—	sideroplesite
Wetlina 2	30.41	0.93	5.52	nd	49.00	1.51	11.55	—	sideroplesite

nd — not determined.

Molecular contents of individual carbonates in all the above samples are presented in the classification diagram (Fig. 4). The siderite concretions from the Dukla and Silesian Units studied are mainly sideroplesites from mineralogical viewpoint, except of manganospheritic character of the Wisłok sample. Similarly sideroplesitic in character are concretions from Paleocene beds of the Dukla Unit (Table 3).

The results of estimations of trace elements in siderite concretions and shales embedding them indicate in general that the former are impoverished in the vast majority of them, namely in Ni, V, Rb, Ba, Cu, Cr, Cs, Pb, Sc and Th, except of Sr (Fig. 5). The content of the latter element is at least two times higher in the concretions, which

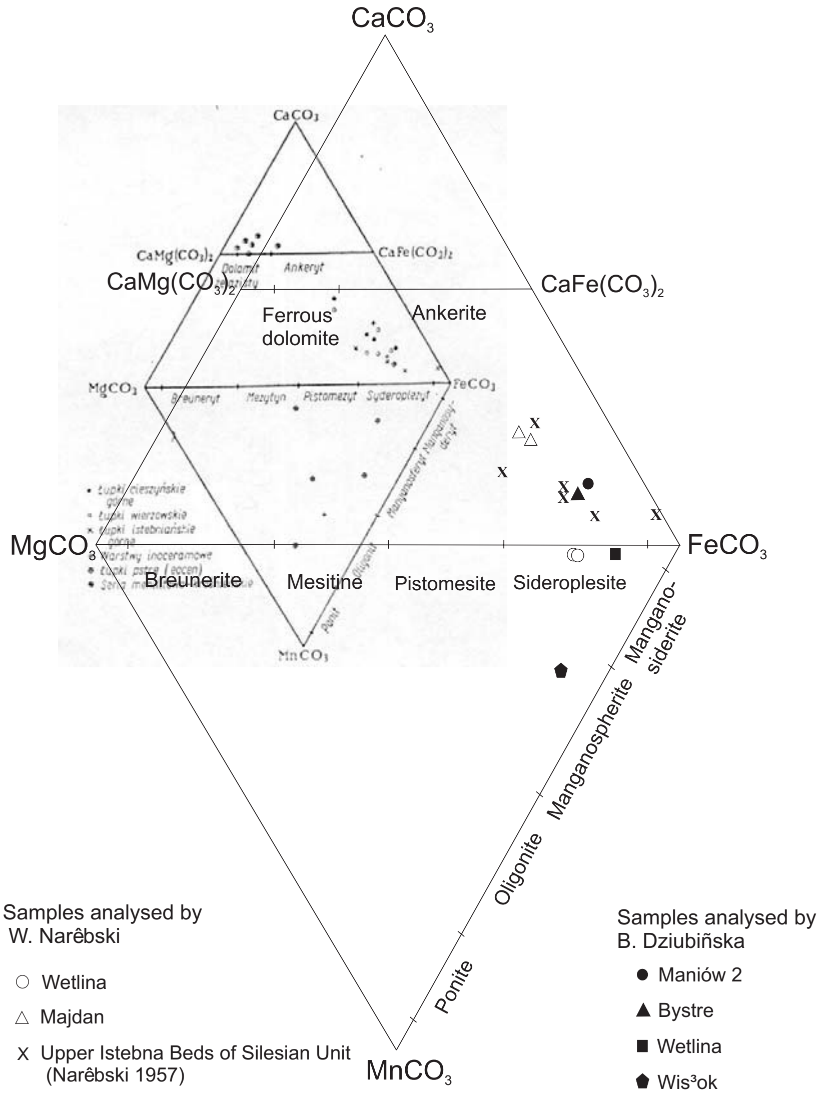

Fig. 4. Concretions from Paleocene series of the Dukla and Silesian Units in classification diagram

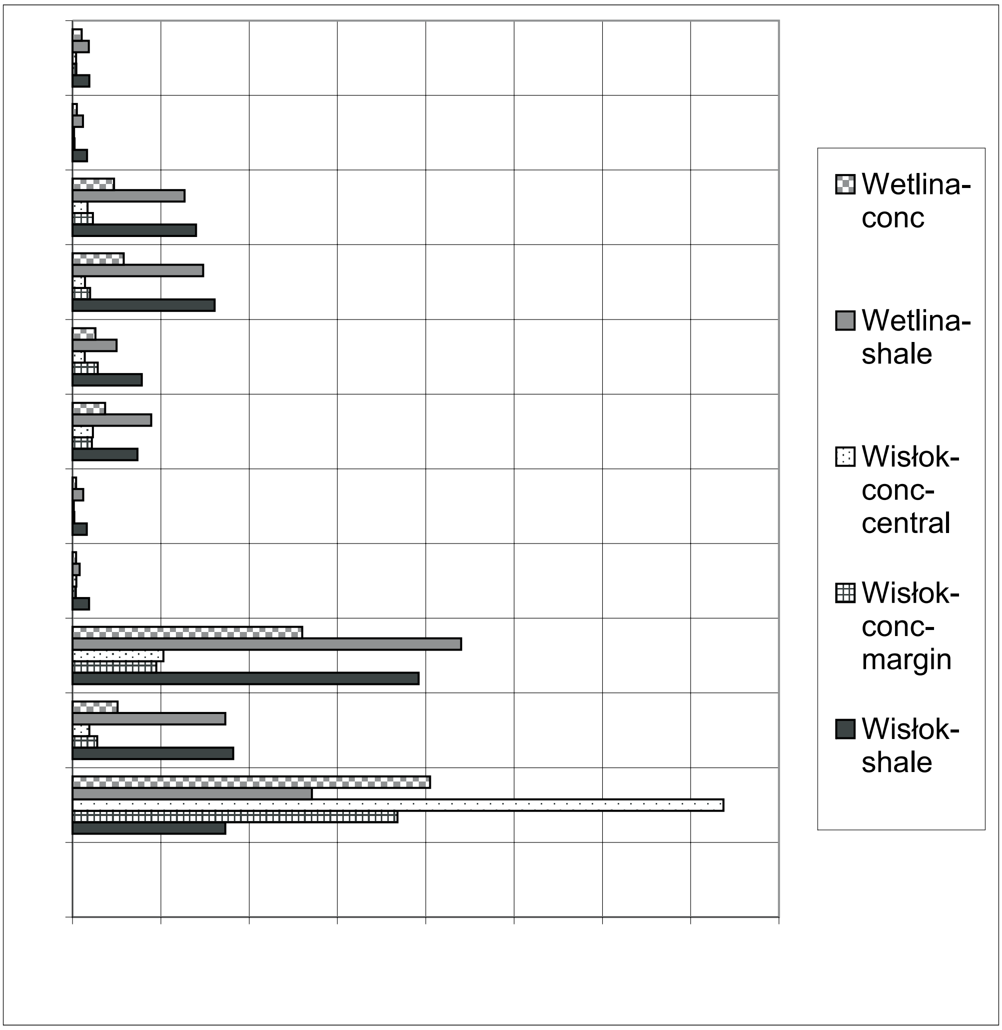

Fig. 5. Trace elements in selected concretions and containing them shales

can be explained by isovalent diadochy of Sr and Ca. Lower contents of trace elements in the concretions studied result from a small admixture of clay minerals, since the latter are usually enriched in them by sorption.

On the other hand, the concentrations of REE (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) in the concretions studied are higher than in the shales embedding them (Fig. 6). This is rather unexpected phenomenon since carbonate rocks and siderite concretions are, in general, impoverished in rare earth elements (e.g. Zodrow, Cleal 1999).

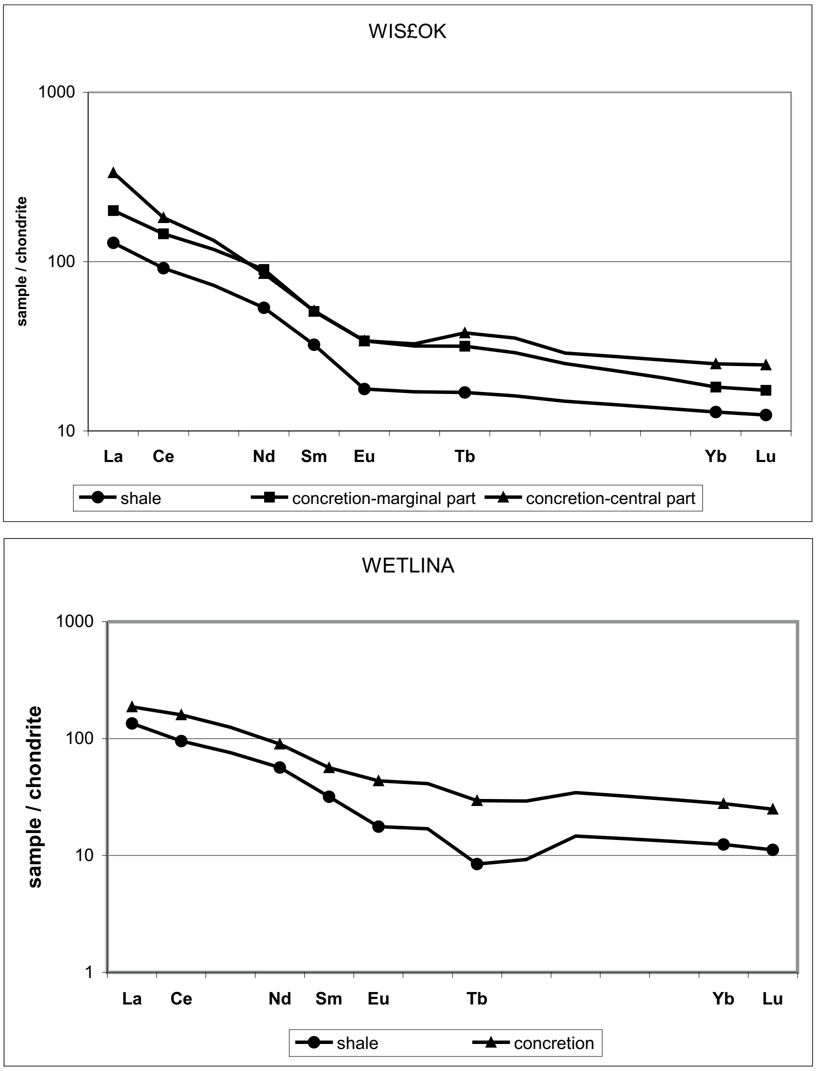

Fig. 6. Chondrite–normalized REE contents in selected concretions and containing them shales

ORIGIN OF SIDERITE CONCRETIONS

Siderites are formed under conditions of negative Eh values and high concentration of ferrous ions in the environment low in sulphate but high in carbonate anions and favouring the mobility of carbon dioxide. Organic matter is generally considered to be the main producer of carbonate ions in clay sediments. On the other hand, the supply of this matter depends on microbiotic activity (Coleman 1985). Moreover, the amount of organic matter trapped in clay sediment depends also on its exposition to oxidizing sea water. Consequently, rapid sedimentation and short exposition of deposited clay minerals to sea water favour the entrapment of organic matter (Coleman 1993). In slowly accumulating sediments the majority of organic matter is, most probably, consumed at the water-sediment interface by sulphate reducing aerobic bacteria and anaerobic organisms (Gautier 1982). The presence of pyrite in slowly depositing clay sediments suggests, by analogy to recent deposits, that the depth of precipitation of siderite depends on the rate of sedimentation.

The genetic model presented follows the concept of Narębski (1957), described in detail in the monograph on mineralogy and geochemical conditions of origin of the so-called siderites of the Carpathian Flysch. It was based on the idea of sedimentary geochemical facies (Teodorovich 1949) and on the method of their identification by estimation of different forms of iron in pelitic deposits as well as on the character of early diagenetic concretions occurring in them (Strakhov 1953). In the opinion of Teodorovich (1949) geochemical siderite facies are usually related to near-shore or peri-insular zones of not very deep basins.

The dominant chemical elements of the concretions studied are iron and manganese. It is, therefore, necessary to characterise their geochemical behaviour in sedimentary environments.

One of typical features of siderite geochemical facies are slight fluctuations of the oxidation-reduction boundary within sedimentary environment, usually situated at the surface. of deposited material. The separation of iron from sialic part of the weathering material needs a transitional environment between reducing, H_2S-bearing, and oxidizing one. The dissolution of iron from weathering material and from surficial layer of sediments takes place in those benthic zones of basins where, due to poor ventilation and partial decomposition of organic remnants, the environment is distinctly enriched in carbon dioxide (Borchert 1952; Taupitz 1954). Iron — in the mobile form of hydroxide — is most intensely deposited in trough-like depressions of the bottom. Since sedimentation in geosynclinal basins is progressing fairly rapidly, the boundary of oxidizing and reducing zones usually moves quickly upwards. Colloidal concentrations of ferric hydroxide are in reducing environment and in the presence of carbon dioxide easily transformed into soluble ferrous bicarbonate $Fe(HCO_3)_2$. This form of iron, mobile in pore solutions of pelitic sediments, can be — under very variable conditions of flysch sedimentation — easily transformed into insoluble, anhydrous ferrous carbonate (siderite) when carbon dioxide is given off. This process, leading to the formation of siderite and similar concretions, proceeds within the freshly deposited sediments during their early diagenetic transformations, ordering chaotic distribution of their components. It should be emphasized that the main factor of these processes is bacterial decomposition of organic matter, being the source of active carbon dioxide and very effective reducing agent.

Manganese is oxidized at considerably higher redox potential than iron and, consequently, can be much more easily reduced to the divalent form. Therefore, its compounds dissolve more rapidly and can migrate at longer distances both in water basin and in pore solutions. These geochemical properties of Mn control its often observed separation from iron and more rapid precipitation from solutions what was confirmed by detailed analytical studies of the concretions in question. As already stated, some unquestionably earlier formed central parts of these carbonate concretions are distinctly enriched in manganese.

Moreover, all the carbonate concretions studied are distinctly enriched in magnesium and, therefore, defined as sideroplesites. This is an important geochemical evidence of their marine origin since similar concretions, e.g. from Tertiary lacustrine fresh-water sediments of the Turów brown coal mine, are composed of nearly Mg-free siderites (Narębski 1974).

Summing up it is concluded that the black shales containing the sideroplesitic concretions studied should be generally assigned to marine siderite-pyrite facies, and, partly — due to local occurrence of manganospherite — to siderite facies.

CONCLUSIONS

Siderite concretions of Paleocene series of eastern part of the Flysch Carpathians are sideroplesites and manganospherites of early diagenetic origin. These series composed of black shale deposits should be assigned to siderite-pyrite and siderite facies.

Common occurrence of framboidal pyrite in the Majdan beds suggests more reducing conditions of their early diagenetic changes.

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Beata DZIUBIŃSKA, Wojciech NARĘBSKI

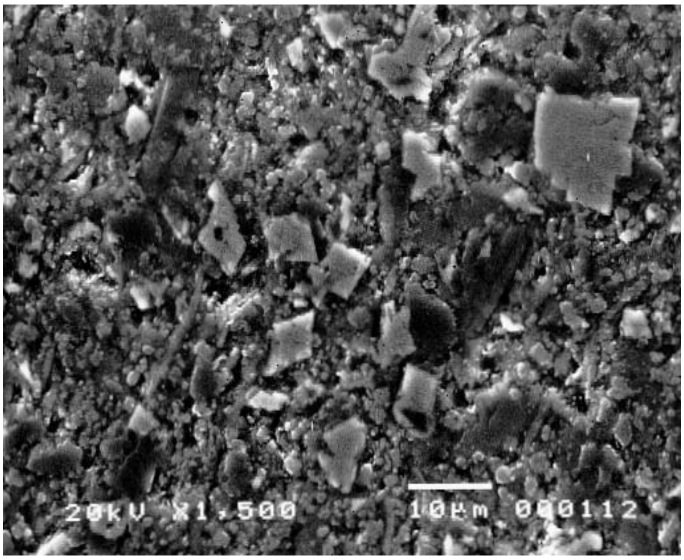
KONKRECJE SYDERYTOWE W WARSTWACH PALEOCEŃSKICH POLSKIEJ CZĘŚCI WSCHODNICH KARPAT FLISZOWYCH

Streszczenie

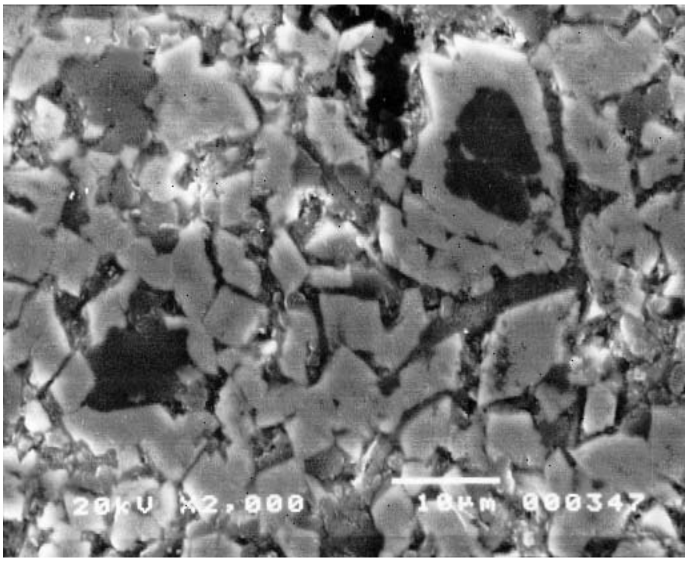
Badaniom poddano konkrecje syderytowe występujące w paleoceńskich czarnych łupkach jednostki dukielskiej i śląskiej — odpowiednio w warstwach z Majdanu i górnych łupkach istebniańskich. Próbki konkrecji poddano obserwacjom mikroskopowym (mikroskop optyczny i skaningowy), badaniom rentgenowskim i analizie chemicznej (SEM-EDS, INNA, ICP i oznaczeniu TOC).

Badania SEM-EDS wykazały, że głównymi minerałami diagenetycznymi są węglany żelaza zbliżone do syderytu, następnie dolomit, dolomit żelazisty i kalcyt. Węglany bogatsze w Mn krystalizują jako pierwsze z roztworów. Badane konkrecje zawierają do 49,15% wag. Fe_2O_3, do 16,46% wag. CaO, do 5,05% wag. MgO i do 8,49% wag. MnO, natomiast zawartość węgla organicznego (TOC) dochodzi do 1,42% wag.

Konkrecje syderytowe warstw paleoceńskich wschodniej części Karpat fliszowych są głównie syderoplezytami i w znacznie mniejszym stopniu manganosferytami pochodzenia wczesnodiagenetycznego. Świadczy o tym m.in. wykazana analizami punktowymi zmienność składu chemicznego konkrecji od środka ku peryferiom, przy wzbogaceniu części centralnej w mangan. Badania geochemiczne wykazały niższe w stosunku do łupków zawartości wszystkich pierwiastków śladowych w konkrecjach z wyjątkiem diadochowego z wapniem strontu. Utwory te wraz z otaczającymi je łupkami można zaliczyć do facji syderytowo-pirytowej i syderytowej.

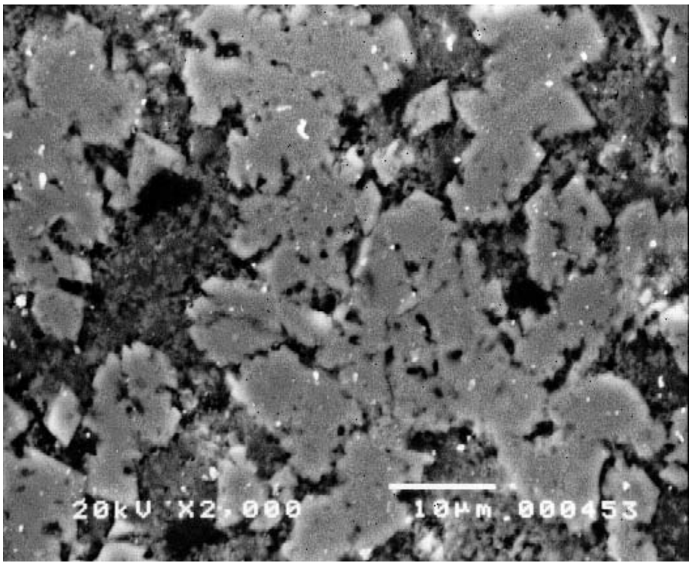


Phot.1. Idiomorphic siderite crystals (Wetlina sample)

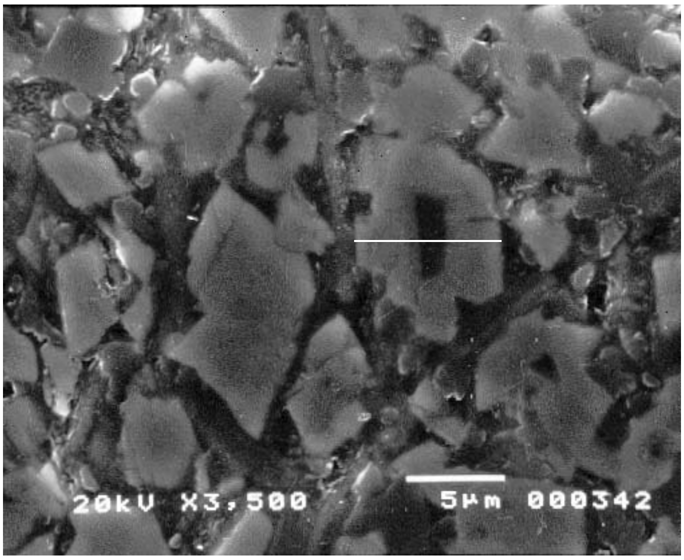


Phot. 2. Idiomorphic siderite crystals rimming detrital grains (Maniów 1 sample)

B. DZIUBIŃSKA, W. NARĘBSKI — Siderite concretions in paleocene series of Polish part of the Eastern Flysch Carpathians



Phot. 3. Idiomorphic siderite crystals, forming irregular aggregates (Wisłok sample)



Phot. 4. Idiomorphic siderite crystals (Maniów 1 sample).
Trace of linear analysis is marked — see Fig. 3

B. DZIUBIŃSKA, W. NARĘBSKI — Siderite concretions in paleocene series of Polish part of the Eastern Flysch Carpathians