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Development of the phosphogenetic processes in the Lower Carboniferous deposits of the Holy Cross Mts.

Concretional and stratal phosphorites from the Lower Carboniferous deposits developed in the Culmian facies of the Gałęzice Syncline and the Kielce – Łagów Synclinorium are described in the present paper. Two generations of phosphate precipitation were observed: a sedimentary and a diagenetic, together with a collophane transition facies into a crystalline apatite. The phosphorites formed in eupelagic deposits directly on the bottom of the basin — at the boundary of the oxidation and reduction environments, i.e., in conditions different from those of phosphorite accumulations in shallow-water shelf deposits.

INTRODUCTION

Similar to the Silurian or the Devonian, the Carboniferous is not a period of abundant phosphate deposits. Distinct accumulations of phosphorites in the Carboniferous are very rare and mostly connected with the Culmian facies. The Lower Carboniferous deposits, already studied at the end of the nineteenth century, were exploited in Ariege in the French Pyrenees Mts. (D. Levat, 1899). Some phosphorite-bearing locations are known from the Culmian of Thüringen, Austria and England (Devonshire). Some phosphorite concretions are also known from the Dinant Syncline in Belgium (Z. Sujkowski, 1933).

The characteristic of the Lower Carboniferous phosphorites from the Holy Cross Mts. presented in this paper are based on the archival samples from the collections of J. Czarnocki, Z. Sujkowski and J. Pawłowska. Those samples have been re-studied together with the thin sections. Thanks to the courteousy of Prof. H. Żakowa, supplementary studies on the concretions from the Łagów region have been also performed.

All the studies listed above resulted in an attempt at re-interpretation of the sedimentary conditions and the genesis of the phosphorite in the Culmian basin of the Holy Cross Mts.

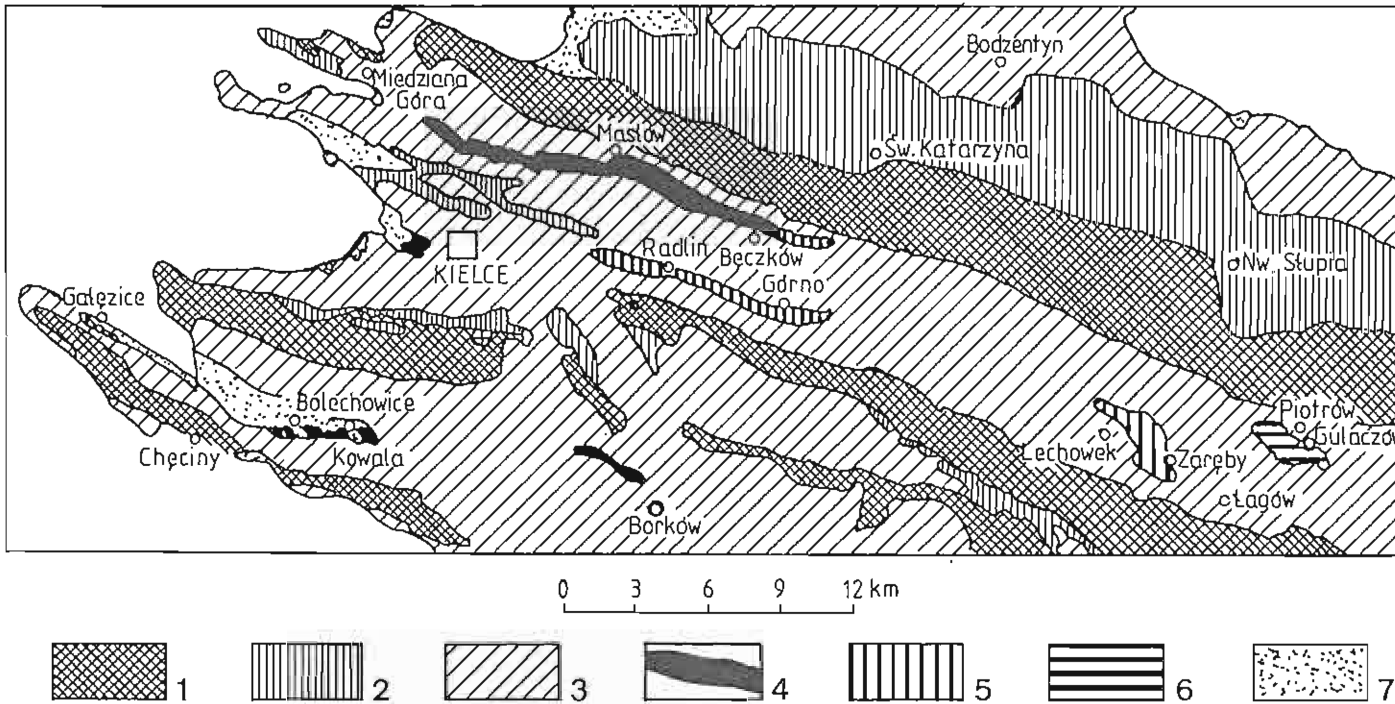

Fig. 1. Map of the occurrence of the Lower Carboniferous on a background of the Palaeozoic of the Holy Cross Mts. — after H. Żakowa (1967)
1 — Cambrian, 2 — Ordovician and Silurian, 3 — Devonian; 4–6 — Carboniferous: 4 — Tournaisian, 5 — Tournaisian and Visean, 6 — Visean; 7 — Permian
Mapa odkryta występowania karbonu dolnego na tle paleozoiku Gór Świętokrzyskich według H. Żakowej (1967)
1 — kambr, 2 — ordowik i sylur, 3 — dewon; 4–6 — karbon: 4 — turnej, 5 — turnej i wizen, 6 — wizen; 7 — perm

The present paper is a fragment of the monograph on Palaeozoic phosphorite-bearing formations in Poland prepared in the Department of Mineral Resources Geology of the Polish Geological Institute, Warsaw.

PREVIOUS WORK

Lower Carboniferous phosphate-bearing deposits occur in the following two regions of the Holy Cross Mts.:

— in the Gałęzice Syncline and its prolongation eastwards, i.e., in the so-called Daleszyce Depression (Miedzianka, Gałęzice, Wola Murowana, Kowala, Bolechowice, Broków – Góra, Jabłonna near Daleszyce),

— in the Kielce – Łagów Synclinorium (Radlin, Górno, Lechówek, Złota Woda, Zaręby near Łagów) — Fig. 1.

The Lower Carboniferous developed in the Culmian facies was discovered by J. Czarnocki (1916, 1928) in the Gałęzice Syncline. Starting from the thirties the phosphorite concretions have been an object of interest. J. Czarnocki and Z. Sujkowski (1932) gave basic information on lithology and stratigraphy of those series. J. Czarnocki (1933) made a search for the phosphorites in Kowala for the purpose of the artificial fertilizer factory in Kielce. The activites described did not bring any positive result. Although the phosphorite-bearing series in Kowala displays, in general, a thickness of about 20 m. The frequently repeated phosphorite interlayers do not exceed 20 cm in thickness and contain 21.3% of P_2O_5 at the bottom, 18.32% in the middle and 10–13% in the upper parts. The background of the source rock is below 1% of P_2O_5. In Kowala, the phosphorites occur only in the Culmian. Their maximum extent covers the lowermost part of the profile which corresponds to the silica and lydite shales, which are widespread from Gałęzice to Łagów. The phosphorites also occur in Upper Devonian deposits in the Miedzianka and Gałęzice regions. Although J. Czarnocki pointed to the low practical significance of the phosphorites from Kowala, he did not exclude the possibility of the depositional concretions in the Kielce – Łagów Synclinorium, e.g., in Górno. These suggestions possibly caused an exploration in the period after the war.

Another paper worth mentioning here is that of Z. Sujkowski (1933) on the Lower Carboniferous radiolarites from the Holy Cross Mts. This paper has a fundamental character for recognition of genesis and sedimentation conditions of the radiolarite deposits. The main purpose of the author was to prove that the radiolarites represent a deep-water facies, a controversial and often denied fact in his times. The phosphorite concretions were especially carefully described by the author quoted and petrographically characterized. Z. Sujkowski gives a detailed description of the organic remnants in the concretions. Based on the comparative studies conducted, he proved that the phosphorites in the Culmian of the Holy Cross Mts. are not a separative event since similar deposit are accompanied by the radiolarite horizons in the geosynclinal sediments of the Lower Carboniferous extending from Thüringen to the Pyrenees Mts. It is a very interesting fact that the phosphorites from the Pyrenees Mts. contain near exlusively spheroidal, crystalline phosphoritic aggregates. This was observed by Z. Sujkowski in the samples delivered by L. Cayeux and is referred by him to more advanced diagenesis than that in the Culmian profiles in the Holy Cross Mts.

The following papers are chronologically connected with the Culmian phosphorites: S. Biskupski (1935) on the chemistry of the phosphorites, J. Czarnocki (1933), Z. Kielan (1949) and S. Kwiatkowski (1953, 1959) on stratigraphy and lithology of the Fammenian and Culmian in Gałęzice. The papers listed have confirmed the phosphorite-bearing potential of the Culmian. These facts together with the positive opinion of A. Morawiecki resulted in 1955 in re-newed exploration done by the Geological Institute. Mining exploration and research had lasted until 1957 covering the area of the Gałęzice Syncline and the Kielce – Łagów region. The results are presented by J. Pawłowska (1957*a*, *b*, 1961*a*, *b*, 1971).

Despite the broad extent of the exploration works no significant accumulations of the deposit were found, mainly because of a distinct dispersion of the concretions in the source rocks.

THE OCCURRENCE OF THE PHOSPHORITES

THE GAŁĘZICE SYNCLINE

The Carboniferous deposits in the Gałęzice region are developed in the facies of Culmian and Carboniferous limestone. The Culmian series correspond to the Lower and Upper Tournaisian and occur at the bottom of red and green clayish shales. The sediments change towards the top into black clay and siliceous shales with lydite intercalations. Phosphorite concretions occur in both types of shales.

The phosphorites found at the bottom of the Carboniferous limestone are distinctly redeposited and originate from the black Culmian shales.

Red radiolarites with the phosphorite concretion occur at the bottom of the Carboniferous syncline in Wola Murowana and Kowala over the Famennian deposits (J. Czarnocki, Z. Sujkowski, 1932). That horizon deserves special attention since it is the only evidence of phosphorite occurrence in the Devonian in the Holy Cross Mts. In the Famennian profile in the Kowala borehole metasomatic phosphorites were found nodular and peloid aggregates in the laminated marls with radiolarians (H. Żakowa, K. Radlicz, 1990).

The Upper Famennian deposits show a gradual transition into grey, fragile Lower Carboniferous shales with intercalations of tuffites and thin packets of lydites and silica shales with phosphorite concretions. Three such horizons of 30 cm thickness were discovered in Bolechowice (J. Pawłowska, 1961*a*).

The detailed analysis of thin sections from the archive samples resulted in a discovery of thin (0.6 cm) intercalations of stratal phosphorites within the clay shales with radiolarians from Wola Murowana and Bolechowice.

In the Borków region (Góra Jabłonna), phosphates of lowermost Tournaisian age have been reported, being present in the mottled reddish-green and black Upper Tournaisian shales (H. Żakowa, 1967).

THE KIELCE – ŁAGÓW SYNCLINORIUM

Exploration drilling for bitumens conducted in the Zaręby region resulted in a complete profile of the Tournaisian deposits displaying a thickness of 200 m and phosphorite horizons (H. Żakowa, J. Pawłowska, 1961).

In general — the Lower Carboniferous member is built of a thick complex of clay and silica-clay shales with tuffogenic interbeds, zones of shalc clasts and phosphorites. Borehole Zaręby 3 displays the most completely developed Tournaisian deposits. Nine horizons with phosphorites in the Upper Tournaisian, while fifteen — in the lower one. The phosphorite coneretions have a diameter of about 0.5–4.5 cm (Pl. I, Figs. 4 ab). The same horizons often contain interlayers of tuffites and are frequently enriched in microflora and plant detritus. H. Żakowa (1967, 1971) also observes the presence of radiolaria in the whole profile of the Carboniferous.

CHARACTERISTICS OF THE PHOSPHORITES

THE STRATAL PHOSPHORITES

Archival materials and papers quoted mostly give information on the concretions from the Culmian deposits from the Gałęzice and Kielce – Łagów Synclines. They neglect, however, the problem of the distinct phosphorite layers important for further discussion.

Such phosphorites are preserved only sporadically in the mottled shales and radiolarites in the lower horizons of the Tournaisian. Relicts of the phosphate layers of thickness varying from 0.3 to 1 cm differ structurally and texturally from the overlain and underlain clay and siliceous shales.

The elongated bands of phosphates and organic matter occur in the shales at the contact, and impregnate the deposit parallel to the lamination. Such small strata were found in Bolechowice (Pl. I, Fig. 2). In Wola Murowana a 0.6 cm thick phosphate lamina was formed cutting the radiolarian shales (Pl. I, Fig. 3). Phosphates are developed there as peloids or irregular aggregates of variable size from 0.05 to 0.75 mm (Pl. I, Fig. 3). Those aggregates are composed of micropeloids indistinct, partly erased texture and diameters varying from 0.006 to 0.01 mm. Also traces of filiform organisms were found, which resemble primary algae. Content of the phosphorites is approximately 40%, other components correspond to skeletons of radiolarians filled with quartz microaggregate, aggregates of shredded organic matter and quartz-clay cement.

PHOSPHORIT CONCRETIONS

Phosphates in the form of small concretions occur in some horizons irregularly distributed in the source rocks. The thickness of those horizons does not in general exceed 20–30 cm. One cubic meter of rock contains from over ten to some tens of concretions. Two main types can be distinguished lenticular and spheroidal. The diameter of the spheroidal concretions equals at maximum 7 cm, the most frequent value varying from 2 to 3 cm. The longer axis in the flattened forms varies from 3 to 8 cm with a thickness in the interval of

0.5–2 cm. Z. Sujkowski (1933, p. 650) writes: "... the spheroidal concretions are more frequent in the shales, while the flat ones — in the lydites. The contrary, however, also occurs. Often both types of concretions are mixed in one stratum..." The co-occurrence of both the forms can be, therefore, accepted. The sample containing two spheroidal forms grown on a flat one and surrounded with one silica overgrowth common to three concretion types (sample no. 17/4, Jabłonna, J. Pawłowska, 1957*b*) is a proof for the suggestion of co-occurrence.

Despite their shape, different concretions can be macroscopically distinguished: the heavy, compact concretions of uneven fracture and light, strongly porous, fragile, crystalline ones. The colour observed on the fracture changes from dark grey to fleshy, light grey. Small edges seen in some samples are the characteristic feature of the concretions, not pointed out until present (Pl. I, Fig. 4).

The external rim is formed either by the chalcedon (up to 4 mm thick — lower horizons) or by the shining black cover of deformed siliceous shales, as well as recrystallized illite. The surface of concretions is sometimes nodular and uneven. In general, however, it is smooth, so that some researches have described the concretions as "well rounded ones".

Worth mentioning is the fact that the concretions do not have a distinctly formed central part or concentrically precipitated phosphate. Only in one case (thin section no. 12, Zaręby) was the nucleus observed, containing laminae enriched in phosphates and in organic matter, as well a dark rim partly built of iron sulphides and presumably of manganese compounds. The spheroidal form of the concretions discussed is only due to the diffusive rings of the hydrated iron oxides and is not confirmed by the distribution of the other components.

The presence of radiolarian skeletons in the interior is the main feature of the concretions. Those skeletons often occur as the main rock-forming element (up to 60% of the total concretion mass) with an exception of the flattened lenticular forms displaying the compact structure. In the bottom parts of the Culmian profile, therefore, there occurs either radiolarian phosphorite or phosphated radiolarite. According to Z. Sujkowski (1933) three types of radiolarites are represented there: *Spumellaria* together with *Collodaria*, subordinately *Nasselaria* and *Phaedaria*. Round Spumellarias with well preserved spines and clear skeleton morphology revealed by pigmentation of the iron oxides are frequent in thin section (Pl. I, Fig. 5). Forms filled with silica are best preserved. Phosphatization of the skeletons is simultaneously observed. Cavities after the leached radiolarians and after their siliceous encrustations are often present, features characteristic for the porous "grain" type of concretion referred to the upper horizon of the black shales. The radiolarian skeletons are less abundant there than in the concretions in the lower horizons. The skeletons occupy 1/4 to 1/3 of the total mass of the concretion.

As is observed in the thin sections the phosphates in the concretions display the following different forms:

1. Anisotropic peloids with no inner structure.

2. Micropeloidal aggregates similar to those described in the phosphate laminae displaying indistinct inner structure, often with a pigment of organic matter.

3. Aggregates of apatite microcrystallites reaching 4 μm in their length and displaying heterogeneous character and isotropy or partly anisotropy. They are disordered in their structure, have the form of needles of needles-spheroids and resemble a rock "cork" (Pl. I,

Fig. 6). Those aggregates are irregular and ameboidal as well, and the size of those forms is about 1–2 x 0.55 mm. They display a characteristic earthy shade under crossed nicols.

4. Isotropic phosphates with some traces of fibroidal structure, whicb form rims around the other types of phosphate aggregates and organic matter, walls limiting the porous space and the covers on the radiolarian skeletons.

5. Well developed phosphate spheroids, seen under crossed nicols. The individual spheroids reach 0.3 mm in diameter. Chains of such spheroids either fill the walls of the radiolarian skeletons or form the rims around them. The similar covers occur in interstitial spaces and on the other phosphate aggregates, which corresponds to the distribution of the isotropic rims and suggests their transition into the crystalline form of the fluorine apatite (Pl. I, Fig. 7; Pl. II, Figs. 8, 9). In the Miedzianka concretions the whole phosphate mass is built of spheroid displaying a radial-fibroidal structure (Z. Sujkowski, 1933).

Many interesting details of the spheroidal covers, as well as the secondary porosity resulting from the crystallization processes (Pl. II, Fig. 10), were discovered in the SEM studies. The spheroids can be formed either from several smaller ones (Pl. II, Figs. 11, 12) or just one individual (Pl. II, Fig. 13). Individual fibres and prisms responsible for the radial and fan-like texture of the spheroids are seen well when strongly magnified.

A distinct zoning of the spheroidal textures creates another problem. It seems from the material studied (which, however, does not represent all phosphate-bearing horizons) that the crystalline forms are more frequent in the bottom parts of the Culmian, while in the upper horizon the other types of phosphate aggregates are dominant, or the spheroids do not occur at all. Those facts can be related to the different degree of diagenesis in the individual horizons. It suggests that the crystalline forms originate from already precipitated isotropic phosphates due to the high pressure conditions and the limited migration of fluids in the porous space.

The organic matter represents, beside the phosphates, an important component of the concretions and of the shales in the contact zones with the concretion horizons. Coal bands and schliers as well as peloid-like accumulations are most frequent. Also sometimes, the radiolarians are filled with organic matter. J. Pawłowska (1957*a*, *b*, 1961*a*) even tells the "coalified" radiolarians and bitumens inside the concretions.

The organic pigment in the phosphate aggregates should also be mentioned. It is possible that some individuals of that organic dust of diameter varying from 5 to 10 μm represent plant material separated from the radiolarians and the concretions by Z. Sujkowski (1933, Fig. 1, p. 653) after HNO_3 treatment. He belived that the material was unidentified spores and pollen made of chitin. There existed a theoretical possibility of the eolian origin of such material transported into the basin by winds from the land. The presence of microflora and the plant detritus in the Culmian shales was observed by A. Jachowicz (1967).

The thread-like and pipe-like forms similar to algae inside the phosphate aggregates should also be attributed to organic activity. These forms are analogous to those in the stratal phosphorites.

The organisms with the siliceous skeletons, however, very frequently must have been the main source of the organic matter in the deposits. Horizons depleted in radiolarian relics are simultaneously poor in organic matter and phosphates (e.g., the upper horizon of the clayish shales from Kowala with P_2O_5 content of about 10%).

It seems that the organic shreds covered or surrounded by the isotropic or spheroidal phosphates are evidence for the local origin of phosphates directly from the biochemical reactions either on the floor of the basin or in weakly consolidated sediments.

The silica in the concretions occurs — outside the radiolarian skeletons — in the form of chalcedony accumulations and impregnations, as well as — in some exceptional cases — recrystallization in pore space. The majority of the radiolarian skeletons in the concretions are built of isotropic dehydrated silica, which also fills their interior. Sometimes, however, the skeletons have preserved their primary opal material.

With an advance of diagenesis a re-mobilization of silica possibly took place, which resulted in the chalcedony rims around the concretions in the bottom parts of the Culmian profile.

The presence of carbonates is of subordinate significance in relation to the main components of the concretions. It may be a result of carbonate leaching following the possible formation of HCO_3^- ions together with CH_4 occurring in the primary deposit. An increase in alkalinity in the pores caused a dislodgement of silica and its partial substitution by calcite, as for example in some radiolarian skeletons. This secondary calcitization occurred possibly in the final stages of the concretion formation.

Iron compounds must have been present in the primary deposit as the pigment of the iron oxides. This fact is proved by goethite and even hematite precipitation which often manifests the morphology of the radiolarian skeletons. The reduction conditions enabled the precipitation of the iron sulphides. The concretions contain pyrite in the form of well-developed cubes or pentagonal dodocahedrons, as well as abundant framboidal aggregates. These last ones are of crystalline character and display a diameter of some micrometres. They form either in marine waters and migrate into the deposit, or in special conditions in the pores.

It is also worth mentioning here that the aggregates of the hydrated iron oxides do not come from the weathering zone since — apart from the shallow horizons — they occur also in the concretions from the deeper Culmian layers (e.g., from depths of 120 and 57 m in the boreholes in Jabłonna and Bolechowice, respectively).

CHEMICAL COMPOSITION

Although the search for the concretions was very intensive, only few chemical analysis were accessible. The lack of total analyses makes it difficult to evaluate the significance of manganese and the quantitative content of the sulphides in the concretions. The results of only one analysis can be quoted from the references (Z. Sujkowski, 1933). This is the case of the "round" concretion from Górno. The results are as follows: P_2O_5 — 32.21% (the highest value determined in the Culmian phosphorites), SiO_2 — 7.86%, Al_2O_3 — 4.38%, CaO — 41.41%, MgO — 2.10%, H_2O — 4.21%, organic matter — 1%, F — traces. Low silica content is characteristic here. The concretion probably correspond to the strongly porous type, where SiO_2 has been partly leached.

The archival materials contain only incomplete or indicatory analyses. For example — for some concretions from the Jabłonna region J. Pawłowska (1957*b*) gives the following average data: P_2O_5 — 14.2%, SiO_2 — 45.8%, CaO — 30.0%, F — 1.5%. The content of P_2O_5 varies from 12.97 to 22.24% in the Gałęzice region, being 27.34% (one concretion) and 10.0–21.3% in Lechówek and Kowala, respectively. The data presented above should be treated as approximate. There exist no data about the other types of concretions.

CONDITIONS OF SEDIMENTATION AND ORIGIN OF THE PHOSPHORITE-BEARING CULMIAN FORMATION

As is evidenced from the radiolarians, the primary deposit of the Culmian series was formed in deep parts of the sedimentary basin. The basin itself was characterized by a limited water exchange and low activity of bottom flows. Per analogy to the present sedimentation zones of radiolarian muds containing no $CaCO_3$ in the open ocean basins, the depth of deposition under discussion was of several thousand metres. In that zone, changes in rate of deposition and lack of the terrigenous material supply were characteristic. J. Pawłowska (1961*a*) relates that in her two analysed samples "clasts of a very fine-grained siliceous rock" were presented in the concretions. She concluded that supply of clastic material was from the shallower parts of the basin. The re-interpretation of the same samples (thin sections no. 6–65 and 12–65), however, resulted in an observation of the aggregates of recrystallized quartz formed *in situ*.

The primary deposit had the character of radiolarian mud with a high content of the organic matter. As has been already mentioned in the previous section, the presence of plant material in the form of microflora and detritus, as well as in some concretions of filiform organismus which may be algal remnants, is very characteristic. According to the opinion of Z. Sujkowski (1933) there could have existed poor pelagic fauna with limestone shells, the remnants of which were dissolved in the initial stages of the deposit formation. (As is generally known, eupelagic radiolarian muds of that type, being theoretically devoid of calcium, can contain up to 4% of $CaCO_3$ and 10–15% of iron oxides.)

The Culmian deposits were in general formed in reduction conditions, which is evidenced by the black colour of the clay-siliceous shales except for the lower radiolarian horizons and the mottled claystones. The layers and phosphorite concretions, however, display a grey, light-grey or even beige colour, which may indicate periodic changes in oxidation in the floor zone and may be tied to the rate of accumulation of the sediments. Due to the lower rate of deposition in the phosphorite horizons, there existed conditions for oxidation and alteration of the organic matter directly at the bottom of the basin. The high rate of accumulation of the deposits from clay suspension resulted in quick burial of the organic remnants and in a rapid change in conditions into reduction (that change is recorded by a sharp boundary between the light phosphorite strata and black clay shales as well as by a contrast between the colours of the flat concretions from Bolechowice and its neighbourhood). The distribution of the organic matter in such conditions was different and corresponded among others to anaeorobic methane formation and oxidation in the presence of SO_4^{2-} ions. The iron sulphides which followed the reaction, were responsible for the black colour of the deposit.

The contrasting changes in colour are generally less distinct, except for the small layers and phosphorite concretions mentioned above. This fact points to a poor oxidation environment with Eh oscillating around zero. Periods of the dominance of the relative oxidation conditions were very short in the Culmian sedimentation cycle. The initial formation of phosphate peloids and their joining into aggregates should be referred to those periods of minimum oxygen content on the floor zone, as well as to the conditions changing from the boundary between the oxidation and reduction environments.

Direct precipitation of the phosphates on the basin's floor has already been suggested by many investigators (R. P. Sheldon, 1963) as the only explanation for a significant thickness of the peloid layers, often reaching even some tens of metres (e.g., the Eocene phosphorites from Morocco and Algeria, the Phosphoria Formation in Rocky Mts.). Such a process was possible under conditions of bacterial participation in the alteration of organic matter. The bacteria destroy the structure of proteins and form the molecules of orthophosphatic acid reacting directly with the calcium ions (J. Lucas, L. Prevot, 1985), which leads to formation of amorphous, collophane aggregates. The Ca^{2+} ions acted probably as the regulator of the process discussed, while their deficiency moderated further reaction.

The problem has been discussed above in a very simplified way not taking into account the significance of such inhibitors as Mg^{2+} ions, as well as their neutralization, and the ratio of Ca and Mg adequate for the reaction. Fluorine was taken directly from the marine water.

The phosphates were the only compound cementing the deposit in its initial diagenetic stage, while their aggregates in the neighbourhood of the relics of organic matter were responsible for the shape of the concretions. The direct formation of the concretions on the floor of the basin is probably evidenced by the delicate hollows or spines along the longest meridian of the samples. Those forms mark a boundary between water and the deposit. Other evidence is the uneven, nodular upper surface, occasionally preserved.

Evident relics of the genesis of the concretions are not very frequent. In general the surfaces and the traces of sedimentation are masked by the deformed shales. Many samples are also damaged since they come from outcrops and drillings done more than thirty years ago.

Z. Sujkowski (1933) suggested the possibility of the concretions growing on the floor of the basin. He did not, however, present details and the evidence. J. Pawłowska (1961*a*) is of the opinion that the concretions formed due to diagenetic differentiation.

In the initial diagenetic stage during burial the silica of the concretion, which must have started to dissolve already during sedimentation of the phosphates (pH = 7.8) parallel to the increase in alkalinity, underwent further leaching, transformation and precipitation in the pore space, or even transportation outside the concretions (the chalcedony rims over the concretions of the Lower Culmian horizons). The main component of the radiolarian shells — opal — was altered into chalcedony in the first turn.

The next stage of phosphate precipitation in the porous space in the second important process in the initial diagenetic phase, following the silica migration. Those phosphates are called isomorphic with some traces of fibres. They form covers either in the pores after the leached radiolarites or over the other phosphate aggregates. Change in conditions from the boundary (Eh = 0) to reduced ones is manifested by pyrite crystallization.

Further phases of the diagenetic changes within the concretions in the conditions of the deposit overburden, compaction and the decrease in porosity correspond, as it has been already suggested, to the alteration of the isomorphic covers into the chains of the spheroidal crystalline apatite forms. The inner structure of the peloid aggregates has been gradually erased. The aggregates join occasionally into an amorphous fabric with some relics of the organic matter. The alteration of some aggregates into the microcrystalline forms displaying a disordered primary structure (filiforms similar to the rock "cork") can be also observed.

Calcite injections, which occasionally replace silica on the local scale, seen to be the last stage of the interior cementation of the concretions.

An increase in pressure leads to the partial recrystallization of illite in the concretion rims and formation of the polished lustruous covers. Rings of the hydrated iron oxides, which underlie the spherical shape of the forms, were formed after the second phosphate generation on the already precipitated concretions.

CONCLUSIONS

Two generations of phosphorus precipitation have been distinguished in the Culmian basins of the Holy Cross Mts., namely: sedimentary and diagenetic, as well as an alteration phase of collophane into crystalline apatite forms.

It should be stressed here that the decomposition of the organic matter in a weak oxidation environment under the influence of bacteria is dominant in the phosphogenetic processes. The calcium ions act as the regulator of phosphate precipitation a process which takes place in boundary red-ox conditions. The form and position of the collophane accumulations in the deposit suggest the occurrence of the processes discussed directly on the floor of the basin.

These processes resulted in the sedimentary-diagenetic type of concretions referred to the eupelagic deposits and different from the phosphate aggregates in the shallow-water shelf deposits. It was impossible to discover phosphorite deposits in the Carboniferous of the Holy Cross Mts. since the Culmian basin did not display conditions suitable for large-scale phosphorite accumulation (too short periods of oxygen maximum, insignificant amount of Ca ions available for reaction, dominance of strong reduction environment).

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ROZWÓJ PROCESÓW FOSFOGENETYCZNYCH W UTWORACH DOLNEGO KARBONU GÓR ŚWIĘTOKRZYSKICH

Streszczenie

Zbadano fosforyty konkrecyjne i warstwowe z osadów dolnego karbonu Gór Świętokrzyskich występujących w facji kulmu w synklinie gałęzickiej i synklinorium kielecko-łagowskim (fig. 1). Podstawą prac badawczych były preparaty mikroskopowe i próbki geologiczne z kolekcji J. Czarnockiego, J. Pawłowskiej i H. Żakowej. W osadach turneju występowanie fosforytów związane jest z łupkami ilasto-krzemionkowymi i lidytami, zaś w osadach famenu rejonu Kowali z facją wapieni gruzłowych i margli laminowanych z radiolariami (H. Żakowa, K. Radlicz, 1990). W najpełniej wykształconym profilu turneju miąższości 200 m w rejonie Zarębów (fig. 1) wyróżniono dwadzieścia pięć poziomów grubości 20–30 cm z konkrecjami fosforytowymi średnicy 5–80 mm (tabl. I, fig. 4a). Obok form konkrecyjnych występują drobnowarstwowe fosforyty grubości 3–10 mm (tabl. I, fig. 2), stwierdzone w pstrych łupkach z radiolarytami dolnego turneju w rejonie Woli Murowanej i Bolechowic. W laminach fosforytowych notowane są kolofanitowe peloidy i agregaty peloidowe średnicy 0,01–0,15 mm, czasem z reliktami nitkowatych glonów. Udział fosforanów w warstewkach wynosi około 40%, zaś reszta składników to radiolarie, skupienia substancji organicznej i masa kwarcowo-ilasta.

Konkrecje fosforytowe są kuliste i spłaszczone (tabl. I, fig. 4a). Makroskopowo wydzielono konkrecje ciężkie, masywne oraz konkrecje lekkie, porowate i kruche. Budowa konkrecji jest najczęściej zróżnicowana. Zewnętrzną część tworzy chalcedonowa otoczka lub błyszcząca powłoka łupków ilasto-krzemionkowych. Część wewnętrzną tworzą koncentryczne laminy fosforanowe i powłoki dyfuzyjne tlenków żelaza i siarczków. W laminach fosforanowych konkrecji kulistych udział szkieletów radiolarii, głównie z rodzajów *Spumellaria* i *Collodaria*, dochodzi do 60%. Ich kształty i budowa wewnętrzna bywa wyraźniej widoczna dzięki pigmentowi tlenków żelaza (tabl. I, fig. 5). W konkrecjach ciężkich szkielety radiolarii bywają krzemionkowe, czasem metasomatycznie zastąpione przez węglan wapnia lub fosforany. W konkrecjach lekkich, silnie porowatych występują negatywy po wyługowanych szkieletach radiolarii i skupieniach krzemionkowych. Udział radiolarii nie przekracza tu 30%.

Fosforany w konkrecjach występują w formach peloidów, agregatów mikropeloidowych, ameboidalnych agregatów krystalitów apatytowych (tabl. I, fig. 6), otulin powłokowych zewnętrznych i wewnętrznych szkieletów radiolarii (tabl. I, fig. 5) oraz łańcuchowych tworzących zlep szeregowy sferolitów apatytowych (tabl. II, fig. 8, 9). Część powłok jest izotropowa, część zaś włóknisto-sferolitowa, apatytowa (tabl. I, fig. 7; tabl. II, fig. 8, 9). W konkrecjach z Miedzianki masa fosforanowa złożona jest z kulistych sferoidów włóknistego apatytu. Skupienia kuliste bywają złożone z pojedynczych (tabl. II, fig. 11, 12, 13) lub kilku (tabl. II, fig. 10) sferoidów. Ułożenie kryształów apatytu w sferoidach bywa sferoidalne lub wachlarzowe. Sferoidy włókniste częściej występują w dolnych partiach kulmu, natomiast w górnych przeważają skupienia amorficzne. Zróżnicowanie diagenezy substancji fosforanowej w dolnych i górnych partiach kulmu spowodowane jest prawdopodobnie różnymi możliwościami migracji roztworów porowych i warunkami wysokiego ciśnienia.

Krzemionka w konkrecjach występuje zarówno w szkieletach radiolarii, jak i w nieregularnych skupieniach włóknistego chalcedonu i agregatowego kwarcu. Przekształcanie i ługowanie krzemionki zachodziło na dnie zbiornika pod niewielkim nadkładem osadów oraz w etapach późnej diagenezy, prowadząc do wytworzenia się powłok chalcedonu wokół konkrecji.

Środowisko depozycji pierwotnej osadów porównano do środowiska głębokowodnych, bezwapiennych mułów radiolariowych zbiorników oceanicznych. Osady kulmu w postaci kompleksu czarnych łupków ilasto-krzemionkowych, z wyjątkiem dolnych poziomów radiolarytowych i pstrych iłowców, tworzyły się w warunkach redukcyjnych. Warstewki i konkrecje fosforytowe bywają szare i jasnoszare, co wskazywałoby na okresowe zmiany natlenienia strefy przydennej. Wolniejsze tempo sedymentacji mogło wytworzyć bardziej utleniające warunki do przemian substancji organicznej. Szybsze narastanie osadów zawiesin ilastych prowadziło do szybszego pogrzebania szczątków organicznych i gwałtownej zmiany środowiska na redukcyjne (ostra granica między jasnymi warstewkami fosforytowymi oraz konkrecjami płaskimi z Bolechowic i czarnymi łupkami ilasto-krzemionkowymi). Rozkład substancji organicznej zachodził tu w wyniku anaerobowej działalności i utleniania metanu w obecności jonu SO_4^{2-}. Tworzące się w następstwie siarczki nadawały osadom czarne zabarwienie. W większości przypadków barwy osadów i fosforytów są mniej kontrastowe, co świadczy o słabo utleniającym środowisku. Inicjalne tworzenie się peloidów fosforanowych i łączenie się w agregaty należy wiązać z krótkimi

okresami pewnego minimum zawartości tlenu w strefie przydennej i z warunkami pośrednimi między środowiskiem utleniającym i redukcyjnym. Bezpośrednia precypitacja fosforanów jest możliwa przy założeniu, że w przemianach substancji organicznej uczestniczyły bakterie, które niszcząc strukturę białka wytwarzającą cząstki kwasu ortofosforanowego reagujące bezpośrednio z jonami Ca^{2+} (J. Lucas, L. Prevot, 1985). Jony Ca^{2+} stanowiły zapewne regulator tego procesu, a ich deficyt hamował dalszy jego przebieg. Fosforany były jedynym elementem cementującym osad we wczesnym stadium diagenezy na dnie zbiornika, a ich skupienia w sąsiedztwie reliktów substancji organicznej określały kształt konkrecji. Dalszy rozwój cementacji zachodził głównie w miejscach ługowania krzemionki ze szkieletów radiolarii w wyniku penetracji roztworów porowych i drugiej fazy precypitacji fosforanów. Dalsze stadia diagenezy doprowadziły do krystalizacji włóknistego, sferoidalnego apatytu.

PLATE I

Fig. 2. The contact of the clay shales with radiolarians with a light grey phosphorite lamina (lower part of the photograph). Bolechowice, thin section 11/65, about x 40, crossed nicols

Kontakt łupku ilastego z radiolariami z jasnoszarą warstewką fosforytu (dolna część zdjęcia). Bolechowice, szlif 11/65, ok. 40 x, nikole skrzyżowane

Fig. 3. Phosphate peloids (black rounded aggregates) from the stratal phosphorite, radiolarians and silica filling the pores (white) are seen. Wola Murowana, thin section 16/30, x 125, without analyser

Peloidy fosforanowe (czarne okrągłe skupienia) z fosforytu warstwowego, widoczne radiolarie i krzemionka wypełniająca pory (białe). Wola Murowana, szlif 16/30, 125 x, bez analizatora

Fig. 4. Sedimentary trace of the contact of the concretion with the floor of the basin (depression running along the concretion periphery). Zaręby, sample no. 3, x 1.5

Sedymentacyjny ślad kontaktu konkrecji z dnem zbiornika (wgłębienie biegnące wzdłuż obwodu konkrecji). Zaręby, próbka nr 3, 1,5 x

Fig. 5. Radiolarian with impregnations of hydrated iron oxides and covers and fillings of isotropic and spheroidal phosphates. Black spots are iron-rich pigment and organic matter. Jabłonna, thin section 16/30, about x 40, without analyser

Radiolarie z impregnacjami uwodnionych tlenków żelaza oraz powłokami i wypełnieniami fosforanów izotropowych i sferoidalnych. Czarne plamy pigmentu żelazistego i substancji organicznej. Jabłonna, szlif 16/30, ok. 40 x, bez analizatora

Fig. 6. Fragment of the aggregate of the apatite microcrystallites displaying spheroidal and needle-like structure similar to rock "cork". Galęzice, thin section 5/65, x 125, crossed nicols

Fragment agregatu mikrokrystalitów apatytowych o strukturze sferoidowo-igiełkowej, przypominającej pilśń. Gałęzice, szlif 5/65, x 125, nikole skrzyżowane

Fig. 7. Peloid aggregates with cementation covers of the spheroidal phosphate. Empty spaces after the leached silica (white) are also covered with cement covers. Intensively black accumulations — organic matter. Gałęzice, thin section 5/65, x 32, without analyser

Agregaty peloidowe z powłokami cementacyjnymi fosforanu sferoidalnego, którymi wysłane są również pustki po wyługowanej krzemionce (białe). Skupienia intensywnie czarne — substancja organiczna. Galęzice, szlif 5/65, x 32, bez analizatora

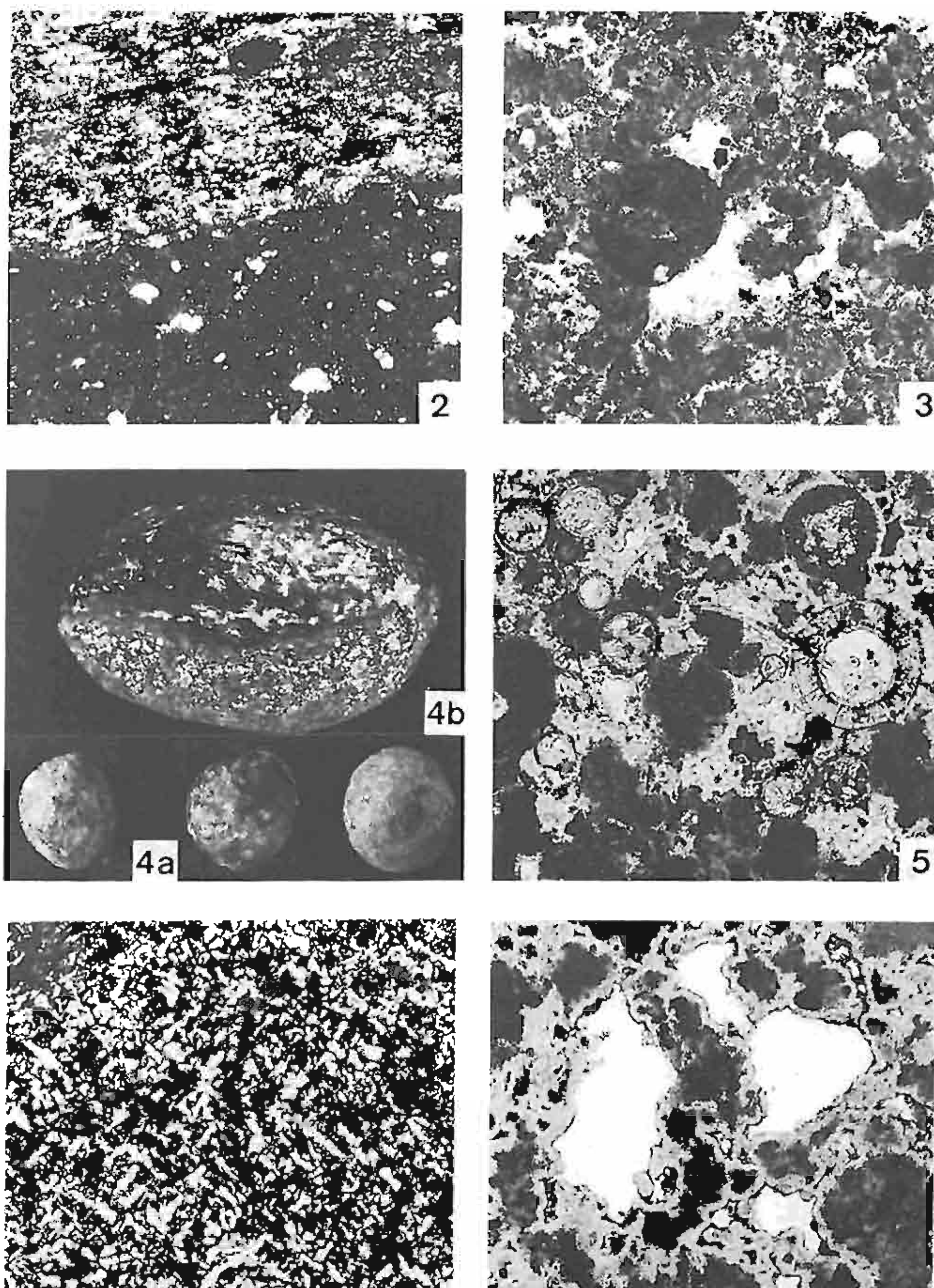

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PLATE II

Fig. 8. Covers of spheroidal phosphate densely filling the spaces between pelloids and the interior of the radiolarians. Pores filled with silica. Jabłonna, thin section 14/65, x 40, without analyser

Powłoki fosforanu sferoidalnego szczelnie wypełniające przestrzenie pomiędzy peloidami oraz wnętrza radiolarii. Pory wypełnione krzemionką. Jabłonna, szlif 14/65, 40 x, bez analizatora

Fig. 9. As above; crossed nicols

Jak wyżej; nikole skrzyżowane

Fig. 10. Phosphate spheroids adjoined one to another and the characteristic porosity between the crystalline structures. Zaręby, sample no. 3, x 7200 SEM

Stykające się ze sobą sferoidy fosforanowe i charakterystyczna porowatość między strukturami krystalicznymi. Zaręby, próbka nr 3, 7200 x SEM

Fig. 11. Phosphate spheroid of diameter about 50 μm filled by over ten forms of feather — fan texture. Zaręby, sample no. 3, x 1000 SEM

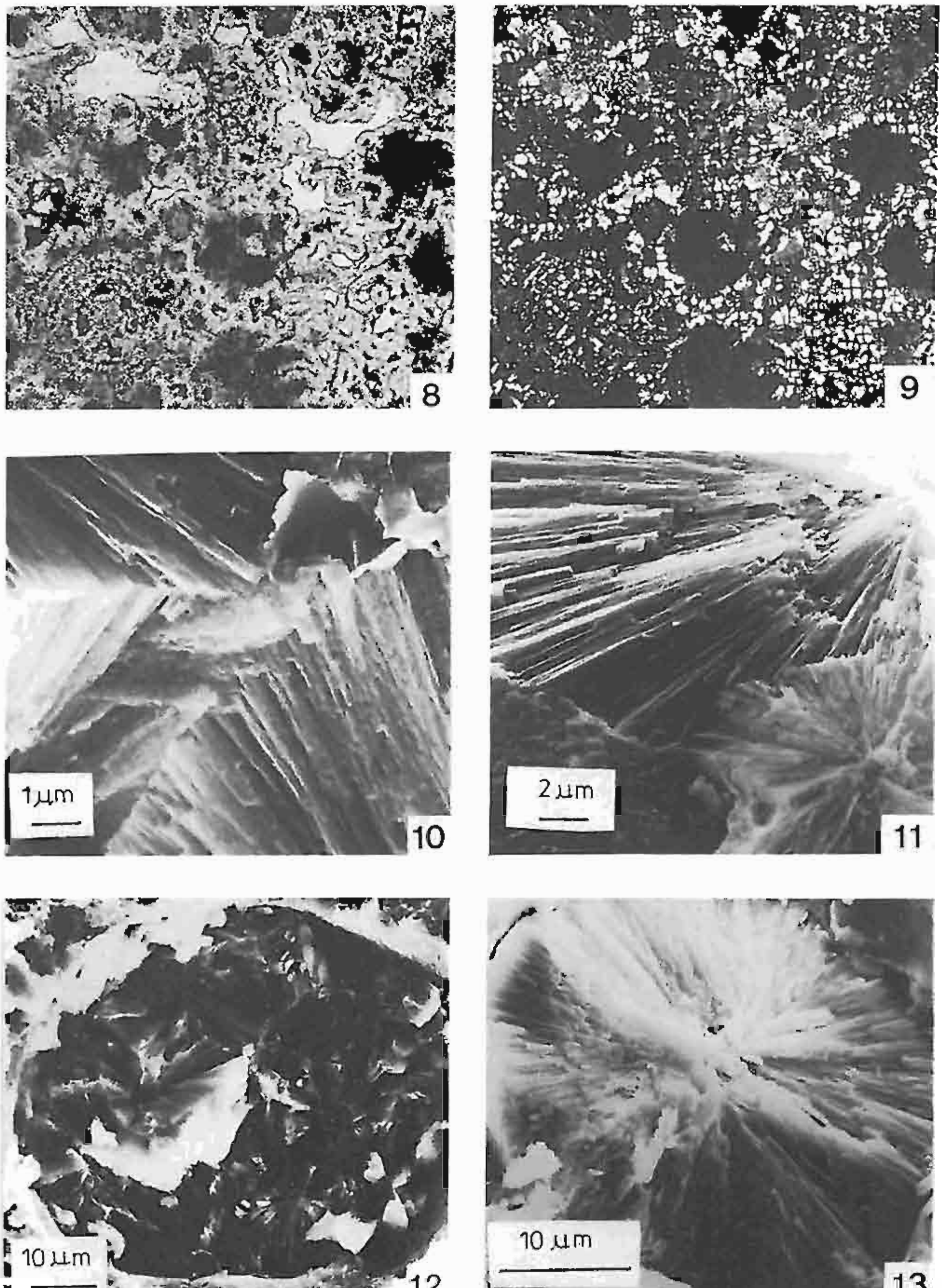
Fosforanowy sferoid średnicy ok. 50 μm wypełniony przez kilkanaście nakładających się na siebie form o strukturze pierzasto-wachlarzowej. Zaręby, próbka nr 3, 1000 x SEM

Fig. 12. Phosphate spheroid with well developed overgrowth. The details of the feather-fan texture seen. Zaręby, sample no. 2, x 3600 SEM

Fosforanowy sferoid z wyraźnie wykształconą otoczką. Widoczne szczegóły budowy pierzasto-wachlarzowej. Zaręby, próbka nr 2, 3600 x SEM

Fig. 13. Phosphate spheroid of diameter 35 μm built of only one feather-fan texture. Zaręby, sample no. 2, x 2000 SEM

Fosforanowy sferoid o średnicy 35 μm zbudowany tylko z jednej struktury pierzasto-wachlarzowej. Zaręby, próbka nr 2, 2000 x SEM



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