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Biostratinomy and Diagenetic Impact on Exceptional Preservation of Coccospheres from Lower Oligocene Coccolith Limestones

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Received: 31 May 2020; Accepted: 6 July 2020; Published: 9 July 2020



Abstract: Lower Oligocene coccolith limestones, known as Tylawa Limestones, in the Polish part of the Outer Carpathians have been analyzed using back-scattered electron (BSE) and charge contrast imaging (CCI) techniques and X-ray diffraction. The aim of the study was to reconstruct the fossilization history of the excellently preserved coccospheres, commonly observed in these sediments, deposited in the Paratethys basin. Multiple petrographic and geochemical analyses indicate that the exceptional preservation of coccospheres has been caused by the special coincidence of biostratinomic processes: pre- and post-depositional processes within the water–sediment interface and possible early cementation. We discuss the origin of the calcite and silica and provide some hypotheses regarding the environment and possible factors responsible for the spectacular preservation process. Based on the observed intermediate steps of calcite and silica alteration, we propose an extended model of biostratinomic processes and diagenesis. The possibility of finding exquisitely preserved coccospheres not only in soft clay-rich deposits but also in heavily lithified rocks extends the possibilities of research on the development and evolution of this group of organisms.

Keywords: taphonomy; silicification; calcification; dolomite cement; redox; pyrite; pellets; Reticulofenestra; Carpathians; Paratethys

1. Introduction

Coccolithophores are a group of unicellular calcifying haptophyte algae living in the photic zone of the oceanic environment. Each coccolithophore cell secretes intracellularly minute calcitic particles, the coccoliths, which after completion are exocytosed and incorporated into the coccosphere. Individual coccospheres may consist of a few or a few dozen coccoliths. Individual coccolith plates are small $(1-10 \ \mu\text{m} \text{ in diameter})$ biomineral structures that consist of interlaced single calcite crystals with a highly complex morphology [1].

Coccoliths are formed of low-Mg calcite, thus, they have a high potential for fossilization process. Therefore, since the Mesozoic up to the present times, coccoliths are an important component of pelagic carbonates covering the basin floor above the calcite compensation depth [2] and a significant source of calcium carbonate in different types of marine deposits [3]. Especially during the Late Cretaceous, a huge accumulation of coccoliths and coccolith debris played a significant role in formation of chalk and opokas lithofacies in most parts of the epicontinental European Basin [4–8].

However, entire preserved coccospheres are rare in the fossil record. Only few publications describe and illustrate complete coccospheres [9–14]. The oldest coccospheres that were found come from the

Toarcian calcareous shales of the Paris Basin [15]. Another example came from the Upper Jurassic Kimmeridge Clay Formation (Dorset, UK) [16,17] from coccolith stone bands which occur within nannofossil subzone NJ17a [18]. Most of the best preserved fossil coccospheres have been found in clay-rich hemipelagic sediments that have not been affected by more advanced diagenesis [13,17,19,20]. Many other examples come also from laminated limestones, e.g., the Kimmeridge White Stone Band [16,17].

A special example is finely laminated coccolith limestones known as the Tylawa Limestones in the Outer Western Carpathians. These deposits contain common pelletal structures composed of excellently preserved coccospheres in strongly lithified laminated coccolith limestones which lie within monotonous siliciclastic turbidite facies [21–25]. The Tylawa Limestones are well known as isochronous regional markers within Lower Oligocene deposits in the Outer Carpathians [23,26–29] and have an important stratigraphic potential [30,31]. They are also known as "taphonomic window for vertebrates" because they contain many excellently preserved fish remnants [32]. In this context the Tylawa Limestones are another example of micro-laminated limestones formed from pellets of coccospheres in euxinic environments [26-29] where taphonomic processes have led to understanding the biological diversity of fossil organisms. In particular such types of limestones are important in the Late Jurassic and Early Cretaceous, the most famous example being the Upper Jurassic Plattenkalk from Solenhofen region of Bavaria (Germany) containing many well preserved fossils, including numerous vertebrates [33] and notably Archaeopteryx [34,35]. Another, probably the best documented example of such type of micro-laminated limestone is the white stone band of the Kimmeridge Clay Formation [16]. The Middle Barremian Munk Marl Bed in the central North Sea area which consists of alternating laminae of calcareous nannofossils and clayey material is another good example [36].

Ciurej [29] first discovered the excellent preservation of the coccoliths and complete coccospheres in the alternating white/dark laminae couplets typical of the Tylawa Limestones, visible both in freshly broken rock-chips and in the scanning electron microscope (SEM). The aim of the study was to reconstruct the fossilization history of these excellently preserved coccospheres in the Lower Oligocene coccolith limestones in the Polish part of the Outer Carpathians via microscopic observations and X-ray diffraction analysis of samples. Based on the observed intermediate steps of calcite and silica alteration, we propose an extended model of biostratinomic processes and diagenesis. We discuss the origin of the calcite and silica and provide some hypotheses regarding the environment and possible factors responsible for the spectacular preservation process. The possibility of finding exquisitely preserved coccospheres not only in soft clay-rich deposits but also in heavily lithified rocks extends the possibilities of research on biology, development, and evolution of this group of organisms. Moreover, such limestones are often very important for preservation of vertebrate fossils.

2. Geological Setting

2.1. General Outline

The studied laminated coccolith limestones, the Tylawa Limestones, occur in the Polish part of the Outer Western Carpathians (Figure 1a), which comprises several units (nappes and thrust-sheets), regarded as remnants of oceanic basins. They were folded and thrusted mainly in the Early and Middle Miocene times [37,38]. The studied deposits form outcrops in localities from three nappes of this region, i.e., the Skole, Silesian, and the Dukla nappes (Figure 1b) consisting of the Upper Jurassic through Neogene (Miocene) flysch deposits. The Tylawa Limestones occur in a synorogenic succession, up to ca. 3 km thick (Late Eocene–Early Miocene) which was laid down in a closing basin (Paratethys), whose communication with the Mediterranean area became periodically restricted [38,39].



Figure 1. Location of study area. (**a**) Simplified geological map of the Outer Carpathians with the location of study area. C.F.—Carpathian Foredeep, I.C.—Inner Carpathians, P.B.—Panonian Basin, PKB—Pieniny Klippen Belt, T.B.—Transylvanian Basin, V.B.—Vienna Basin (after [38]); (**b**) simplified geological map of Polish part of the Outer Carpathians (after [37]) with the localities of the studied sections.

2.2. Lithostratigraphy and Biostratigraphy

The Upper Eocene and Oligocene strata consist of variable facies, from black shales to coarse-grained sandstones representing gravity-driven mass-flow deposits [40], locally with olistostromes and slump sediments [41–43]. The lower part of the Oligocene sequence is represented by the conglomeratic Mszanka Sandstones [44] and Globigerina Marls [45], overlaid by Menilite Beds, which are dominated by mostly non-calcareous, organic-rich, brown or black mudstones, and dark grey siltstones. Laying above is thick series of micaceous calcareous sandstones and grey marlstones, known as the Krosno Beds and the Kliwa Sandstone which are diachronous across the Outer Carpathian subbasins (Figure 2). The Krosno Beds appeared first in the internal subbasins (Dukla subbasin) and prograded outwards, while the Kliwa Sandstone prograded from the external margin to the Skole basin. Due to restricted connections of the Paratethys Sea with the surrounding deep basins of the Mediterranean Sea [46], this sequence is poor in stratigraphically useful fossils and the presence of many endemic faunas and floras, assigned to the Paratethys bioprovince [47,48], limits precise biostratigraphic correlation with the coeval strata of the open ocean [49].

The Tylawa Limestones is one of four isochronous coccolith limestone horizons present within the Oligocene sequence ([23] and citations herein) (Figure 2). Others are the Jasło, Sokoliska and the Zagórz limestones. The Tylawa Limestones lies in the middle of the nannoplankton NP23 Zone in the regional scheme of Martini [23,24,26,27,29,50]. The former Jasło, Sokoliska and Zagórz limestones were laid down during the Rupelian-Chattian transition within the NP24 zone [27,51–54].





3. Materials and Methods

3.1. Sampling

The samples were collected continuously from the Tylawa Limestones from the Polish part of the Outer Carpathians, in five sections as follows: a—Duszatyn (DUSZA), b—Tylawa (TYL), c—Rudawka Rymanowska (RR), d—Iwla (IWLA), and e—Janowice (JAN) (Figures 1 and 3). Duszatyn and Tylawa sections belong to the Dukla unit, the Rudawka Rymanowska and Iwla sections represent the Silesian unit, while the Janowice section comprises deposits of the Skole unit (Figure 1b). The detailed location, geology, and lithological logs of the studied sections with locations of studied samples were presented by Ciurej [29] and Ciurej and Haczewski [24].

For a detailed study we divided the collected samples into three groups: (1) samples with clearly visible alternating white-dark laminae couplets typical of these deposits, with a nodular structure, but without any macroscopic sign of silicification (Figure 4a), (2) samples with packages of light and dark laminae covered by dark silica or chert, where both the laminae and nodular structure are barely recognizable with the naked eye and only slightly better under optical microscopy and SEM (Figure 4b), and (3) samples with packages of laminae that are nearly completely obliterated by dark cherts (Figure 4c).

Twenty-five standard uncovered petrographic thin sections with a size of approximately $3 \text{ cm} \times 5 \text{ cm}$ were made from representative samples. Twenty thin sections were cut perpendicular to the lamination, and five were cut at angles from 30° to 50° to the lamination to obtain various perspectives. The thin sections are stored at the Pedagogical University of Cracow (UP), Kraków, Poland.



Figure 3. Natural outcrops of the Tylawa Limestones: (**a**) Rudawka Rymanowska (RR), Wisłok river, in the higher part of profile, intercalated by shale and sandstone. State as of 2006; (**b**,**c**) Tylawa (TYL), Jasiołka river, in the higher part of profile intercalated by series dominated by nonlaminated limetones (**b**) and in the lower part within series dominated by shales (**c**). State as of 2007; (**d**) Duszatyn (DUSZA), Osława river; within shale-sandstone series. State as of 2007; (**e**) Iwla (IWLA), Iwełka river, within dominated by black shale series. State as of 2007; (**f**) Janowice (JAN), within series of shale intercalated by cherts. State as of 2004. Scale: hammer—30 cm or tape measure with centimeter scale. Detailed logs with locations of presented samples are presented in Ciurej [29] and Ciurej and Haczewski [24].

3.2. Transmitted Light Microscopy (TLM) and Scanning Electron Microscopy (SEM)

All thin sections were observed under a conventional transmitted light microscope (TLM) using an Olympus SZX9 polarizing microscope with a digital camera (Olympus U-TVO.5XC-2), housed at the Faculty of Geology, Geophysics, and Environmental Protection of the AGH University of Science and Technology, Kraków, Poland. Images were obtained from transverse and longitudinal thin sections of samples. Fifteen thin sections were mapped and studied under SEM using the method described by Ciurej [56]. The study was carried out using two modes of observation: back-scattered electron (BSE) mode, which provided information on chemical composition, and charge contrast imaging (CCI), which provided structural information on the components ([56] and references therein). The combination of both CCI and BSE modes for the same area allowed us to observe the biogenic particles, such as the coccolithophore material, their state of preservation, the presence of cement and the chemical/mineral composition. Additionally, the chemical/mineral composition of the studied components and cement were determined using energy dispersive spectroscopy (EDS). Rock chips were observed on SEM using the SE and BSE modes. Three different SEM instruments were used: (M1) FEI Quanta 200 FEG, housed at the AGH University of Science and Technology, Kraków, Poland, (M2) HITACHI 3-4700 housed at the Institute of Geological Sciences of the Jagiellonian University, Kraków, Poland, and (M3) FEI Nova NanoSEM 200 housed at the Institute of Ceramics and Composites, Warsaw, Poland. The parameters of observation were different for each instrument and are given on each image.



Figure 4. Tylawa Limestones composed of alternating light/dark of laminae, with a nodular structure and three types of silicification: (**a**) macroscopic and optical microscope (**a1,2**) views of samples with clearly visible alternating light-dark laminae couplets (LL/DL) typical of these deposits, with a nodular structure, that usually consist of closely packed pellets (red arrows) in LL. Silicification is observed in all LL, mostly as infilling of pelletal structures (Si on **a1,2**) located near the border with DL. Note that silicification is not visible in macroscopic images, however it is well visible in optical microscope. Sample TYL 9B/07; (**b**) macroscopic and optical microscope (**b1,2**) views of samples with packages of light and dark laminae covered by dark silica or chert (green arrows), where both the laminae and nodular structure are barely recognizable with the naked eye and only slightly better under optical microscopy (red arrows). Sample IWLA 5/07; (**c**) macroscopic and optical microscopic and optical microscope (**c1,2**) views of samples with packages of laminae that are nearly completely obliterated by dark cherts (red arrows). Sample JAN 5A/04. **a–c**—polished rock sections; **a1–c2**—thin sections; 1N—plane-polarized light, XN—crossed-polarized light. All samples cu perpendicular to the lamination, except the sample a1—cut at angles to the lamination.

3.3. X-ray Powder Diffraction

The mineralogy of eight selected samples was determined on randomly oriented powder specimens (Table 1). The aim was to obtain information on individual laminae and their packages in laminated limestone and selected non-laminated surrounding rocks. Two samples from individual laminas were obtained with a dental scalpel, using an optical magnifier. Packages of several laminas and selected laminated rocks were crushed and milled using an agate mortar and then agate mill. X-ray diffraction measurements were carried out using Philips X'Pert PW 3020 diffractometer, equipped with graphite monochromator—located in the X-ray diffraction laboratory in the Faculty of Geology, Geophysics, and Environmental Protection, AGH University of Science and Technology, AGH, Kraków, Poland. Diffractograms were recorded with Cu radiation in the range of 2–73° 2Θ, with a step size of 0.05°, registered every 1 s.

Sample	Lithology	Quartz	Plagioclase	Calcite	Pyrite	Siderite	Ankerite	Kaolinite	Muscovite	Illite-Smectite	Smectite	SUM
RR 2/06	Laminated limestone	10.3 (0.192°)		85.6			0.5			3.6		100.0
RR 6/06	Laminated limestone	24.7 (0.198°)		62.0	0.8		0.6			11.9		100.0
IWLA 5/07	Laminated limestone	30.9 (0.181°)		67.9	0.3		0.3			0.6		100.0
IWLA 6/07	Laminated limestone	28.2 (0.193°)	1.1	53.4	1.2	1.0	0.7	0.6		8.4	5.4	100.0
DUSZA 2B/07	Laminated limestone	25.5 (0.187°)		52.1	1.1	0.5	6.3		9.7	4.8		100.0
DUSZA 6/07	Laminated limestone	13.9 (0.173°)		82.4			2.0			1.7		100.0
TYL 3/07	Dark lamina	10.5 (0.171°)		74.8	0.5		1.8		4.8	7.6		100.0
RR 4-3	Dark lamina	33.3 (0.185°)	1.2	35.0	2.5	0.4	3.5	6.7	8.3	9.1		100.0

Table 1. Results of mineralogical analysis of selected samples. Angles in brackets are lower full width at half maximum (FWHM) of quartz peaks in degrees.

Q-MIN software (M. Szczerba, Institute of Geological Sciences PAS, Kraków, Poland) was used for quantitative analysis. Determination of mineral composition was achieved by matching of the sum of the diffraction patterns of mineral standards to the pattern of analyzed rock sample. During the matching some parts of diffraction pattern were excluded from analysis. These were the ranges where reflections of clay minerals that are significantly affected by humidity are located (2Θ below 15°). Additionally, there was discrepancy in level of background between registered diffractograms and diffractograms in the database in the Q-MIN program, as these have been registered on different diffractometers

4. Results

4.1. General Sedimentary Features of the Tylawa Limestones

The Tylawa Limestones (TL) are present as single bed or as groups of several beds, with bed thicknesses generally ranging from 0.5 to 4 cm up to a maximum of 28 cm (Figure 3). The total thickness varies between the sections. The host sediments are usually much thicker than the coccolith limestones, so the entire interval with coccolith layers attains thicknesses slightly above 100 m. The intercalated sediments are typically black shales, hemipelagic limestones, siliciclastic turbidites, and other types of gravity mass-flow deposits.

In the sections studied, the Tylawa Limestones have the following characteristics: (1) Rudawka Rymanowska—18 layers with a total thickness of 38.7 cm in an 18.6 m thick profile (Figure 3a); (2) Tylawa—12 layers with a total thickness of 18 cm thickness within a 115.3 m thick profile (Figure 3b,c); (3) Duszatyn—four layers with a total thickness of 24.7 cm within a 50.45 m thick profile (Figure 3d); (4) Iwla—five layers with a total thickness of 9.7 cm within of a 92 m thick profile (Figure 3e); and (5) Janowice—three layers with a total thickness of 39.9 cm within a 4.15 m thick profile (Figure 3f). In all sections, the TL display typical fine lamination with a nodular structure (Figure 4). Within some layers, cherts are visible and occur as layers or nodules within individual laminae or within packages of several laminae (Figure 4c). Such layers are seen sporadically in the studied section, except in the Janowice section, where these are more common. In samples with cherts, the laminae structure is obliterated to varying degrees and variously recognizable. In all sections (except Janowice), the typical surrounding sediments are black, non-calcareous shales (Menilite Shales), mudstones, non-laminated limestones, dark brown marls of the Dynów Marls type and several thin layers of black cherts. In the Janowice section, silicified shales and black cherts dominate.

4.2. Microtexture of the Tylawa Limestones

The millimeter-scale white-dark grey laminae couplets observable with the naked eye in the Tylawa Limestones are composed of alternating light and dark laminae in submillimeter- to micrometer-scale when viewed in the light microscope or SEM (Figure 4). The light laminae in all of the studied samples are bioclastic wackestone/packstone, with thicknesses of 20–600 μ m (Figure 5). They consist predominately of coccospheres, coccoliths, and coccolith debris. Coccolithophore material is usually packed into nodular structures which are fusiform to lenticular in shape (red arrows in Figures 4 and 5a). Presence of the nodular structure generates wavy lamination visible both in micrometer- and milimeter-scale (Figure 4). The nodular structures (Figure 4, Figure 5, and Figure 6a–d) vary in sizes from 30 to 300 μ m in cross section and up to 1000 μ m in length. SEM observations show that these structures are not homogenous and usually consist of several closely packed pellets (Figure 5a). All examined pellets consist predominately of coccolith mass and whole coccospheres (Figures 5 and 6a–d). Complete coccospheres are concentrated predominantly in pellets which are located in the central part of light laminae. Coccoliths and coccolith debris occur more often in more peripheral parts of light laminae (Figure 5a and 6).



Figure 5. The scanning electron microscope (SEM) images showing details of coccolithophore material and cementation within pellets within light laminae: (a) SEM-back-scattered electron (BSE) image showing spatial relationships between components within light laminae (LL) separated by dark laminae (DL, dashed lines). The closely packed pellets (p), composed of calcite coccospheres (b enlarged on b1,2), coccoliths, and coccolith debris are the main components of all LL The various mineral phases of calcite (light gray) and silica (dark gray) are visible within LL. Sample JAN 3/04; (b1,2) the same area in SEM BSE and SEM charge contrast imaging (CCI) images, respectively, and (c,d) SEM CCI images showing the morphological details of variously oriented cross sections of coccospheres and individual coccolith plates, in samples with different types and state of cementation: silica (Si on b1,2), calcareous cement (Cal on (c)), and free of cement (d). In perpendicular coccospheres the tight interlocking of adjacent coccolith plates (placoliths) with well visible distal (di) and proximal (pr) shields. The shields of placoliths are joined by wide central area (ce) closed by parallel calcite crystallites, as seen in perpendicular, and as the reticular structure (ce1) in the horizontal cross sections. Proto-coccolith rings are visible in some of the coccospheres (ri). Note the exquisite state of preservation of all specimens, with neither dissolution marks nor replacement by silica, and lack of advanced diagenetic compaction. Samples: JAN 3/04 (b), TYL 3/07 (c), RR 2/06 (d).



Figure 6. The SEM images of the cococospheres and cementations inside of the pellet. (a) SEM BSE image of light lamina (LL) with the pellet (p) located in the external part of the fusiform structure with complete coccospheres, near the contact with dark lamina (DL); note that the silica cement (dark gray circular) is more common in the outer parts of the LL and gradually infiltrated into pellet, and calcite cement dominate in the central part of LL; (b) close up view of figure (a) in SEM-BSE mode, showing that nano- α -quartz (black arrows, Si) and micro- α -quartz crystal (green arrow) infill the voids in coccospheres (yellow arrows) and space between micrite particles, the caltite (Cal) cement is also observed; (Si, Cal—points examined by energy dispersive spectroscopy (EDS), shown in (f); (c) close up view of (a) in SEM CCI mode, showing the exquisitely preserved calcite coccospheres filled with quartz crystals pseudomorphoses after calcite crystals with rhombic cleavage (white arrows); (d) close up view of (c) in SEM CCI mode, showing the exquisitely preserved coccospheres filled with micro- α -quartz (green arrow), and quartz pseudomorph after calcite crystal (white arrow). Note lack of dissolution marks, nor replacement by silica of any coccolith plates from coccospheres; (e) close up view of (a) in SEM BSE image showing of boundary (yellow dashed line) between dark lamina (DL) and pellet (p). Components are indicated as follows: coccolith debris (black arrows), subhedral calcite crystal (red arrow), quartz pseudomorph after calcite crystal (white arrow), pyrite framboid (blue arrow); (f) EDS analyses of the points Si and Ca in (b). Sample DUSZA 2B/07.

The dark laminae, with thicknesses usually ranging from 3 to $100 \ \mu\text{m}$, are much thinner than light laminae. They surround lenticular and nodular structures composed of coccolithophores material. Very thin dark laminae are usually composed of parallel oriented fibers and sheets of clay minerals and organic matter, fine siliciclastic detrital grains, micrite, and authigenic minerals (Figure 6e).

4.2.1. Biogenic Fraction

The biogenic content of the Tylawa Limestones corresponds to biogenic particles (or fragments and voids after skeletons) observed in SEM images (Figures 5–7). It is composed of coccolithophore skeletons material and diatoms.



Figure 7. The SEM BSE images showing the voids after diatoms observed within dark laminae. (**a**,**b**) Variously preserved lenticular and cylindrical voids (yellow arrows) with the inner walls covered by cristobalite spherulithes interpreted as remnants of frustules of pennate diatoms, which were intensively dissolved. The pyrite crystals and framboids (pyr) are present inside some voids. Note the "discontinuity structures" (x), which are coming out from the voids and spreading to different distances. That may indicate the circulation of silica released during dissolution of diatoms frustule. The deformation of clay mineral sheets and micas flakes are observed (green arrows). Sample TYL 3/07.

The coccolithophore material is the most common biogenic fraction in the studied deposits. Coccolith density was quantified manually on SEM images at magnification $2000 \times [57]$. It was graded from high (10,000–15,000 specimens per mm²) inside pellets where the whole coccospheres are absent, to medium (5000–10,000) in pellets where complete coccospheres are present. In the dark laminae coccoliths and coccolith debris are absent. Coccoliths observed in a cross-section (in coccospheres and as singular particles), are predominantly very well-preserved with clearly observable structure (Figure 5b–d). Only less than 30% of the coccoliths population is partly or completely overgrown by calcite or quartz crystals (Figure 5b,c).

Within numerous specimens of coccospheres the morphological details are very well preserved, with well visible interlocking of adjacent coccolith plates (placoliths), and well visible distal and proximal shields. The shields of observed placoliths contain a wide central area closed by a reticular structure (Figure 5c,d).

In addition to complete coccospheres, there are also forms containing proto-coccolith rings (the initial calcite crystal of coccolith) [58] and partially formed coccoliths prior to completion of growth and exocytosis onto the cell surface (Figure 5d).

Diatom frustules are rarely present in the Tylawa Limestones. They occur only in the dark laminae. Diatoms occur as separated parts of frustules, or more commonly as characteristic angular voids after dissolved frustules. Voids might be compacted and/or have secondary infills by pyrite framboids (Figure 7).

4.2.2. Abiogenic Micritic Fraction

The micritic fraction corresponds to particles smaller than 10 micrometers, including no identifiable structures of biogenic origin. Micrite is present in both types of laminae. It is composed of disintegrated coccolith plates, and calcite crystals. Micrite morphology is predominantly isometric to rhombohedral, sometimes ovoid to elongated. Micrite shapes are usually subhedral and anhedral. Euhedral crystals are rare. There are also small (<1 μ m) rounded grains which are termed pseudomicrite.

4.3. Mineralogical Composition

In total, eight samples were analyzed by X-ray powder diffraction for mineralogical purposes (Table 1, Figure 8). The six samples from limestones containing light and dark laminae from different localities have similar mineral composition. The dominant mineral is calcite, which is found in the range 52.1–85.4% (Table 1). The second most common mineral is quartz: 10.3–30.9%. All the samples contain illite-smectite (0.6–11.9%) and ankerite (0.3–6.3%); some in very small amounts, like the samples IWLA 5/07 and RR 2/06. Pyrite is also very common mineral, found in amounts of 0.3–1.2%, with exception of the samples RR 2/06 and DUSZA 6/07. Plagioclase (sodium form), siderite, kaolinite, muscovite, and smectite are minerals less common and found only in some of the studied samples opal-CT has not been detected.



Figure 8. Comparison of experimental and calculated diffractograms of samples selected for mineralogical analyses. Part of the patterns below 15° 2 Θ were excluded from analysis because of existence of smectite/illite-smectite minerals, which have peak positions that are significantly affected by humidity, and because of discrepancy in level of background between registered diffractograms and the ones from database of the QMIN program. Sm—smectite, M—muscovite, I/S—illite-smectite, Kln—kaolinite, Cal—calcite, Q—quartz, Pl—plagioclase, Pyr—pyrite, Ank—ankerite, Sid—siderite.

Two samples extracted from dark laminae, RR 4-3 and TYL 3/07, both contain muscovite, along with dominating calcite and quartz minerals. The sample RR 4-3 is relatively rich in kaolinite (6.7%) and pyrite (2.5%), compared to the laminated limestones. It contains also the lowest content of calcite (35.0%) and the highest of quartz (33.3%). The sample TYL 3/07 has simpler mineralogical composition and is more similar to other samples from laminated limestones.

Additionally, the most intensive quartz peak was analyzed for peak broadening. There is however no clear trend. It is visible that samples from dark laminae do not have significantly different quartz

crystallinity (Table 1). These two analyzed samples seem to have slightly more crystalline quartz population (lower full width at half maximum (FWHM) of the quartz peaks), compared to its equivalent in the laminated limestones.

SEM-EDS analyses show the location of individual mineral phases in the samples studied (Figures 9–11). The most diverse mineral composition occurs in dark laminae and in light laminae near the contact with dark laminae.



Figure 9. SEM images of the mineral composition in the light laminae near the contact with dark laminae. (a) SEM charge contrast imaging (CCI) image showing the outer parts of pellets (p) with tightly packed coccoliths and coccolith debris, without any dissolution marks (yellow arrows) and some etched ones (green arrows), located mostly near the pellet boundary (dashed line), separated by various mineralogical phases, such as the silica cement (Si,), calcite grains (Ca), and quartz (Qtz). Sample RR 1B/06; (b) SEM BSE image showing components on the contact (dashed line) of light laminae (LL) and dark laminae (DL), as follows: muscovite (Mus), ankerite (Ank), organic matter (OM), pyrite (Pyr), dolomite (Dol), quartz (Qtz). Sample RR 1B/06.

Calcite is the main mineral component of light laminae because it is the primary ingredient of coccolith plates, which are densely packed in pellets (Figure 9a). Mica flakes and quartz grains are detrital components randomly distributed and rarely present in pellets (Figure 9a,b). Authigenic crystals are present in light laminae usually in the 10-50 micrometers thick outer zone of pellets (red arrows in Figure 11). The rhombohedra of dolomite, ankerite, siderite, and calcite are common and randomly distributed in the outer parts of pellets and in the peripheral parts of light laminae (Figures 9b, 10 and 11). Some of them possess zonal internal structure (Figure 11a,b). EDS analyses showed that some cross sections of rhombic minerals which can represent dolomite or calcite possess brighter borders visible in BSE, which indicates composition with heavier elements. One of examples is light lamina in sample DUSZA 2B/07—where, according to EDS analysis, in point 3 on Figure 11a there is increased iron content. This indicates the process of replacement of dolomite by ankerite (or siderite) on the edges of these rhombic minerals. Some of the rhombohedral crystals, usually with subhedral and anhedral shapes, are quartz pseudomorphs after dolomite, calcite, or ankerite (Figure 6). Pyrite framboids are rarely present in the pellets. They are up to 10 micrometers across and occupy the space between biogenic grains in the outer part of the pellets (Figures 9–11). The chemical/mineral composition of the studied components and cement in light laminae were determined using energy dispersive spectroscopy (EDS) and are shown on Figures S1–S5 on the Supplementary Materials.



Figure 10. The SEM BSE images showing mineralogical composition and the diagenetical changes on a contact of dark laminae and pellet in respect of mineralogical changes and silica migration from dark lamina into pellet. (a) Peripheral zone of pellets (p) separated by dark laminae (DL). Common silica cement (dark gray), coccoliths, and coccolith debris with advanced dissolution and recrystallization marks (green arrows) are observed. Clay minerals such as illite-smectite (III-Sme) are observed within DL. Sample RR 1B/06; (b) common silica cement (dark gray, Si) in dark laminae (DL), and in the outer parts of light laminae (LL), suggesting the silica migration from DL into pellets. The minerals of ankerite (Ank) and dolomite (Dol) are seen within DL, on a direct contact with LL. Sample IWLA 6/07.



Figure 11. The SEM BSE images showing composition and diagenetic changes in contact zone of light laminae and dark laminae. (**a**) Various components such as illite (III), siderite (Sid), and crystals with zonal internal structures (red arrows) such as dolomite (Dol) replaced by ankerite and/or siderite (Ank-Sid) are observed in a zone of contact of light laminae with dark laminae. Sample DUSZA 2b/07; (**b**) the peripheral parts of pellets (p) in contact with dark laminae (DL). The advanced dissolution of coccolith material and various minerals are dispersed as follows: rhombic crystals of calcite, dolomite, and pseudomorphic calcite after dolomite crystals (yellow arrows), ankerite (blue arrows), and area (dotted line) with zonal crystals displaying replacement of dolomite by ankerite or siderite (red arrows). Sample RR1A/06.

The dark laminae consists mainly of authigenic crystals which are dolomite, calcite, siderite, ankerite, and pyrite framboids (Figures 9–11). The most common component is authigenic quartz which may form pseudomorphoses after carbonates. Dark laminae contain remnants of organic matter and rare flakes and sheets of clay minerals as illite-smectite (Figures 9b and 10a). The chemical/mineral composition of the studied components and cement in dark laminae were determined using energy dispersive spectroscopy (EDS) and are shown on Figures S1–S5 on the Supplementary Materials.

4.4. Cement Types

Scanning electron microscopy (SEM) observations indicated that light laminae are lithified mostly by calcareous cement and a small amount of quartz cements, while dark laminae are predominately lithified by quartz cement (Figures 5, 6 and 9–11). The cement fraction contains small (even less than 5 μ m) authigenic crystals of calcite, dolomite, ankerite, siderite, and pseudomorphoses after these crystals and quartz crystals. Cement is present as small clusters of crystals, as dispersed singular crystal specimens, or may form patches of anhedral homogeneous zone which is more characteristic for dark laminae (Figure 11b). The characteristic feature of cementation of the Tylawa Limestones is strong quartz cementation of the dark laminae and strong calcitic cementation of internal part of light laminae. In the external part of the light laminae there is a mixing zone of different types of cements (Figures 5 and 11b).

Cementation inside Pellets with Coccospheres

In all pellets studied by scanning electron microscopy, cementations by calcite and quartz prevail. However, the frequency and position of different types of cement inside pellets with coccospheres depends on the thickness of the pellet-bearing lamina in relation to the thickness of the surrounding dark laminae.

Detailed SEM observations reveal that calcite cement dominates in light laminae, especially if they are thicker and consist of packed pellets. Rhombic crystals usually infill internal parts of coccospheres, often with one crystal infilling the whole empty space. Small calcite crystals are observed between biogenic particles and may form tiny overgrowths on coccoliths or coccolith debris.

Silica cement is observed in all of the studied samples. There are different types of development of quartz cement. In all of the studied samples silica cement occurs which infills coccospheres or binds coccolithophore material inside the pelletal structures. It is located in samples where the typical parallel lamination is visible and there are no displayed signs of silicification in handmade specimens (Figure 4a(a1,2)). The silica cement is readily visible under optical and scanning electron microscopes (Figures 5 and 6). Quartz crystals may replace carbonate rhombohedra, precipitate in empty spaces of coccospheres or between grains and crystals in the form of nano- or micro-quartz aggregates. Their concentration changes from high to moderate in individual pellets. Silica cement is more common in the outer parts of the light laminae and is gradually infiltrated into pelletal structures. Calcite cement is more common in the central part of the light laminae (Figures 4(a1,2) and 6a). Most pellets with silica cement in the outer zone do not display any damage. They have sharp boundaries and have oval, lenticular, or circular shapes when observed in cross section. The pellets as described above, are composed of coccolithophore material dominated by excellently preserved coccospheres. The observed quartz crystals can be divided into two subtypes: nano- and/or micro-quartz (Figure 6b,d) and single quartz crystals in the form of rhomboedra which are pseudomorphoses after calcite or dolomite (Figure 6c-e). Both subtypes of nano- and/or micro-quartz are located within the inner parts of intact coccospheres. In most cases, nano- and microquartz aggregates conform well to the space inside the coccospheres, taking on the round shapes of coccosphere interiors (Figure 5(b1,2) and Figure 6b,d). The coccosphere shape and the morphological structures of the coccolith plates, that make the coccospheres, are very well preserved.

Single quartz crystals are also located inside the coccospheres and exhibit various shapes, from isometric to irregular (Figure 6c–e). These crystals are usually pseudomorphoses after rhombic crystals of carbonate minerals, such as calcite or dolomite. The crystals partially or fully fill the space inside of coccospheres and range in size from 5 to 10 μ m. Calcite cement also occurs within the coccospheres, even when quartz cement partly infills their interiors. Coccolithophores with two types of cement also show a good state of preservation.

Locally in some TL samples quartz cement occurs, which is visible in handmade specimens, as a packages of silicified laminae or chert, however, both the laminae and nodular structures are barely recognizable with the naked eye and, in some cases, these are slightly more easily observable under

optical and scanning electron microscopes (Figure 4b). The quartz cement entirely or partially fills the pellets. It partially or totally replaces the calcite crystals in coccolith plates. The morphological structures of these silicified coccolith plates (in which the calcareous component has been replaced with quartz) are not obliterated and are readily recognizable (Figure 12).



Figure 12. SEM images of silicified coccospheres. (**a**,**b**) the same area in combination of the BSE and CCI modes (respectively), where the calcite (Ca and light grey, on (**a**), and Ca on (**b**)) in coccolith plates in coccospheres are partially or totally replaced by quartz cement (Si and dark grey on (**a**), and Si on (**b**)). Note the well visible morphological structures of silicified coccolith plates (compare Si on (**a**) and (**b**)). Sample IWLA 5/07.

These replaced coccolith plates are similar in size to the coccolith plates composed of calcite that has not been replaced. The coccospheres with silicified coccolith plates display a circular shape and are up to 10μ m in diameter when observed in variously oriented cross sections. The shape and size of these coccospheres are similar to the coccospheres with no replacement of calcite by quartz. This suggests that silicification did not change the volume/size of the coccospheres or individual plates. The quartz may also occur as a micro-quartz phase between coccolith plates and coccospheres, when this coincides with replacement of calcite by quartz, the morphological details of coccolith plates are partially or completely erased.

Locally in some of the TL samples the lamination and nodular structures are strongly or totally obliterated by the silicification (Figure 4c). Such samples are commonly observed in the Janowice section. The pellets in these samples, if possible to recognize, display damage of their boundaries and shapes. They contain silica in the form of a micro-quartz phase and also completely replace the calcite in the coccolith plates. Pseudomorphs with weakly visible morphological structures and imprints of coccolith plates are only locally observed.

5. Discussion

Preservation of coccospheres in the geological record is undoubtedly linked to many factors concerning phylogenetic relationships [10], ecology of living coccolithophores, as well as environmental circulation of $CaCO_3$ in relation to ocean CO_2 uptake and its atmospheric concentration. However, biostratinomy and diagenesis are two of the taphonomic processes that have the greatest impact on the possibility of preserving of fossilized coccospheres. As a phase of fossilization, biostratinomy comprises all processes occurring after the death of an organism until its burial [59]. However, because living coccolithophores float passively as plankton in the surface part of the water column, we considered the beginning of the biostratonomic processes, the beginning of the transport of coccolithophores to the seabed regardless of whether they were already dead then. From this point of view, we used in this

paper a concept of Seilacher [60] and according to this, we treated coccolithophores as sedimentary particles. Thus, biostratinomic processes (include physical, mechanical, or sedimentary processes, such as disarticulation, abrasion, transport, dispersal, sorting, and resedimentation) took place in the time interval, between the biogenic production of coccolithophores and its burial. In this meaning, diagenesis includes physical and chemical changes in sediments as they get buried.

5.1. Species Taxonomic Affiliation in Relation to Coccospheres Preservation

Previous studies on fossilization of complete coccospheres indicate that the phylogenetic relationship of coccolithophore is largely responsible for their preservation potential [10]. In our study, all complete specimens of coccospheres that we observed belong to spherical, monomorphic, placolith-bearing species of *Reticulofenestra ornata*, Müller [23,25,27,29]. Coccolithophores from the genus *Reticulofenestra* are capable of maintaining structural integrity after death and after removal of cellular organic material. It is possible due to the special construction of the coccosphere, in which the adjacent coccoliths overlap and interlock forming a mechanically robust structure (Figure 5). Thus, the presence of placolith-bearing forms increased frequency of occurrence of complete and excellently preserved coccospheres in the fossil record.

5.2. Factors Affecting the Coccolithophore Remains before Settling on the Bottom

5.2.1. Role of the Zooplankton Grazing

The high abundance of coccolithophores remnants and also complete coccospheres in lenticular and fusiform structures within the light laminae of the Tylawa Limestones suggests that they were formed by zooplankton grazing. These structures have been also previously interpreted as the remnants of zooplankton fecal pellets or remnants of marine snow [23,24,29].

Presently, coccolithophores live in large numbers throughout the upper layers of the ocean and their skeletal remains are transported downward mainly in the form of fecal pellets and aggregates [61]. The sinking coccolithophores have been usually observed to reach the sea-floor highly altered [43,62,63]. Detached coccoliths have negligible sinking rates, thus their sedimentation flux must be mediated by larger aggregates [64] such as fecal pellets produced by planktonic herbivores feeding directly on coccolithophores [65]. Small fossil zooplankton fecal pellets usually consist of isolated coccoliths or coccolith debris. Articulated coccolithophores are known in modern marine environments as incorporated in calanoid copepods fecal pellets [66] which are big enough to contain the whole specimens. The high abundance of coccolith-rich, zooplankton fecal pellets and fecal aggregates in the Tylawa Limestones indicates that pelletization represents a significant mechanism for the delivery of coccoliths to the sea floor.

Pellets' shapes indicate that they reached the bottom as consistent but soft and plastic particles (Figure 5a). Thus, the pellets' integrity which is necessary to preserve whole coccospheres, must be due to individual organic peritrophic membranes surrounding each of the pellets during the transport through the water column. Such organic peritrophic membranes are described on fecal pellets of modern zooplankton [67,68]. These membranes provide some kind of protection for pellets against rapid disintegration in the water column [69].

5.2.2. Contribution of Oxygen Minimum Zone in the Water Column

As the studied pellets contain large amounts of undigested or partially digested coccolithophores' material, they are interpreted as derived from primary consumers that lived in surface-waters [70]. More intensive zooplankton activity through the water column should generate pellet degradation and their repacking within the deeper part of the water column. It would cause an increase in amount of homogenous pellets with skeletal destruction and dissolution [71,72]. In the studied material, even in smaller pellets there are no homogenous intrinsic constituents, which would indicate secondary ingestion by deeper-dwelling microzooplankton. It could have been related to existence of oxygen

minimum zone widely dispersed in the water column in the central Paratethys [25,46,73–75]. Unlike oxygenated water column, where organic-rich aggregates are rapidly consumed by detritivores and micro-organisms at the sediment/water interface [76], the anoxic conditions were an important factor for the preservation of fecal pellets and aggregates [77,78]. Such conditions could prevail during most of the Oligocene in the central Paratethys Basin which was a landlocked, marginal sea, where stagnation and oxygen deficiency prevailed in deep water [25]. Such environmental conditions were an important factor for formation of the light, coccolith-rich laminae in the light–dark laminae couples of the Tylawa Limestones.

5.3. Factors Affecting the Remains after Settling on the Bottom but before Burial

The pellets are rather randomly distributed in the light laminae and inside lenticular structures. The pellets differ in sizes and forms, although they contain the same type of coccolithophore material. The lack of sorting indicates that the pellets were not transported horizontally. The pellets also have no signs of feeding on them by any organisms living on the bottom. The exception is irregular or even jagged edges of some of the pellets which may indicate that they have undergone the process of coprorhexy (fragmentation of pellets), most probably by copepods feeding in the water column which are known to be highly efficient at breaking down their own fecal pellets while ingesting only a small proportion [79–81]. Coccoliths and coccospheres also do not reveal any signs of dissolution which may take place even during copepods gut passage. The low rate of microbial degradation can be confirmed by SEM observations. We can observe that some pellets are tight, indicating that organic peritrophic membranes existed on the pellets after settling at the bottom, and protected the pellets content after burial. The membranes themselves were not preserved, they could have been colonized by bacteria on different biostratinomic stages (even possibly after burial), and degraded after burial.

5.4. Mineralization of Voids and Pores inside and outside of Pellets

5.4.1. Calcite

SEM pictures revealed (Figure 5) that many intact coccospheres are empty while calcite cement is present mainly around crushed coccolith plates or coccolith debris located usually in the outer part of the pellets. This debris was probably the main source of solutions containing calcium carbonate ions which might have infiltrated from the outer part of the pellet and precipitated inside some of the empty coccospheres located in interiors of pellets. The calcite cement was the first generation of cements inside well preserved coccospheres, making them more resistant to further compaction. Additionally, early precipitation of calcite between coccolith debris particles might have influenced pellet mechanical resistance. The dissolution of coccolith debris could be graded and begin even during copepods gut passage, in the case of acid digestion. Such process has been observed in experiments on copepods feeding on coccolithophores [82,83].

Many rounded calcite crystals which are located inside coccospheres as well as in space between pellets and dark laminae (Figure 6, Figure 5, and Figure 9a) indicate that the process of calcite dissolution/precipitation must have been repeated several times and mostly occurred at the water/sediment interface as reported in earlier publications [84]. As light–dark laminae couples are thought to be a sedimentary record of seasonal, likely annual, biotic changes in the photic zone [23,24] each layer consisting of pellets with coccospheres was probably quickly covered with a layer of falling particles containing predominately organic matter and diatoms coming from the subsequent seasonal cycle of biogenic production in the upper part of the water column. Bacterial degradation of organic matter and concomitant production of CO_2 acidity would cause dissolution of calcite crystals in coccolith debris in the outer parts of the pellets. However, when the pH of the solution is lowered due to bacterial activity, the CaCO₃ present in the sediments begins to buffer further reaction [85] according to the following formulas:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \tag{1}$$

$$\text{CO}_3^{2^-} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{OH}^-$$
 (2)

$$HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^-$$
(3)

As a consequence of this reaction, the close contact between calcite crystals and organic matter, even within the empty chambers of coccospheres could relatively rapidly buffer the pH of the pore waters and thus prevent further dissolving of coccoliths inside the pellets in one cycle of light–dark lamina sedimentation. However, this cycle of dissolution and buffering could be repeated during the next cycle of sedimentation of light–dark lamina couplet, when the next pellets flux could deliver the next portion of calcite coccolith plates to the bottom environment.

5.4.2. Dolomite

The calcite is also present outside the pellets in the form of pseudomorphoses after dolomite crystals. Such dolomite crystals have never been observed inside the pellets. It indicates that dolomite is authigenic and may have crystallized very early after setting of the pellets at the sea bottom, during dissolution of outer layers of the pellets, in contact with seawater supplying enough Mg for this reaction. The low amount of dolomite formed in the Tylawa Limestones probably depended on low Mg flux into the sediment, which is proportional to the rate of dolomite precipitation and inversely proportional to the sediment accumulation rate [86]. The accompanying sedimentation of the organic layer with diatom frustules might be an additional source of Mg for dolomite formation and additionally, the source of Fe for formation of siderite crystals (FeCO₃) and pyrite crystals (FeS₂). Such crystal associations are visible in SEM observation within the thin interlayer space between pellets and lamina with organic matter (Figures 10 and 11).

5.4.3. Pyrite

The pyrite crystals and framboids are present inside voids after diatom frustules within organic layers (Figure 7) and also inside empty spaces between grains in the outermost part of some of the pellets located close to the dark laminae (Figures 10 and 11). This indicates that iron ions were relatively common and easily accessible in bottom environments. It also indicates that decomposition of organic matter was anaerobic and probably took place within the bacterial sulphate reduction zone, very close to the sediment–water interface, overlain by anoxic-sulfidic bottom water [87]. The bacteria utilized seawater sulphate and produced hydrogen sulphide (H_2S) [88] which partially precipitated as pyrite.

The precipitation of iron sulphides was very important in preservation of pellets with coccospheres because these reactions can act as pH buffers [89] according to Equation (4) and was another process which minimizes coccoliths dissolution.

$$2FeOOH + 3H^+ + 3HS^- \rightarrow FeS + FeS_2 + 4H_2O$$
⁽⁴⁾

5.4.4. Siderite

The coexistence of pyrite and siderite within the light–dark laminae couplets occurring in the Tylawa Limestones, indicates that anoxic conditions prevailed in the sediments [90,91]. Siderite can be precipitated below the sulfate reduction zone in the presence of CaO, where dissolved sulfide is absent, the iron is still present, and the Fe/Ca-ratio of pore water is high enough to stabilize siderite over calcite [92]. Thus, the coexistence of siderite and pyrite attributes to the changes of microenvironments resulting in consecutive reactions, next to each other, within the same sediment depth [93,94]. Such changes of bottom environment could be a consequence of cyclic seasonal biotic production in the surface waters coinciding with delivery and remineralization of particular organic matter and could response for post-depositional migration of local redox boundary [88,95].

5.4.5. Quartz

Different quartz crystallinity observed in the studied Tylawa Limestones and different shape and position of authigenic quartz crystals indicate that silica precipitation/dissolution occurred in several cycles and might be attributed to different sources. The authigenic quartz crystals that occur in different positions, dark laminae, between dark and light laminas, and inside coccospheres in the most outside part of the pellets are interpreted as derived from dissolution of diatoms frustules sedimented during organic matter flux. The quartz crystals crystallized directly in the coccospheres interior or in the empty space inside light lamina and also as pseudomorphoses after calcite or dolomite. These different quartz positions indicate that precipitation of soluble silica was not directly related to pH changes within the local microenvironment but rather depended on the difference in the solubility of silica polymorphs at any pH due to its precipitation (see discussion in van der Weijden) [89].

The total silicification of the dark–light laminae couplets, which is observed in some samples is interpreted rather as late diagenetic process, where the silica derived from later diagenesis of thick sequence of clastic deposits surrounding the Tylawa Limestones. These later processes usually contributed to dissolution of coccospheres in the studied deposits.

5.5. Timing and Depth of Diagenetic Processes Protecting Coccospheres

The timing of cement crystallization which protected the coccospheres from destruction within the light-dark laminae couplets of the Tylawa Limestones and overlying deposits, can be inferred from compaction characteristics, using preserved texture [96,97]. The SEM images show that only a small number of complete coccospheres are partly crushed and/or cracked (Figure 5a). The presence of uncrushed delicate nannofossils indicates forming micro-concretions around pellets aggregates to resist compaction, due to early cementation. Significant compaction prior to precipitation of the cement would have destroyed such delicate features [98]. It can be a result of very early diagenesis of pellets due to very early crystallization of calcite cement inside coccospheres. The pellets which were cemented very early stayed intact inside lenticular structures forming these micro-concretions. The micro-size of concretions reflects short duration of concretion growth and suggests an early initiation of this process [99]. It is possible that excellent preservation is closely related to the early cementation process. The lenticular structures are surrounded by laminae containing organic matter, clay minerals, and diatoms, which form wavy lamination (Figure 4). The significant deflection of strata around the lenticular structures, plastic deformation of laminae fragments (Figure 11b), and deformation of clay mineral sheets and mica flakes (e.g., Figure 7) indicates differential compaction, and growth of micro-concretions in relatively uncompacted sediments [100], and also suggesting that the micro-concretion formed prior to compaction [101].

Petrography (especially of authigenic minerals) and texture of the studied Tylawa Limestones couplets can be used to interpret the depth where the micro-concretions could be finally formed to protect the well preserved coccospheres against degradation. XRD results reveal that all calcite crystals inside coccospheres are non-ferroan. Ferroan iron in the pore waters was most probably sequestered by pyrite and formation of ferroan carbonates like ankerite and siderite [102,103]. The studied deposits also contain calcite pseudomorphoses after dolomite located outside of the pellets, very close or inside the layer that contained organic matter. It would suggest that the dolomite was primary in origin and precipitated within the organotrophic sulfate reduction zone where the sulfate reducers may use carbon compounds [98]. Thus, the Fe-poor calcites inside the studied coccospheres could have precipitated during sulfate reduction [104].

6. Conclusions

Excellently preserved coccospheres have been found in the Tylawa Limestones that occurred as an isochronic lithological horizon in the Lower Oligocene deposits of the Outer Carpathians. Multiple petrographic and geochemical analyses indicate that the exceptional preservation of coccospheres has been caused by the special coincidence of biostratinomic processes and pre and post-depositional processes within the water-sediment interface.

The environmental conditions in the surface waters of the Paratethys-a semi-closed basin with limited circulation—stimulated coccolithophore blooms and production of diatoms and organic flux which repeated in hydrographical cycles. Grazers feeding on coccolithophores (most probably large copepods) produced pellets enhancing vertical transport of coccospheres and their further preservation within the sediment. The anoxic conditions prevailing in the water column could have protected sinking pellets from fragmentation or eating by deeper swimming zooplankton. The coccospheres of Reticulofenestra ornata found in the studied fecal pellets, are particularly thick-walled, for this reason these forms avoided digestion and stayed intact after copepods gut passage. Possibly, it can also be dependent on the genre of copepods, which can have significant morphological variation, and thus different digestive systems and pH inside. The pellets with excellently preserved coccospheres have been calcitized prior to the rest of the studied light-dark laminae couplets and thus stayed almost non-compacted. These processes took place mainly in shallow sediments, in the bacterial sulfate reduction zone, during the very early stages of diagenesis. The water column overlying the depositional environment was euxinic. The micro-concretions containing pellets with coccospheres were formed in a partially closed system, with a limited supply of sulfate and formation of calcite cement inside coccospheres. The pH changes did not have such a wide range to cause the dissolution of silica and calcium carbonate, which also favored the preservation of the coccospheres. The total silicification of the dark-light laminae couplets which is observed in some samples was late diagenetic process, where the silica derived from later diagenesis of the thick sequence of clastic deposits surrounding the Tylawa Limestones. These contributed to total destruction of coccospheres (dissolution) in parts where mentioned silicification is present in studied deposits.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/7/616/s1, Figure S1: Energy dispersive spectroscopy (EDS) peaks of silica cement (Si), quartz (Qtz) and calcite grains (Ca), from Figure 9a, Figure S2: Energy dispersive spectroscopy (EDS) peaks of muscovite (Mus), ankerite (Ank), likely organic matter (OM), dolomite (Dol) and quartz (Qtz) from Figure 9b, Figure S3: Energy dispersive spectroscopy (EDS) peaks of illite - smectite (Ill-Sme) from Figure 10a, Figure S4: Energy dispersive spectroscopy (EDS) peaks of ankerite (Ank) and silica cement (Si) from Figure 10b, Figure S5: Energy dispersive spectroscopy (EDS) peaks of illite (Ill), dolomite (Dol), ankerite-siderite (Ank-Sid) and siderite (Sid) from sample 11a.

Author Contributions: Conceptualization, A.C. and M.B.; methodology, A.C. and M.B.; validation, A.C. and M.B.; formal analysis, A.C.; and M.B.; investigation, A.C.; M.B. and M.S.; data curation, A.C. and M.B.; writing—original draft preparation, A.C. and M.B.; writing—review and editing, A.C.; M.B. and M.S. All authors have read and agreed to the published version of the manuscript.

Funding: The study was funded by the Statutory Funds of Department of General Geology and Geotourism, the Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Kraków, Poland No. 11.11.140.005 to Marta Bak and the Ministry of Science and Higher Education to Agnieszka Ciurej (Project BN.610-408/PBU/2020).

Acknowledgments: We would like to thank two anonymous reviewers and the journal editor for constructive comments and suggestions.

Conflicts of Interest: The authors declare no conflict of interest.

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