

PYRITIZED RADIOLARIANS FROM THE MID-CRETACEOUS DEPOSITS OF THE PIENINY KLIPPEN BELT — A MODEL OF PYRITIZATION IN AN ANOXIC ENVIRONMENT

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Abstract: Excellently preserved, pyritized radiolarian skeletons have been found within the Upper Cenomanian deposits in the Pieniny Klippen Belt (PKB—Carpathians, Poland). On the basis of a study of their chemical composition, structure of replacing skeletons and exceptional preservation of all morphological details, we propose a new model where the pyritization process took place not in sediment but while the radiolarian skeletons were suspended in the anoxic water column. The radiolarians rich in organic matter, sinking through the upper (iron-rich) part of an anoxic water column, became the sites of organic matter decomposition and enhanced bacterial sulphate reduction. Dissolved iron in this zone diffused into the radiolarians and precipitated as iron sulphides replacing the opaline skeletons. This process was controlled by the rates of opal dissolution and of bacterial sulphate reduction, and the availability of dissolved iron. The preservation of radiolarians in the Upper Cenomanian deposits from different depth sub-basins of the PKB was compared. We found that the extent of pyritization and preservation of radiolarian skeletons may be dependent on the depth of the basin and the position of the oxic-anoxic interface.

Key words: Carpathians, Pieniny Klippen Belt, anoxic event, pyritization, Radiolaria.

Introduction

Pyritized organic remains are common in the sedimentary record. Pyrite may form moulds of diatoms (Geroch 1978; McNeil 1990), fill empty spaces and/or replace carbonates in echinoderms (Jensen & Thomsen 1987), ammonites (Hudson 1982), gastropods and bivalves (Fisher 1986) or whale bones (Bang 1994), delineate tubes and burrows of polychetes (Thomsen & Vorren 1984) and replace soft-bodied trilobites (Briggs et al. 1991). Pyrite has also been found in recent foraminifers (Seiglie 1973). Pyrite can adopt various forms, from massive to aggregated, euhedra and framboids. Generally pyrite replaces the organic matrix ("soft parts") and carbonate skeletons during all stages of sediment burial history. Excellent descriptions of mechanisms of fossil pyritization (but not of silica skeletons) were given by Canfield & Raiswell (1991), Briggs et al. (1996) and Raiswell (1997).

While pyritized radiolarian skeletons are relatively common (e.g. Pessagno 1977; Thurow 1988; M. Bąk 1995, 1996b), this phenomenon has only been recorded in the taxonomic literature. In this paper we present the results of the first non-taxonomic study and propose an original model of radiolarian pyritization in the water column. Perfectly and poorly preserved pyritized radiolarian skeletons from the upper Cenomanian deposits of different successions in the Polish part of the Pieniny Klippen Belt were also compared.

Geology

The Pieniny Klippen Belt (PKB) represents a zone of strongly deformed Mesozoic and Paleogene sedimentary rocks

which separates two major structural units of the Carpathians: the Inner and the Outer Carpathians (Fig. 1). During the Cretaceous, the Pieniny Klippen Basin consisted of several sub-basins representing realms from the outer shelf (the Czorsztyn Succession), to the lower and middle bathyal zones, (the Branisko and Pieniny successions) (Birkenmajer 1977; Birkenmajer & Gasiński 1992; K. Bąk 1993). The Upper Cenomanian deposits in the Pieniny Klippen Basin, which belong to the foraminiferal Rotalipora cushmani Zone are represented by two facies. These are black marly shales with radiolarians (Birkenmajer 1977; Birkenmajer & Jednorowska 1987), which can be correlated with an anoxic event, well developed in the Pieniny and Czorsztyn successions, and grey-green shales with thin sandstone intercalations represented by the shaly flysch deposits belonging to the Branisko Succession (Birkenmajer 1977; K. Bąk 1993). All these deposits contain pyritized radiolarians (M. Bąk 1995, 1996a,b, 1999). For the purpose of this study the rocks belonging to the Czorsztyn, Branisko and Pieniny successions were sampled and the pyritized radiolarian skeletons compared.

Method

The material studied includes 33 samples, from four profiles in the Polish part in the Pieniny Klippen Belt. Eleven samples have been taken from black shales of the Magierowa Member in the Magierowa Skała section of the Pieniny Succession (M. Bąk 1999). Ten samples have been taken from grey-green shales of the Jaworki Formation (Trawne Member and Snežnica Siltstone Member) in the Kietowy stream section of the Branisko Succession (M. Bąk 1995, 1996a), and twelve

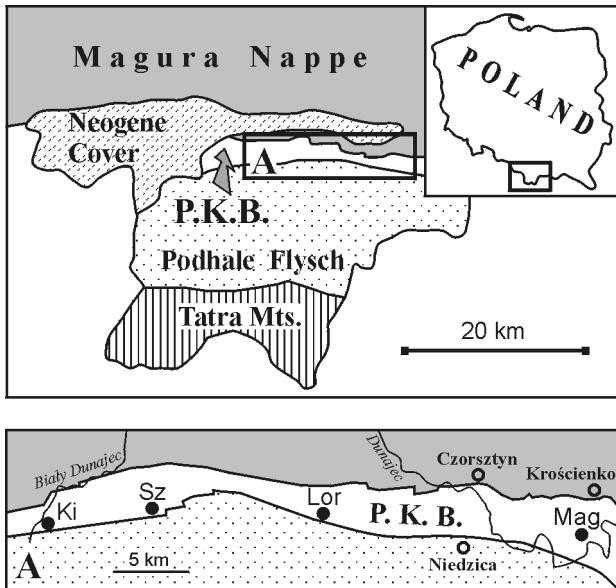


Fig. 1. The geological position of the Polish part of the Pieniny Klippen Belt (P.K.B.) within the Carpathians. Tectonic elements mainly after M. Książkiewicz, simplified by K. Birkenmajer (1985); A: Location of the investigated sections in the Pieniny Klippen Belt (geology after Birkenmajer (1977) — simplified). Designation of the sections: Ki — Kietowy, Lor — Lorencowe Klippes, Sz — Szaflary quarry, Mag — Magierowa Skałka.

samples have been collected from black shales of the Altana Shale Bed in two profiles of the Czorsztyn Succession (Szaflary quarry and Lorencowe Klippes sections — see M. Bąk 1996b). The samples were collected in the sections every 10 to 80 cm (depending on the changes of lithology and the quality of exposure), especially near lithological boundaries. Marls and marly shales were the dominant lithotypes. A few samples were taken from mudstones.

Samples of about 1 kg were taken for preparation. Each sample was broken into pieces 1–2 cm across and dried out under a temperature of 105 °C. Next the samples were soaked in a hot solution of glauberic salt and boiled, usually for several days. Hard cemented parts of samples were soaked in hot acetic acid for 7–8 hours. Then the residue was washed through a 63 µm sieve.

Radiolarians were first examined under a binocular microscope. They were picked out manually from the residue (maximum 300 specimens per sample). The best preserved specimens were mounted on Scanning Electron Microscope (SEM) stubs for photography.

Radiolarian association and description of pyritized skeletons

Radiolaria are generally common in the samples studied. Specimens are well to poorly preserved, silicified or pyritized. The above mentioned data suggest, that the type of preservation of pyritized radiolarian skeletons depends on the depth at which they were formed in the sub-basins.

Radiolarian skeletons from the black marly shales of the Pieniny Succession (the deepest part of the PKB) (Fig. 2A) are usually moderate to poorly preserved. Pyritized skeletons with poorly preserved outer structures (due to dissolution) dominate in the radiolarian association which consists of numerous Nassellaria (mostly cryptocephalic and cryptothoracic forms), belonging to genera such as *Holocryptocanium*, *Hemicryptocapsa*, *Squinabollum* with only a few forms of Spumellaria (genera *Archaeocenosphaera*, *Orbiculiforma*). Siliceous skeletons are rare here. Pyrite microconcretions, possibly pseudomorphs after radiolarian skeletons, are also present.

Radiolarian skeletons from the black shales of the Czorsztyn Succession (the shallowest part of the PKB basin) (Fig. 2C) are usually poorly preserved (although often sufficiently for taxonomic determinations), and seem to be formed exclusively of pyrite. However, the examination of cross-sections shows that irregular masses of pyrite grains cover various parts of the majority of the siliceous skeletons of radiolarians. This radiolarian association comprises both Nassellaria (genera *Holocryptocanium*, *Hemicryptocapsa*, *Dictyomitra*, *Stichomitra*) and Spumellaria (genera *Patellula*, *Crucella*, *Cavaspongia*) (forming about 60 and 40 per cent of the association, respectively).

The majority of the radiolarians in one sample (Kietowy section — sample Ki-14 — see M. Bąk 1995) from the grey-green shales of the Branisko Succession (Fig. 2B) (lower to middle bathyal, K. Bąk 1993) consist of pyrite, with only a few siliceous skeletons. The radiolarian assemblage consists predominantly of Nassellaria. The pyritized forms belong mostly to the cryptothoracic Nassellaria (Pl. I) such as *Holocryptocanium barbui*, *Hemicryptocapsa tuberosa* and *Hemicryptocapsa prepolyhedra*. *Xitus mclaughlini* and *Thanarla pulchra* are less abundant. The rare siliceous specimens, all corroded, also include the Nassellaria (*Cryptamphorella conara*, *Sethocapsa* sp.) (Pl. II: Fig. 2), with only one specimen of Spumellaria (*Haliommura* sp.). The above mentioned radiolarian taxa do not occur in both siliceous and pyritized forms. Pyrite very faithfully replaces all the original silica skeletons in the studied sample, even the finest details of ornamentation (Pl. II: Figs. 3, 4). Even in cryptothoracic forms with a thick abdomen wall (e.g. *H. barbui*, *H. tuberculatum*) of four layers, the internal layers are perfectly preserved (Pl. II: Figs. 7, 8). SEM-EDS study showed that pyrite is actually the only sulphide mineral present, without the presence of silica or silicates. At lower magnifications (below 1000×), SEM images reveal very even surfaces of pyritized skeleton elements. However, higher magnifications (5000–10000×) show that these skeletons are built of masses of small irregular grains of pyrite (size about 0.5 µm), intergrown or closely packed, sometimes with pores (Pl. II: Fig. 1). Secondary dissolution of the pyritized skeletons caused corrosion, resulting in fine to coarse-granulated surfaces, or partly destroyed walls (Pl. II: Fig. 6). Dissolution sometimes enhances a primary granulated structure of the walls. The observations of corroded surfaces of some preserved silica skeletons suggest that the primary skeletons were built of silica grains of the similar size to the pyrite grains. Pyrite framboids are common in the pyritized radiolarian skeletons. They typically occur in

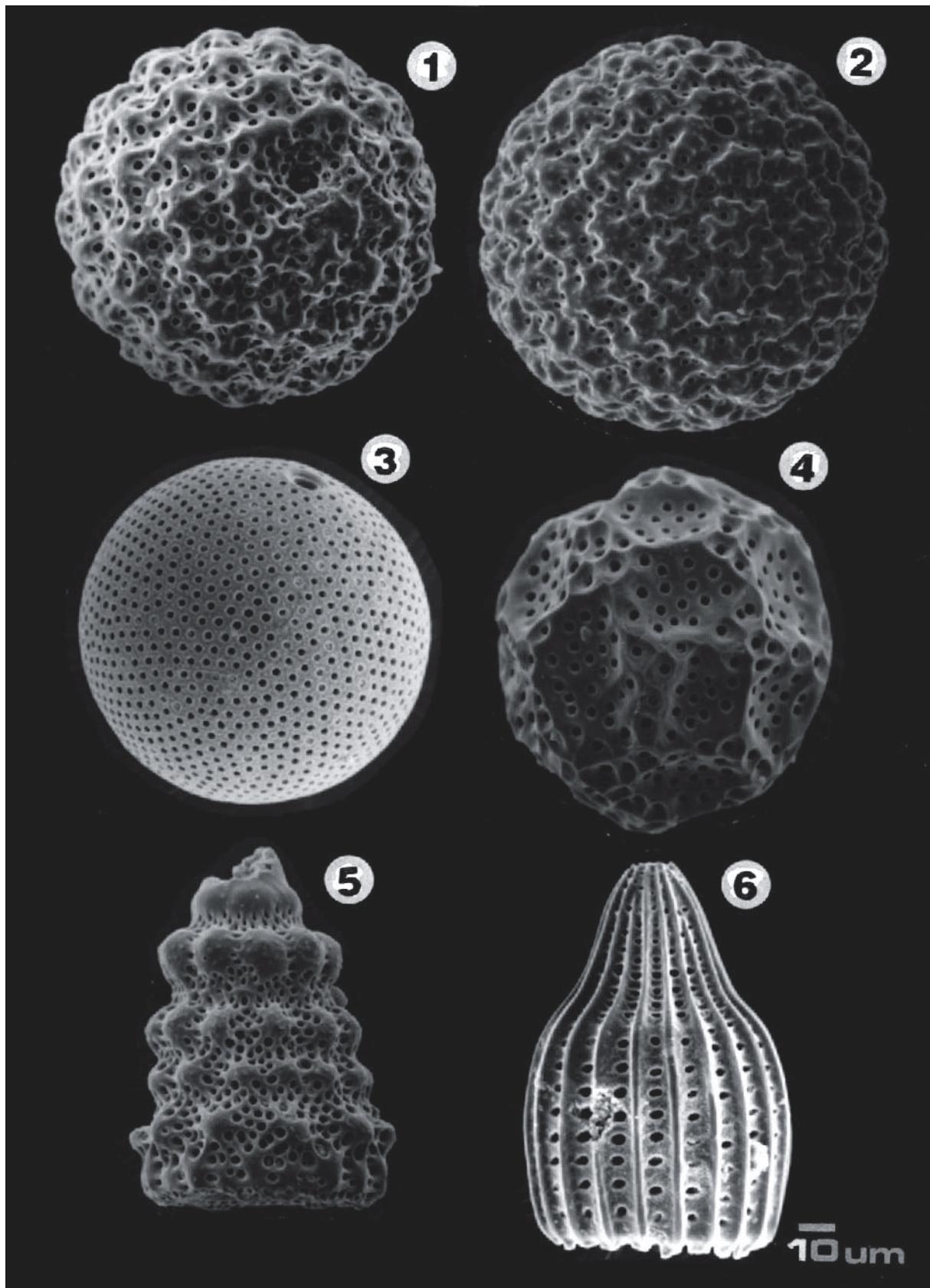
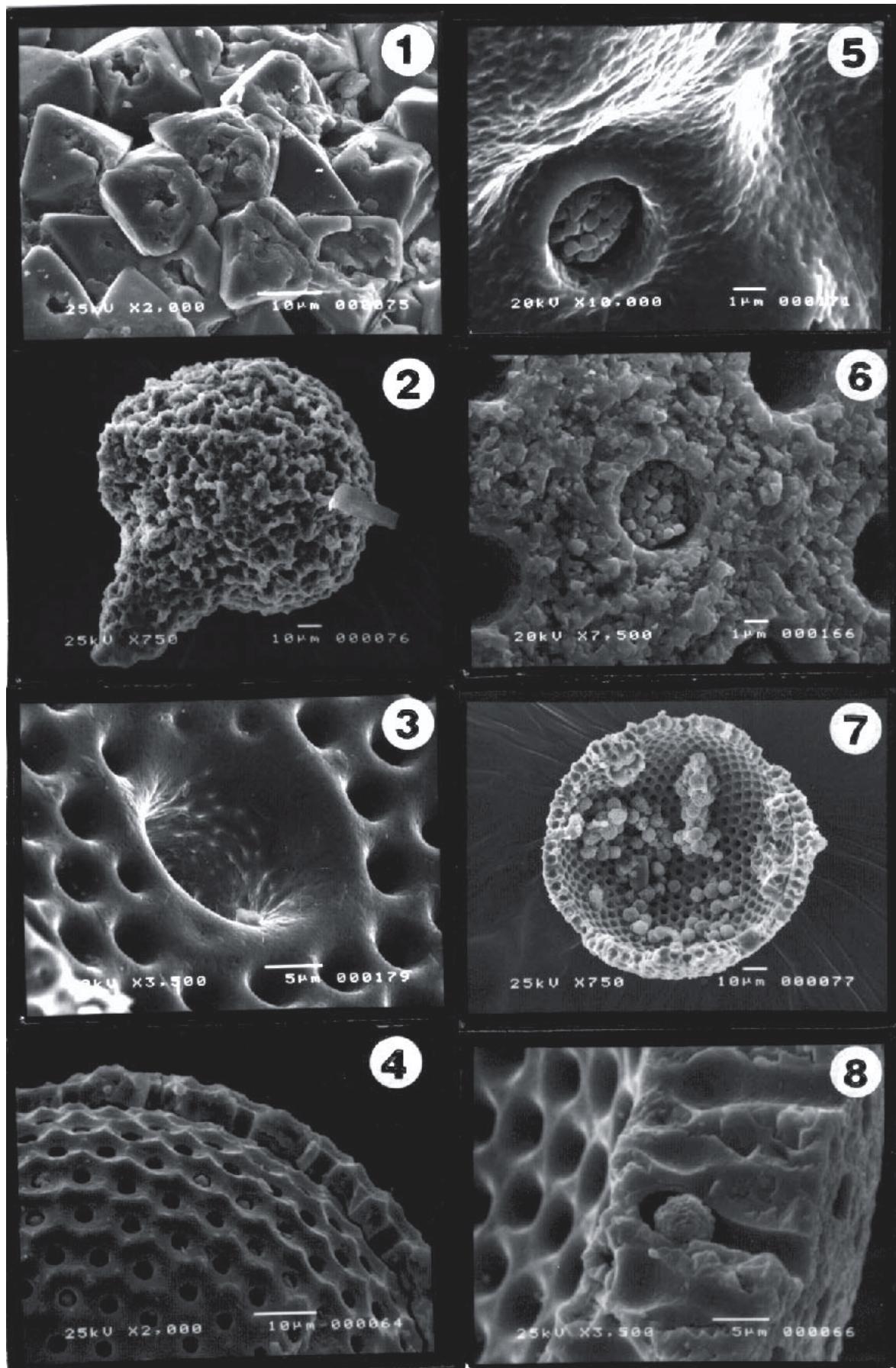


Plate I: Pyritized Radiolaria: **Fig. 1.** *Hemicryptocapsa tuberosa* Dumitrică. **Fig. 2.** *Holocryptocanium tuberculatum* Dumitrică. **Fig. 3.** *Holocryptocanium barbui* Dumitrică. **Fig. 4.** *Hemicryptocapsa prepolyhedra* Dumitrică. **Fig. 5.** *Xitus mclaughlini* Pessagno. **Fig. 6.** *Thanarla pulchra* (Squinabol).



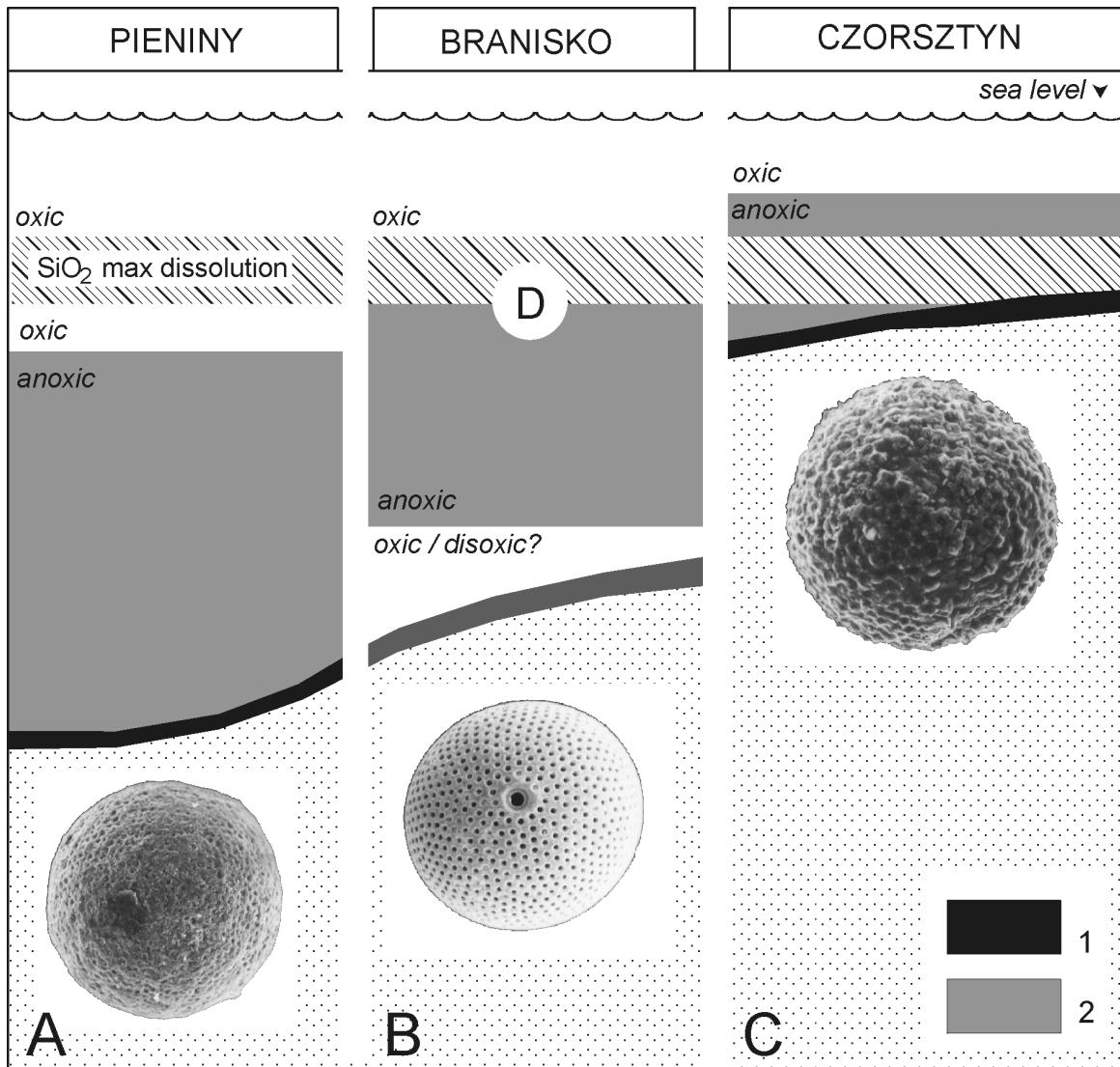


Fig. 2. An idealized cross-section through different depths of sub-basins of the PKB showing various modes of radiolarian skeleton preservation (species *Holocryptocanum barbui*, magnification for all illustrated forms: $\times 300$). The most faithful replacement by pyrite is expected where the chemocline is just below the SiO_2 dissolution zone (Branisko Succession); A — Pieniny Basin — example of pyritized, poorly preserved skeleton; B — Branisko Basin — excellently preserved, pyritized skeleton; C — Czorsztyn Basin — siliceous skeleton covered by pyrite grains. 1 — black shales, 2 — grey-green shales; D — place of ideal pyritization of radiolarian skeletons in an anoxic water column.

Plate II: **Fig. 1.** Pyrite octaedra (with growth defects or partly dissolved) forming microconcretions replacing radiolarian skeleton. **Fig. 2.** Siliceous, partly corroded, skeleton of *Sethocapsa* sp. **Fig. 3.** Inner side of abdomen chamber with aperture, perfectly replaced by pyrite. **Fig. 4.** Pyritized, partly removed the external layer and completely preserved the internal layer of abdomen wall (*H. barbui*) with pyrite frambooids inside of the pores. **Fig. 5.** Granulate pyritized surface of abdomen wall of *H. tuberosa*, with pyrite frambooid in a pore. **Fig. 6.** Partly corroded pyritized surface of *H. barbui*, revealing granulated texture, also seen in a pore, note the similar size of grains forming abdomen wall and frambooid in a pore. **Fig. 7.** Interior of the abdominal chamber of *H. barbui*, with individual frambooids and their clusters attached to the inner surface. **Fig. 8.** A cross-section of the abdomen wall of *H. barbui* with lamp chimney shape of pores, sometimes hosting a pyrite frambooid.

two different positions: (1) — in channels (pores) (Pl. II: Figs. 4, 5, 8); (2) — inside the abdomen of cryptothoracic forms, attached to an internal surface, often at a channel exit (Pl. II: Fig. 7). The size of frambooids is around $5 \mu\text{m}$. The average size of grains and crystals in the frambooids is similar to that of the opal “grains”, forming the radiolarian skeleton. Sometimes the frambooids contain silicate minerals in the interstices. In some pyrite skeletons pores are filled by aggregations of aluminosilicates.

A 0.5 mg combined sample of excellent pyritized radiolarian skeletons was subjected to a sulphur stable isotope study (preparation after Robinson & Kusakabe (1975), analysed on a modified MI-1305 mass spectrometer). The $\delta^{34}\text{S}_{\text{CDT}}$ value was $-1.88 \pm 0.07 \text{‰}$.

Proposed model of radiolarian pyritization

Pyrite can be formed either directly or indirectly (via iron monosulphides, mainly mackinawite and greigite) although the latter pathway is more typical for sediments (Rickard 1975; Howarth 1979; Berner 1980; Rickard et al. 1995). Pyrite may also form in an euxinic water column but its formation during diagenesis is more common.

We assume that the pyritization of skeletons resulting in excellent preservation of the radiolarians described here took place in the anoxic water column. A comparison of the degrees of preservation of skeletons from different environments suggests that such perfect (exceptionally well preserved details, etc.) and "clean" (no silicate admixtures or silica remains), replacement of silica by pyrite as observed in the sample (Ki-14) of the Branisko Succession is unlikely to have occurred in a sediment during and/or after burial. This origin is supported by observations on the formation of sulphides and pyrite framboids in the anoxic water column of the Black Sea and Framvaren Fjord (Skei 1988; Canfield et al. 1996). Sulphur isotope data from the Black Sea also suggest a rapid water-column formation of Fe-S (Lyons 1997). Further evidence for pyritization of radiolarian skeletons in water column could be derived from close spatial and genetic association of skeletons with pyrite framboids. Pyrite framboids typically form in euxinic water column and/or during early diagenesis in a sediment (Lyons 1997; Wilkin & Barnes 1997). Their occurrence in pores or attached to the internal surface of pyritized radiolarian skeletons suggests that pyritization of skeletons took place before framboids formation. If framboids formed in siliceous radiolarian skeletons, the subsequent process of skeleton pyritization would cause infilling of framboid interstices, overgrowths on framboid or framboid growth to euhedra (see Sawłowicz 1993) which was not observed in the studied sample.

It has been suggested that settling organic matter becomes sites for elevated rates of sulphate reduction (Muramoto et al. 1991; Canfield et al. 1996). We propose that siliceous radiolarian skeletons, rich in organic matter, settling in the upper (iron-rich) part of an anoxic water column were the sites of organic matter decomposition and enhanced bacterial sulphate reduction (BSR), producing sulphide (Fig. 3). Dissolved iron in this zone diffused into the radiolarians and precipitated as iron sulphides replacing the opaline skeletons. The chemical properties of the water column were important factors in the pyritization. The process requires a water column undersaturated with respect to SiO_2 and saturated with respect to iron sulphides (appropriate ratios of iron to sulphide, see Canfield & Raiswell 1991). According to Raiswell (*written comm.* 1997), the amount of dissolved iron in the reservoir below the oxic/anoxic interface would only need negligible sulphur for saturation. Thus, as opaline skeletons with organic matter sink through the Fe-rich zone, they are replaced by Fe-sulphides. A simplified reaction could be: $\text{SiO}_2 + \text{Fe}^{2+} + 2\text{H}_2\text{S} \rightarrow \text{Si}^{4+} + \text{FeS}_2 + 2\text{H}_2\text{O}$, although pyrite formation was probably preceded by formation of mackinawite and greigite. It is possible that only iron monosulphide formation took place in the water column with subsequent pyritization during/after burial. On the basis of the similarity between siz-

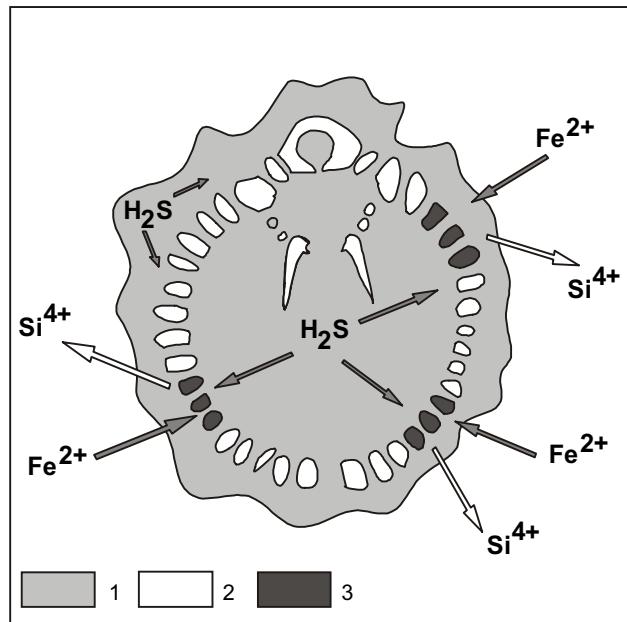


Fig. 3. Model of pyritization of radiolarian skeletons in an anoxic water column. Pyritization, resulting from H_2S formation in the organic matter of the radiolarian and iron supply from the Fe-rich water column, must be matched by dissolution of the opal skeleton; 1 — organic matter; 2 — siliceous skeleton; 3 — pyritized parts of the skeleton.

es of grains forming the silica and pyrite skeletons, we suggest that replacement of opal by iron sulphides could be "grain for grain". The primary and necessary condition for excellent preservation is that the living level of radiolarians (the beginning of the opaline skeleton dissolution process), the rate of sulphide production by BSR and the oxic/anoxic interface with the iron-rich zone below (low in H_2S and with relatively high pH) must be correlated (Fig. 2B). Typical dissolution of radiolarians begins in the upper hundreds of meters of the water column, which suggests that the pyritization process began very early and high up in the water column. For comparison, the oxic/anoxic interface in the Black Sea varies from 60 to 200 m depth (Brewer & Spencer 1974). If the chemocline is much below a silica dissolution level, then well pyritized but poorly preserved skeletons (or microconcretions), without preservation of all morphological details (Fig. 2A), result from the pyritization of silica remnants during sinking or in the sediment. On the other hand, pyrite encrustation on silica skeletons may form when the chemocline is high in the water column (pyritization proceeds opal dissolution), or when skeletons are buried before dissolution, for example in a shallow basin (Fig. 2C). The processes described above are also controlled by the ratios of dissolved sulphide and iron concentrations (compare with the diffusion-with-precipitation model of Raiswell et al. 1993).

Discussion

In discussing the main factors influencing the model presented above, we are aware that most available data are re-

lated to the present day ocean, and that care is required when applying them to past environments.

The most difficult problem is to evaluate a possible rate of opaline skeleton dissolution, especially as the available data are often contradictory. Present day oceans are highly undersaturated with dissolved silica. The mean concentration of silicon in seawater is 1×10^{-4} mol/kg (Broecker & Peng 1982). Dissolution of the silica in radiolarians during settling through the water column is a very common process. The amorphous mineralogically unstable opal, which forms radiolarian skeletons, is dissolved in a silica-undersaturated marine environment (Hurd 1974). However opal skeletal remains have a variable resistance to dissolution, due to differences in structure, chemical composition, geometrical construction and specific surface area (Bohrmann 1986). According to Goll & Bjorklund (1974) most biologically produced opal in the oceans dissolves before reaching the bottom and, for example, in the present central Pacific, radiolarians suspended in the water column dissolve most rapidly in the upper 250 metres. On the other hand, Broecker & Peng (1982) found that only a little silica dissolution occurs during settling of the particles through the water column, and inferred that most of the opal dissolution occurs on the sea floor. There is a possible relationship between radiolarian opal preservation and oxygen minima in the water column (Goll & Bjorklund 1974). A semi-closed anoxic basin with little exchange and increased concentrations of dissolved silica may probably lower silica undersaturation in the water column and slow down dissolution. The rate of opal dissolution could also be modified by some other factors. Production of HCO_3^- ($2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$) inside radiolarians during organic matter decomposition and bacterial sulphate reduction may enhance opal skeleton dissolution. On the other hand, the early formation of iron sulphide coatings may slow down dissolution. It is interesting to note that higher concentrations of iron salts may reduce the solubility of radiolarians (Lewin's experiments with diatoms — see Goll & Bjorklund 1974). The depth of the Branisko Basin has been estimated at approximately 1500 m (K. Bąk 1993). Radiolarians which are not transported in fecal pelets, reach the bottom during several days to about one month, based on sinking rates and residence time calculated by Takahashi & Honjo (1983), and Berger & Piper (1972). This seems to be a reasonable period of time for pyritization of skeletons to proceed.

Bacterial sulphate reduction is the most common source of sulphide for pyrite formation and often occurs at the site of the decomposing organic matter (Berner 1980). Decay of readily metabolizable organic matter in radiolarians produces an anaerobic microenvironment in which sulphates from surrounding seawater are being reduced by anaerobic bacteria (Berner 1970, 1984). As the skeleton of living radiolarians is encased in a soft cytoplasm, not even the most protruding parts of the skeleton are ever in direct contact with seawater. The proteinaceous material comprising the soft bodies of radiolarians decomposes rapidly, probably together with symbiotic bacteria and algae. There is no consensus as to the rate of organic matter decomposition, estimates ranging from days to years, depending on dominant organic compounds (Westrich 1983). Studies of Radiolaria

from the South Atlantic suggest that bacterial decay of cytoplasm may progress to completion long before burial (Goll & Bjorklund 1974). Canfield et al. (1996) explained a process of iron mineral sulphidation in the euxinic Black Sea as the result of local sulphate reduction during decomposition of settling organic material. H_2S generation could be a very localized process restricted to radiolarians, especially when coupled with contemporaneous iron sulphide formation. In such a case the water column would be iron-rich and anoxic but not euxinic. Concentration of the free H_2S in the water column would have to be low otherwise the samples would contain extensive pyrite framboids formed in the water column or at the sediment-water interface, which was not observed.

The $\delta^{34}\text{S}_{\text{CDT}}$ of Upper Cretaceous seawater sulphate was about +17 ‰ (Claypool et al. 1980). The typical maximum of microbial sulphate reduction fractionation varies from -45 to -60 ‰ (Goldhaber & Kaplan 1974), but it is much lower in the absence of the oxidative sulphur cycle (Canfield & Thamdrup 1994). In our study, $\delta^{34}\text{S}$ is around -2 ‰ indicating fractionation of about 19 ‰. It is worth stressing that a readily metabolizable proteinous material stimulates higher rates of sulphate reduction, which in turn may cause a smaller fractionation. Thus, fractionation of around 20 ‰ could be typical for pyritization of radiolarians. It is also possible that the radiolarians themselves could form a semi-closed system to sulphates. Part of the isotopically light H_2S formed during BSR may be removed from the radiolarians faster than the rate of iron sulphide formation. Thus, heavier residual sulphates remain in the radiolarian body and are used for continued BSR. As the result, the pyritized skeleton may be relatively enriched in heavy sulphur. It cannot be excluded that $\delta^{34}\text{S}$ varies across the skeleton wall.

The concentration of iron in recent ocean water is generally very low and varies from 0 to 0.007 mg/l, with mean concentration of 1×10^{-9} mol/kg (Broecker & Peng 1982). However, high maxima are typically found in an iron-rich zone below the oxic/anoxic interface, reaching 50 ppb in the Black Sea (Brewer & Spencer 1974). Iron concentrations in some anoxic basins may conform to mackinawite-greigite solubility limits (Morse et al. 1987). The major sources of iron could be iron oxides, like goethite, hematite, lepidocrocite and ferrihydrite (Canfield 1989), which are then reduced in the anoxic water-column. Some iron may be adsorbed on radiolarians (especially those still covered with organic material) as oxides and hydroxides and dissolved *in situ*.

Pyritization of only specific radiolarian species may be explained by their variable "living levels" and/or different skeleton structure. The position of the living zone in relation to the chemocline could be crucial for the degree of pyritization and preservation. We cannot exclude radiolarian taxa selection by bottom currents, but the diversity of the shapes (e.g. spheres and cones) of pyritized skeletons speaks rather against this possibility.

Pyrite framboids present in Radiolaria were probably formed after the pyritization of skeletons. They occur in free spaces within the skeletons and could form during diagenesis (even late diagenesis if only BSR was active) of the sediment, like pyrite concretions. The latter could replace the silica of radiolarians or recrystallize earlier pyritized radiolarians during

diagenesis. Pyrite encrustation on silica skeletons could form both during the short period of sinking in shallow water, or later, after burial.

Conclusions

The results of the studies presented here are based on micropaleontological and mineralogical analyses of radiolarian skeletons from 33 samples from four profiles.

For the purpose of this study the Upper Cenomanian deposits belonging to the Czorsztyn, Branisko and Pieniny successions were sampled and the radiolarian skeletons compared.

Samples have been taken from black shales of the Magierowa Member (Pieniny Succession), grey-green shales of the Jaworki Formation (Branisko Succession), and black shales of the Altana Shale Bed (Czorsztyn Succession).

Radiolarian skeletons from the Pieniny Succession are usually moderately to poorly preserved. The pyritized skeletons with poorly preserved outer structures (due to dissolution) dominate the association. Siliceous skeletons are rare here. Pyrite microconcretions, possibly pseudomorphs after radiolarian skeletons, are also present.

Radiolarian skeletons from the Czorsztyn Succession are usually poorly preserved and seem to consist exclusively of pyrite. The examination of skeleton cross-sections show that irregular masses of pyrite grains cover various parts of the majority of siliceous skeletons of radiolarians.

Excellent preserved, pyritized radiolarian skeletons have been found within the grey-green shales of the Branisko Succession. On the basis of a study of their chemical composition, structure of replacing skeletons and exceptional preservation of all morphological details, we proposed a new model where the pyritization process took place not in sediment but while the radiolarian skeletons were suspended in the anoxic water column. The radiolarians rich in organic matter, sinking through the upper (iron-rich) part of an anoxic water column, became the sites of organic matter decomposition and enhanced bacterial sulphate reduction. Dissolved iron in this zone diffused into the radiolarians and precipitated as iron sulphides replacing the opaline skeletons. This process was controlled by the rates of opal dissolution and of bacterial sulphate reduction, and the availability of dissolved iron.

Preservation of radiolarians in the same deposits from different depth sub-basins of the Pieniny Klippen Belt (Pieniny, Branisko, and Czorsztyn) was compared. We found that the extent of pyritization and preservation of radiolarian skeletons may be dependent on the depth of the basin and the position of the oxic-anoxic interface.

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