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SELECTIVE SILICIFICATION OF CALCITIC FOSSILS AND BIOCLASTS IN THE WEST-CARPATHIAN LIMESTONES

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Abstract: Fibrous microquartz replacing the bioclasts belongs always to quartzine and lutecite, while fibrous chalcedony (length-fast chalcedony) was found only as the filling of sponge spicules. Silicification displaying the orbicule structure ("beekite") occurred exclusively in the Liassic limestones and was limited to oyster shells and belemnites. A file of susceptibility to the silicification of calcite skeletons of the various organisms was derived. The frequency of dispersed silicification within the shallow-water limestones of the Upper Jurassic and Barremian-Aptian proceeding from various tectonic units was compared and utilised for source analyses of pebbles in conglomerates. The zones of recrystallized shell first described by Maliva & Siever (1988) were confirmed by our study.

Key words: Western Carpathians, Mesozoic, Tertiary, silicification, limestones, calcareous fossils, bioclasts.

Introduction

There are two different kinds of authigenic silica in the carbonate rocks: the first is very fine-grained microquartz ("chalcedony" s.l.), the second is the megaquartz, forming mostly euhedral crystals. These two kinds of silica have different sources. Microquartz and its fibrous varieties (chalcedony s.s., quartzine and lutecite) occur within the chert nodules and in the silicified bioclasts; they proceed from the dissolved sponge spicules and radiolarian tests. The source for the megaquartz crystals is almost always dissolution of clastic quartz or alumosilicates, exceptionally also volcanic glass.

The origin of chert nodules and silicification of the bioclasts takes place during the early diagenesis from the highly concentrated silica solutions. The crystals of authigenic megaquartz grow during the late diagenesis to achimetamorphosis from the very diluted solutions.

The time relation between the formation of the microquartz (included chalcedony, quartzine and lutecite) and authigenic mostly euhedral quartz (megaquartz) can be directly observed in some cases where from the last portions of silica causing bioclast silicification, or along the peripheral part of small chert nodules the microquartz passes into partially euhedral quartz crystals. The peculiar difference between the both kinds of silica is that the clastic quartz enclosed within the chert nodules never bears syntaxial overgrowths; it was indifferent to the highly concentrated solutions. On the contrary, the silica precipitated from the very diluted solutions forms syntaxial rims on the clastic quartz grains. The qualitative difference of both solutions is also obvious from the fact that the formation of carbonate rhombohedra and metasomatic veinlets in chert nodules is limited only to the early stage of highly concentrated solutions in chert nodules (Mišík 1993). The term microquartz designates an aggregate formed by tiny individuals under 20 microns (Folk & Pittman 1971) of isometric grains or fibrous aggregates: chalcedony, quartzine, lutecite and zebra quartz. Their source is almost always radiolarian tests and sponge spicules formed by opal-A. Recently Hesse (1989) summarized the data concerning silica diagenesis. Opal-A is dissolved at the beginning of diagenesis and after the migration it is precipitated as opal-CT (CT = cristobalite + tridymite) often in the tiny spherules - lepispheres. The transition in opal-CT may rarely take place without any migration, e.g. in the spicule or radiolarian test. During diagenesis, after some tens of millions of years, opal-CT is completely changed into microquartz still containing a considerable amount of water, especially in the fluid inclusions. The formation of microquartz through the opal-CT transformation has been well documented in the layered silicites (rocks consisting mainly of opal-CT are designated as porcelanites), but it took place also in the chert nodules, as was proved by the relics of lepispheres found in them (Maliva & Siever 1988; Mišík 1993; Lintnerová & Peterčáková 1994).

The topic of this contribution will be limited to the selective silicification of bioclasts. Authigenic euhedral quartz, chert nodules, macroscopic silica, spherulites and silcretes in the West-Carpathian carbonate rocks will be treated separately. The hydrothermal replacement by SiO_2 connected with the volcanic activity is not involved.

Selective silicification of calcitic bioclasts in the West-Carpathian rocks

Dispersed silicification also occurred in the carbonate layers devoid of chert nodules. It is almost always represented by selective silicification of the calcite skeleton fragments; rarely also other allochems are affected, e.g. selectively silicified ooids. The microstructure of tests is highly convenient as a trap for the migrating solutions.

Selective silicification of the biodetritus is most frequent in the shallow-water limestones and allodapic intercalations in the pelagic limestones (Pl. I: Fig. 1). Its rarity in the proper pelagic limestones contrasts with abundant chert nodules in them. In the pelagic Tithonian-Lower Cretaceous limestones a selective silicification of the dinocysts *Cadosina* occurs; in the basinal Triassic Reifling limestones lagenid foraminifers and ostracodes have been replaced by quartz.

The selective silicification of wood (plant tissues) will not be treated here because it represents a different process, so-called petrification in which silica reacts with the organic compounds, with cellulose fibres (new results were summarized by Hesse 1989, from the territory of Slovakia by Forgáč et al. 1990). The source of silica for the silicification of Neogene wood fragments in the Carpathians was dissolution of the volcanic glass of pyroclastic rocks by ground waters. A similar exceptional syngenetic silicification is known from some chitinous animal remains, e.g. silicified spiders from the Mohav Desert (Müller 1962).

Mineral composition

Fibrous aggregates replacing calcitic bioclasts belong in all cases to the quartzine (length-slow chalcedony) or lutecite; chalcedony (length-fast chalcedony) was never found. We already arrived at this conclusion some years ago (Mišík & Sýkora 1981, p. 72). On the contrary, the spherulitic aggregate filling the spicules of siliceous sponges is always chalcedony; but here only a transformation within the silica skeleton took place. Quartzine (length-slow chalcedony) was formerly considered to be mainly a sign of the evaporite silicification (Folk & Pittman 1971), but Jacka (1974) correctly stated that quartzine is also indicative for the silicification of fossils. The replacement of biodetritus by quartzine-lutecite (microquartz) occurs frequently, but its replacement by megaquartz crystals is rare.

Replacement by megaquartz

The replacement of organic remains by megaquartz occurs only exceptionally. Thin tests of lagenid foraminifers and ostracods have been replaced by one optic individual of the authigenic quartz in the Middle Triassic Reifling limestones (biomicrites) and in the Liassic spotty limestones ("Fleckenmergel").

An aggregate of authigenic megaquartz with ghosts of growth lines replaced the inner layer of the oysters *Liogryphea* (Pl. III: Fig. 3); their outer layer was replaced by the annular-concentric structure (see further).

Rare occurrences of the authigenic megaquartz in bioclasts is mostly connected with the pre-metamorphic processes. They were observed e.g. in the Paleogene Šambron conglomerates; they are associated there with other pre-metamorphic signs as abundant authigenic feldspars (Mišík 1994). The inclusions in the crystals of euhedral quartz preserve phantoms of the nummulite test structure (Pl. I: Fig. 2) as well as the cellular tissue of the coralline algae, usually resistent to the silica replacement (Pl. I: Fig. 3). The replacement by authigenic megaquartz was sometimes provoked by the syntaxial overgrowth on the clastic quartz grain (Pl. I: Figs. 4, 5). Syntaxial overgrowths on the clastic quartz at the expense of micrite within agglutinated tests of *Orbitolina* are a similar case (Mišík et al. 1981, p.33). The authigenic quartz formed within a collapsed worm tube proved its post-compactional origin (Pl. I: Fig. 6).

Replacement by quartzine and lutecite

Maliva & Siever (1988, p. 392) pointed out that the direct precipitation of microquartz without the intermediation of opal-CT in the silicified skeletal fragments is most probable, as they lack the remnants of tiny globules-lepispheres, found sometimes in the chert nodules (Maliva & Siever 1988; Mišík 1993; Figs. 2H, 3G, H, I).

Bioclast silicification takes place either by filling of voids after dissolved parts of the shell by clear quartzine spherulites without inclusion, or by ion-by-ion replacement (in this case inclusions in the silica reproduce the skeletal structure forming ghosts). Noble & van Stempwoort (1989, p.96) used for the first process without preservation of the original structure the term "spherulitic replacement" and for the second one with preserved ghost structure "pseudomorphic replacement". Maliva & Siever (1988) believe that the silicification progrades through a tiny film of solution and the force of microquartz crystallization plays an active role. Elorza & Orue-Etxebarria (1985) suppose that the replacement of calcitic skeletal fragments by quartzine and lutecite takes place in the zone with mixing of marine and fresh waters according to the model of Knauth (1979). If in the pore waters the proportion of marine water sinks to 70-40 %, they become undersaturated with respect to calcite and oversaturated with respect to the opaline silica.

Recrystallization of shells at the contact with the silica

The accumulation of opal-CT or microquartz in a chert nodule provokes the recrystallization of the micritic calcite in rhombohedra (Mišík 1973, 1993). The recrystallization also takes place in the process of selective silicification of calcitic shells. The recrystallized parts of the shell in the immediate contact with silica were described by Maliva & Siever (1988) as "zones of recrystallized shell" (ZRS) consisting of somewhat coarser calcite filled with inclusions. I observed such recrystallized zones with ghosts of original microstructure on the rudist fragments (Pl. III: Fig. 3) and worm tubes (Pl. II: Figs. 5, 6). On the contrary, the ZRS of echinoderm plates of monocrystal nature are formed by the aggregate of finer calcite grains.

Silicification of individual groups of fossils (examples from the Mesozoic of the Western Carpathians)

Silica penetrates into the fossils mostly along their structural elements like growth rings, lamellae and prisms of bivalvian

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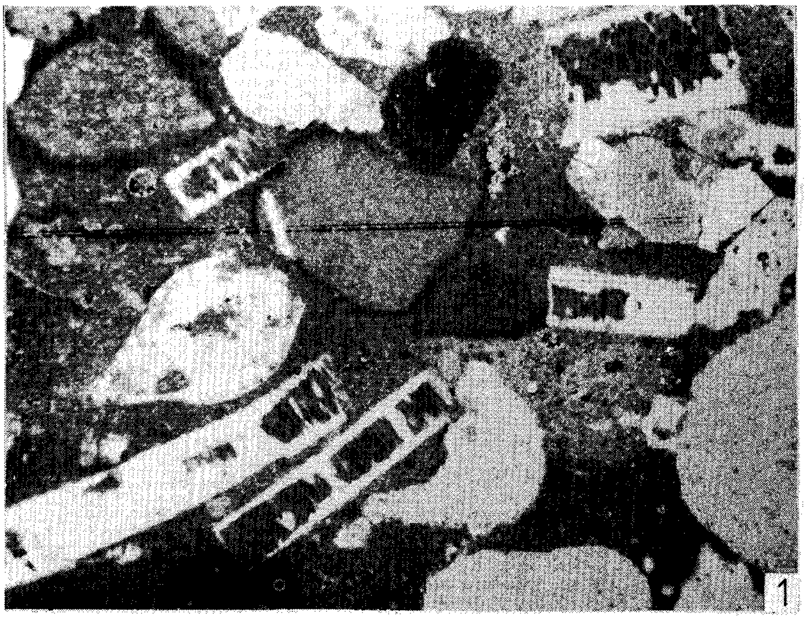
Plate I: Fig. 1 - Selective silicification of bivalvian fragments containing calcite relics of prismatic layer; calciturbidite intercalation in the pelagic Upper Tithonian limestones of Kysuca Unit, Pieniny Klippen Belt. U Belanských, near Turá Lúka; thin section No. 8746, ×26. **Fig. 2** - Authigenic euhedral quartz in a nummulite test; pebble of Lutetian limestone in the Priabonian Šambron Conglomerate. Ľubovnianske kúpele; thin section No. 1089, ×19. **Fig. 3** - Euhedral quartz formed within a fragment of coralline alga; pebble of Lower Eocene Limestone in the Priabonian Šambron Conglomerate. Jakubovany; thin section No. 4214, ×136. **Fig. 4** - Syntaxial overgrowth on a grain of clastic quartz formed at the expense of coralline alga (ghosts of cellular structure are visible in the overgrowth); fine-grained intercalation in the Šambron Conglomerate. Hromoš; thin section No. 4343, ×55. **Fig. 5** - Syntaxial overgrowth on the clastic quartz grain formed at the expense of a nummulite test; Paleogene Šambron Conglomerate. Šambron; thin section No. 14/2, ×43. **Fig. 6** - Authigenic quartz formed within the tube of a serpulid worm, collapsed during the compaction; Paleogene Šambron Conglomerate. Hromoš, thin section No. 4575, ×30.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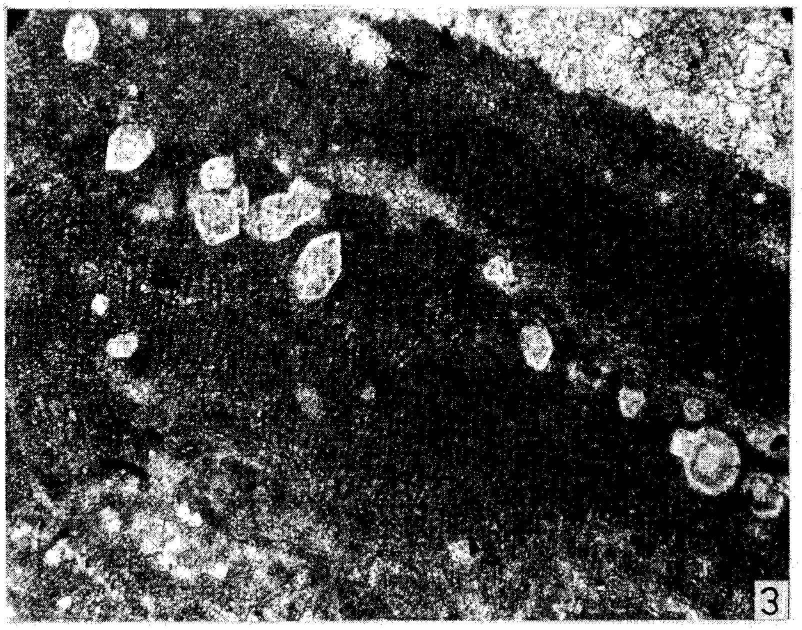
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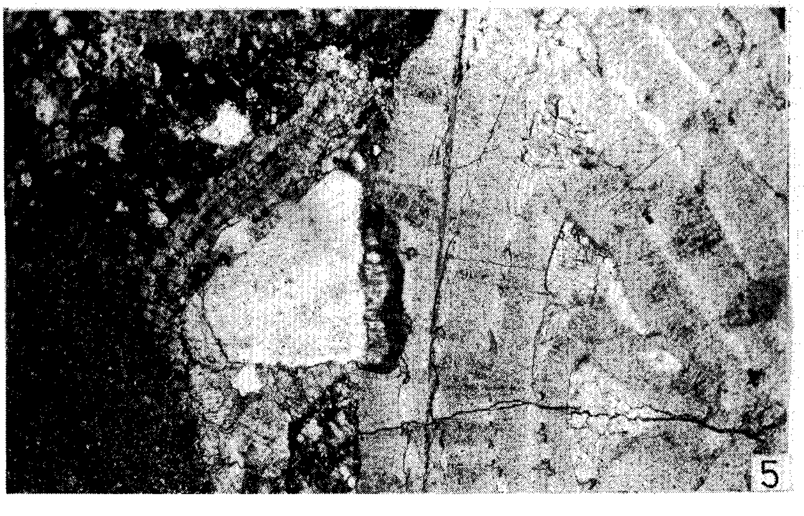
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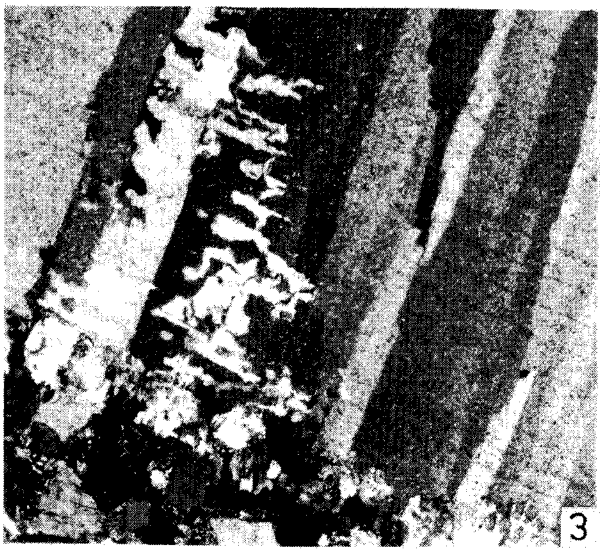
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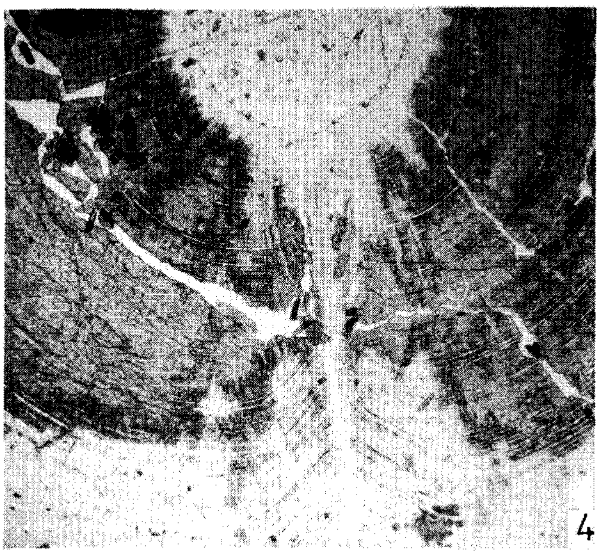
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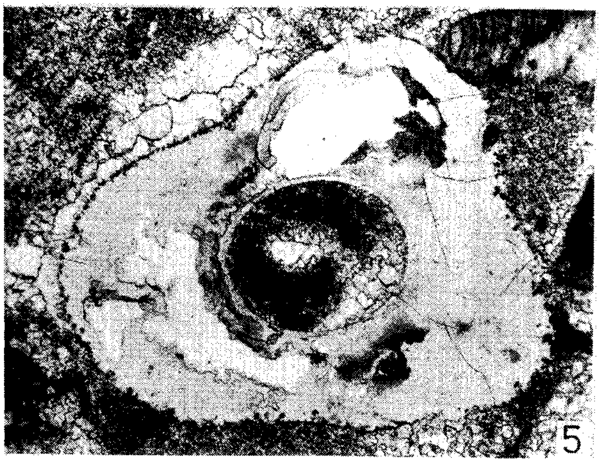
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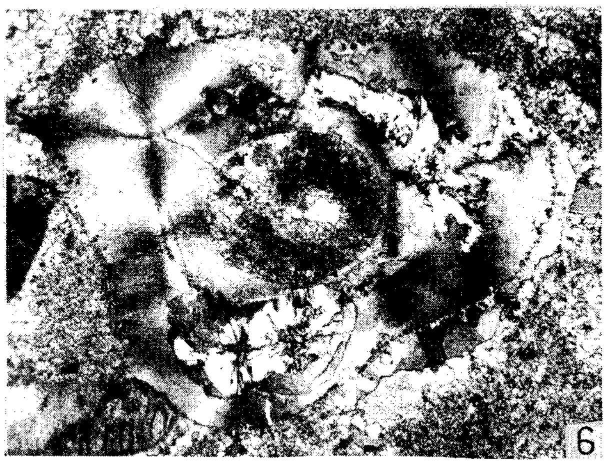
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and brachiopod shells (Pl. I: Fig. 1; Pl. III: Fig. 5) or belemnite rostra (Pl. II: Figs. 3, 4).

The paleontologists paid attention to the selective silicification of fossils in limestones long ago since the dissolution in acids yields loosened specimens sometimes with well preserved details, e.g. the Liassic brachiopods possess well preserved crura (Siblík 1962). Silicified Cenomanian to Santonian corals were redeposited in the Paleocene Klokočov Beds of the Flysch Belt and described by Eliášová (1989). I also found rare silicified corals in the Oxfordian bioherm limestones at the locality Drienková Hora near Krivoklát (Czorsztyn Unit).

The selective silicification of lagenid foraminifers and ostracods by authigenic quartz occurs currently in the pelagic Triassic and Liassic limestones (e.g. Carnian with *Osteocrinus*, locality Turňa nad Bodvou). Silicified foraminifers (*Endothyra*, *Gaudryina* etc.) were quoted from the Reifling limestones by Papšová & Jendrejáková (1984).

The Zámostie Formation (Upper Pelsonian-Lower Illyrian) contains silicified brachiopods, molusks and foraminifers in the Nízke Tatry Mts. (Rakús 1986; Kochanová & Michalík 1986) as well as in the Malé Karpaty Mts. (Buček et al. 1986). Triassic limestones near Demänová Caves contain silicified terebratulid brachiopods; in the Upper Triassic Korytnica Limestone near Liptovská Osada (both Nízke Tatry Mts.) silicified bivalves occur.

Echinoderm plates in the Lower and Middle Jurassic crinoidal limestones often display a silicification in the form of sheaf-like and spherulitic aggregates (Pl. II: Figs. 1, 2). The silicification almost always prograded from the inside. That may be caused probably by the fact that the pores of a plate had been filled by syntaxial growth of calcite beginning from the outer part so that the porosity in the inside persisted for a longer time. Silica solutions penetrated inward along the submicroscopic cracks. Replacement in the form of spherulites was aslso found in the worm tubes (Pl. II: Fig. 6).

A special case of replacement concerning shells of the oysters *Liogryphaea* and belemnite rostra requires an individual description.

Concentric-annular silicification ("orbicules", "beekite")

It is typical for the oysters *Liogryphea* (Pl. III: Fig. 1) and belemnites (Pl. III: Fig. 2) in the Liassic limestones of the Western Carpathians. The surface of the affected fossils is covered by the peculiar patterns of concentric rings with a diameter about 10 mm (5-13 mm). Double or up to twofold double cores occur sometimes.

Plate II: Fig. 1 - Echinoderm plate partially replaced by the fibrous microquartz (quartzine-lutecite) with ghosts of the original porous structure; crinoidal sandy limestone of Liassic age, Nižná Succession of the Pieniny Klippen Belt. Krásna Hôrka, Orava; thin section No. 6283, ×43. **Fig. 2** - The same in the polarized light. **Fig. 3** - Partial silicification of a belemnite rostrum penetrating along the growth lines; pebble of the Liassic sandstone in the Paleocene Proč Conglomerate. Nižné Ladičkovce; thin section No. 16015, ×48. **Fig. 4** - Partial silicification following growth lines as well as radial-fibrous structure of a belemnite rostrum; Bajocian crinoidal limestones of the Czorsztyn Unit, Pieniny Klippen Belt. Vršatec; thin section No. 5915, ×26. **Fig. 5** - Partial silicification of a worm tube by the quartzine aggregates; thin recrystallized zones were formed along their periphery. Pebble of Barremian-Aptian limestone with the detritus of corals and rudists from the Cenomanian conglomerates of the Manín Unit; thin section No. 7120, ×26. **Fig. 6** - The same in the polarized light.

Such silicification rings on the belemnite rostra were described and illustrated by von Eichwald (1886, fide Seilacher 1968) as fossilized belemnite embrya. According to Lacroix (1962), A. Brogniart found them already in the year 1831, named them orbicules ("orbicules siliceux") and correctly discerned their inorganic nature. These small concentric rings of silica were quoted by Hughes (1898) under the name "beekite". Elorza & Orue-Etxebarria (1985) also described from the Liassic calcitic sandstones of Spain the silicification of *Gryphaea* analogic to our cases as beekite. But the American authors use the term beekite for spherulites of a different aspect and genesis; e.g. King & Merriam (1969) applied it for the so-called welded cherts of the Jurassic Morrison Formation which originated from an vitritic tuffite intercalation in the limestones. According to them the red colour is typical for beekite. Taking it into consideration and also for the reason of priority I prefer the term orbicules.

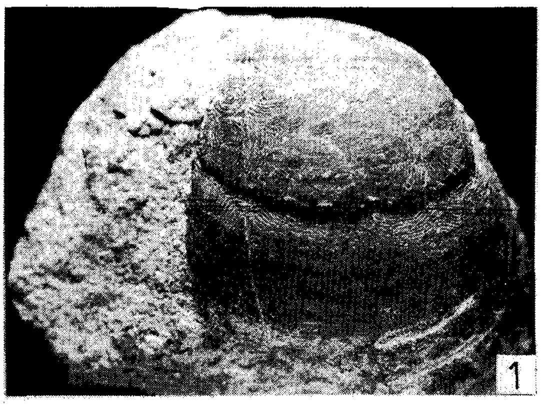
Orbicules - concentric rings from quartzine and lutecite originated on the shell around the central papillae. They replace only the outer part of the shell - ectostracum (Pl. III: Fig. 4); the remaining test is silicified by a mosaic of megaquartz with ghosts of the original microstructure and also by euhedral crystals (Pl. III: Fig. 3).

The described type of silicified shells *Liogryphaea* (mostly *L. arcuata*) from the Sinemurian or Hettangian-Sinemurian limestones was identified at the following localities and tectonic units (Fig. 1): 1 - Manín Unit s.l. - (*a*) Butkov, (*b*) Tunežice (Pl. III: Fig. 1), (*c*) Trenčianska Teplá, (*d*) Opatovská Dolina, (*e*) Dubodiel; 2 - Tatricum - (*a*) Lubochnianska Dolina, (*b*) Kečka (both belong to Veľká Fatra Succession), (*c*) Bobrovecká Dolina (Vysoké Tatry Succession); 3 - Choč Nappe - dam Čierny Váh, Nízke Tatry Mts. (a part of informations was kindly granted by M. Kochanová, M. Rakús, J. Kysela and M. Siblík).

Silicified belemnites with the concentric annular structure (orbicules) come from the following localities: 1 - Czorsztyn Unit of the Pieniny Klippen Belt, Liassic crinoidal limestones, quarry near Beňatina (Pl. III: Fig. 2 - leg. J. Jablonský), 2 - Tatricum of the Veľká Fatra Succession, spotty marly limestones ("Fleckenmergel" facies) near Podhradie (leg. M. Sýkora).

The same concentric-annular structure on unidentified skeletal fragments was found in the localities: 1 - Tatricum, Liassic limestones of the Veľká Fatra Succession (*a*) near Pàrnica, E from the elevation point 837.6 m, (*b*) near Podhradie, 2 - Krížna Nappe, Liassic limestone, Suchý Potok Valley, West Tatra Mts., 3 - Nižná Unit of the Pieniny Klippen Belt, Liassic "Gresten Formation", quarry near Krásna Hôrka, Orava.

All the specimens with orbicules ("beekite") from the Western Carpathians were found in the Liassic rocks. It is possible that not only special type of skeleton but also particular diagenetic conditions are needed for this type of silicification. Elorza & Etxebarria (1989) claimed that it was formed in the freatic fresh-water zone according to the model of Holdaway & Clayton (1982). CO$_2$ produced by the bacterial decay of organic matter should caused the dissolution of calcite. Relicts of the protein sheaths in the *Gryphaea* shells served as the centers of nucleation. Then a penecontemporaneus silicification is supposed to be analogic to the silicified plant tissue (wood), where a reaction of silica with organic molecules takes place (Hesse 1989). The shells of oysters appears to be extraordinary favorable objects with regard to silicification. Gidon (1959) documented preserved muscle tissue in the silicified Lower Cretaceous *Exogyra*.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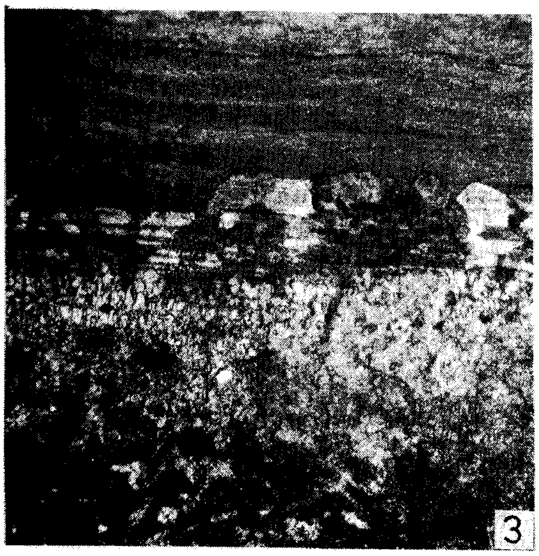
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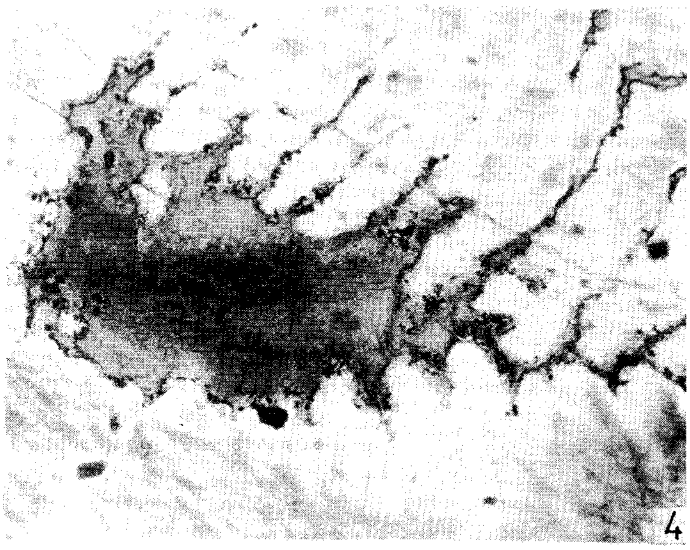
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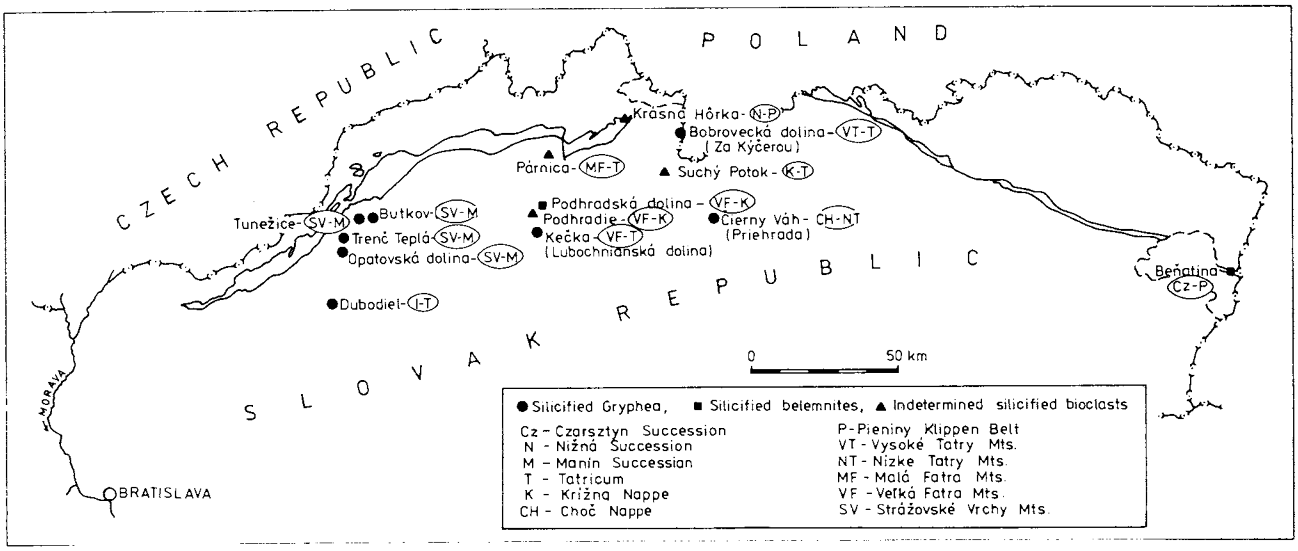

Fig. 1. Localities with the annular-concentric silicification of bioclasts (orbicules, beekite) in the Liassic limestones of the Western Carpathians.

Degree of susceptibility of individual taxa to selective silicification

Sets of thin sections (2 × 2 cm) from several lithotypes affected by dispersed silicification of fossil fragments were checked. The number in numerator indicates in how many of them the followed fossil group was affected by silicification; the number in denominator represents the cases of untouched fragments.

Fifty pebbles of the Barremian-Aptian limestones of the Urgonian facies coming from the Cretaceous "Upohlav" conglomerates (Pieniny Klippen Belt and Peri-Klippen Zone) display the following order in terms of decreasing susceptibility: bivalves 41/0 - brachiopods 5/2 - echinoderm plates 21/23 - corals 4/5 - orbitolinas 2/8 - other foraminifers 7/25 - *Tubiphytes* 1/10 - serpulid worms 0/2 - coralline algae 0/13. Bivalves were the most susceptible, to silicification and coralline algae the most resistent. From the 19 thin sections of the Upper Jurassic Barmstein Limestone (calciturbidites) the following order of susceptibility was derived: bivalves 11/1 - brachiopods 14/2 - hydrozoans 14/5 - bryozoans 4/9 - echinoderm plates 4/15 - aptychi 0/6 - dasyclad algae 0/16 - *Tubiphytes* 0/18.

The results are roughly similar but the degree of susceptibility for a specific group cannot be generalized. In the just mentioned case aptychi were not silicified, while in the Berriasian-Valanginian Horná Lysá Limestone of Pieniny Klippen Belt (Mišík et al. 1994) only aptychi were silicified, while echinoderm plates and foraminifers remained untouched. In the first case only rare thin aptychi ex gr. *Lamellaptychus* occurred associated with abundant bivalves and brachiopods capable of "catching" all the available silica, while the second limestone contained abundant aptychi with cellular structure (*Laevaptychus* type) and more convenient "traps" were absent. The bivalves with calcitic shells are very susceptible to silicification, but no case of silicification of originally aragonitic shells was observed in our material. The dissolution of the aragonitic shells and the filling of their molds by drusy calcite preceded the silicification. Wilson (1966) exceptionally found silicified aragonitic shells in the Portlandian Limestone with ghosts of microstructure.

For the purpose of comparison orders of susceptibility deduced by other authors will be cited (beginning with the most susceptible). Noble & van Stempwoort (1988): coral + brachiopods - stromatopors + echinoderm plates - bryozoan + trilobites. Newell et al. (1953): bryozoans - corals - brachiopods - mollusks - echinoderms - foraminifers - calcareous sponges - dasyclad algae. Dott Jr. (1968): brachiopods - corals - bryozoans - echinoderm plates - foraminifers. Dapples (1967): bryozoans - brachiopods - corals - gastropods - cephalopods - echinoderm plates. Kochanová & Michalík (1986): brachiopods - mollusks - foraminifers; ostracods, echinoderm plates and conodonts were untouched.

Frequency of dispersed silicification of the biodetritus in some Carpathian limestones

The set of thin sections of a lithotype was studied with regard to the occurrence of the dispersed silicification. The number of all thin sections is in the numerator; the number in the denominator indicates in how many of them dispersed silicification was observed. The frequency of silicification can be expressed in percentage terms for the purpose of comparison.

The abundance of silicified bioskeletons in a specific lithotype from the pebbles and outcrops can help us to identify the possible source or select among several alternatives.

1 - Upper Jurassic limestones with shallow-water biodetri-

Plate III: Fig. 1 - Annular-concentric structure (orbicules, beekite) in the selectively silicified oyster shell *Liogryphea* sp.; Sinemurian sandy limestone of the Manín Unit. Quarry by Tunežice; weathered surface, natural size. **Fig. 2** - Belemnite rostrum with the same type of silicification. Quarry in a klippe near Beňatina; natural size. **Fig. 3** - Detail from the annular-concentric silicification of the shell of *Liogryphea*. Quartzine-lutecite aggregate passes downward into the megaquartz grains; ghosts of the growth lines are preserved due to the calcite inclusions. Lower Liassic limestones of Tatricum. Kľak, Veľká Fatra Mts., ×22. **Fig. 4** - Detail of the annular-concentric silicification; grey patterns are relics of the calcite shell within the orbicules. As Fig. 1; thin section No. 17958, ×30. **Fig. 5** - Partial silicification of a rudist shell; silica penetrated along the structural elements of the shell. Aptian limestones of the Drietoma Succession, Klippen Belt. Bošáca, ×11. **Fig. 6** - Partial silicification (white) of a rudist shell; zones of recrystallized shell (grey) were formed along the periphery of the silicified parts. Senonian Široké Bradlo Limestone, Brezová Group. Hrombaba near Brezová pod Bradlom. Thin section No. 20395, ×26.

tus. Their pebbles occur in the Senonian Valchov conglomerates of the Brezovské and Čachtické Karpaty Mts. (Mišík 1991, p.14). Two sources should be taken into consideration. The first possibility are the outcrops of the Barmstein Limestone (calciturbidite intercalations) in the Čachtické Karpaty Mts. (Mišík & Sýkora 1982, p.58). The second possibility is the redeposition of pebbles from the nearly occurrences of the Albian to Senonian "Upohlav" Conglomerates (Mišík & Sýkora 1981), the material of which was derived from an exotic source. Let us compare the frequencies of dispersed silicification for the sets of the mentioned Upper Jurassic limestones with the shallow-water biodetritus:

Pebbles of Valchov Conglomerates - 22/24 = 92%
Outcrops of Barmstein Limestone - 31/38 = 82%
Pebbles of "Upohlav" Conglomerates - 24/52 = 46%

The result of the comparison is that the greater part of the pebbles from the Valchov Conglomerate was derived from the outcrops of Barmstein Limestone.

Pebbles of Upper Jurassic limestones with shallow-water biodetritus also occur in the Senonian conglomerates of Dobšinská Ľadová jaskyňa and Lower Miocene conglomerates near Chvalová (Mišík & Sýkora 1980). They were derived from the Silica Unit, where these highest, youngest strata are now totally absent due to erosion. The dispersed silicification was present only in three of thirty pebbles - 3/30 = 10%. If we compare it with the Barmstein Limestone of a calciturbidite nature (31/38 = 82% - the preferential silicification of calciturbidite is generally known) we can admit with a certain degree of probability, that the Upper Jurassic limestones of the Silica Unit containing the shallow-water detritus did not represent a calciturbiditic intercalation in pelagic strata but came from a carbonate platform comparable to the Plassen Limestone of the Eastern Alps. The supposition was later confirmed by the finding of preserved outcrops of limestones with *Protopeneroplis striata* from Bükk (Bérczi-Makk & Pelikán 1982).

2 - Urgonian facies of Barremian-Aptian age. Pebbles of the *Orbitolina*-bearing limestones from the "Upohlav" Conglomerates of the Pieniny Klippen Belt and Peri-Klippen Zone coming from an exotic source (Mišík & Sýkora 1981, p.38), display dispersed silicification in 10/83 = 12% specimens. Limestones with echinoderm and bivalvian fragments pertaining to the same Urgonian facies show a higher share of dispersed silicification 16/38 = 42%. The bioclast silicification was present in all twelve studied thin sections of the Urgonian facies from the Nižná Unit of the Pieniny Klippen Belt - 12/12 = 100% (Mišík 1990, p. 44). Urgonian pebbles from the Paleogene Strihovce conglomerates of the Magura Zone (Flysch Belt, Eastern Slovakia) had it in the third part of thin sections - 3/9 (Mišík et al. 1991a, p.31). Pebbles with *Palorbitolina* from the Paleocene Proč Conglomerate (Pieniny Klippen Belt, Eastern Slovakia) gave approximately the same result - 11/35 = 31%; Barremian-Aptian biosparites without orbitolinas - 5/25 = 20%, biomicrites only 4/31 = 13% (Mišík et al. 1991b). It is noteworthy that from 20 pebbles of *Orbitolina*-bearing limestones identified in the Albian Ludrová Conglomerate of Tatricum and Križna Nappe not a one contained quartzine or lutecite (Mišík et al. 1981, p. 31).

Timing of bioclast silicification

The silicification can be dated with regard to other diagenetical processes. It was already mentioned that the silicification is always younger that the filling of voids after the dissolved aragonitic bivalvian shells with drusy calcite. The filling of such voids with silica was never found; silicification affected only those bivalvians with original by calcitic shell.

The silicification is older than the tectonic twinning in echinoderm plates. Some crinoidal plates separated by silicification or recrystallized zones (ZRS) do not contain the continuation of the twinning lamellae, or their orientation is different (Mišík 1993, Fig. 3A).

The dispersed silicification is younger than the initial syntaxial filling of pores in echinoderm plates which begins along their periphery. The plates were replaced by silica almost always from inside where pores had remained empty. The silica solutions penetrated into the inner part of plates along the submicroscopical cracks. The silicification is sometimes younger than the growth of syntaxial rims; in such cases the rims can be replaced by silica (Mišík 1993, Fig. 2F).

As was already mentioned, replacement of oysters and belemnites by the concentric-annular aggregates of silica (orbicules, beekite) should be the oldest (almost syngenetic), if the nucleation of such rings is really conditioned by the proteins still present in the skeleton.

Youngest cases of the bioskeletal silicification in the Western Carpathians

In the Mesozoic limestones of the Western Carpathians the selective silicification of fossils is frequent; in the Tertiary ones it occurs only exceptionally. Among the numerous localities studied by thin sections the partial silicification of nummulites and *Rotalia* by quartzine occurred only at the locality Stránske (Rajec Basin). As already mentioned, the replacement of nummulites and coralline algae by authigenic megaquartz is indicative for the thermal effects of the pre-metamorphic stage. We observed it in the Šambron Zone of Eastern Slovakia (Pl. I: Figs. 2-6). A similar replacement of coralline algae was signalized from the Paleogene Flysch of the Alps by Badoux (1954). In the thoroughly studied Paleocene biohermal limestones (Kambühel Limestone) of the Peri-Klippen Zone silicification phenomena were totally absent.

A partial replacement of *Operculina* by quartzine-lutecite in Eggerian (Lower Miocene) limestones near Strelnice (South Slovakia) was ascertained. The youngest case - partial silicification of bivalves by quartzine occurred in the Eggenburgian sediments at the locality Rakša (Turiec Basin). Abundant algal (*Lithothamnium*) limestones of Badenian age including their biohermal facies (localities Rohožník and Láb) as well as Sarmatian limestones entirely lack the silicification of bioclasts.

The above mentioned data concern Neogene sediments not influenced by volcanic activity. Hydrothermal postvolcanic silicification leads to the formation of nummulitic silicites at first found in the paleolithic artifacts (Mišík 1975). The whole nummulitic limestone was replaced by silica. The hydrothermal origin is obvious because nummulites were replaced by chalcedony s.s., while all cases of diagenetic silicification of bioclasts are from quartzine-lutecite.

Conclusions

The selective silicification of calcitic bioclasts by the fibrous aggregates of quartzine and lutecite occurred during the early diagenesis; fibrous chalcedony can be found only as the filling of sponge spicules. A special concentric-annular silicification (orbicules, beekite) was limited to the oyster shells and belemnite rostra in the Liassic limestones. Euhedral quartz crystals (megaquartz) replace the bioclasts only in cases of thermal affection during the late diagenetic (pre-metamorphic) stage.

The main source for the bioclast silicification were sponge spicules. Bivalves appear to be most susceptible to silicification, algae most resistent. The study of the frequency of bioclast silicification in the shallow-water Upper Jurassic and Barremian-Aptian limestones helped to decide between two possible sources of pebbles for some Cretaceous and Paleogene conglomerates in the Western Carpathians. The youngest case of the silicification of biodetritus was ascertained in the Lower Miocene (Eggenburgian) limestone.

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