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SILICA SPHERULITES AND FOSSIL SILCRETES IN CARBONATE ROCKS OF THE WESTERN CARPATHIANS

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Abstract: Tiny spherulitic balls ("Hornsteinkugelchen") were found exclusively in the Triassic micritic limestones and dolomites; they originated partly by the silicification of gypsum microconcretions. This is supported by various signs of hypersalinity. Another origin is supposed for aggregates of spherulites arranged along the polyedric faces; they were formed during the late diagenesis along the network of hair-thin cracks.
Rare red cherts in Keuper dolomite probably represent climatic silcretes; they contain scarce lepisphere-like relicts. Silcretes from the Berriasian limestones of the Czorsztyn Unit (Pieniny Klippen Belt) are described. Paleocene silcrete from the locality of Drienovec was formed on pelitic regolite; its chemical composition indicates the connection with the underlying redeposited products of the Upper Cretaceous lateritization.

Key words: Western Carpathians, Mesozoic carbonates, silcretes, silica spherulites.

Tiny spherulitic chert balls

They weathered out from limestones and rarely from dolomites in the form of mm-size protuberances (Pl. I: Fig. 1). They are named "Hornsteinkugelchen" in the German literature and "pustules" (warts) in French publications. They are formed by fibrous or prismatic silica aggregates. Sometimes only relicts of spherulites are discernible.

In the Western Carpathians such tiny spherulitic silica balls are known only from the Middle and Upper Triassic micrites and dolomicrites. They are absent from younger micritic limestones of Jurassic and Cretaceous age. The tiny chert balls originated by micrite replacement. The most perfect spherulites with the best crystallized silica aggregates occur in dolomites; their possible origin by the replacement of micronodules or stellate aggregates of gypsum or anhydrite will be analysed further.

The source of the silica in the Gutenstein Limestone and Dolomite is not clear, as radiolarians, sponge spicules and clastic quartz are absent and the clay minerals are also reduced to a minimum. A description of the localities will follow.

Middle Triassic limestones

1 — Malé Karpaty Mts., olistolites of the Triassic limestones in the Liassic Korenec Fm (Plašienka 1987). The typical locality is the rockwall under the ruins of Pajštún castle near Borinka, 10 km N of Bratislava (Fig. 1). Grey micrite contains locally weathered-out tiny chert balls, dolomite intercalations, pseudomorphoses after the crystals of gypsum and anhydrite. All these phenomena are typical of Anisian Gutenstein Limestone. In the western part of the rockwall and in other places they are overlain by Liassic carbonate breccia with belemnites of Lotharingian age according to Čiňčurová (1971, p.16). Those breccias also contain clasts of Triassic limestones with tiny chert balls. The following occurrences were ascertained in olistolits of Triassic limestones and their clasts in Liassic breccias (Fig. 1): *a* — rockwall near the entrance to the Pajštún castle, *b* — on the crest 150 m W of the ruins, *c* — small abandoned quarry 1 km N of the ruins, *d* — Vápenický potok valley NE from the ruins, *e* — small abandoned quarry S of Stupava Park (found by V. Havrila), *f* — Kozlisko elevation point, *g* — abandoned quarry of cement works, *h* — 1 km NE of the church in the Borinka village, *i* — between Červený domček and Lintovy (near Lozorno), *j* — hill Prostredný vrch E of Lozorno (found by D. Plašienka), *k* — Rozglabská dolina Valley near Pernek, *l* — northern slope of the hill Pleš near Pernek.

The chert balls occur in a well-defined area with consistent physicochemical parameters of sedimentary and diagenetic evolution. They are already missing in the area of Medenné Hámry-Propadlé, in the Urbár quarry above the village of Záhorská Bystrica, and in the Middle Triassic limestones of the Devín Succession (Mišík 1986, p.88). The locality of Pleš was attributed by Michalík et al. (1994) to the Kuchyňa Succession. As all occurrences of tiny chert balls are in the Borinka Succession and they are absent in the successions of other tectonic units in the Malé Karpaty Mts., it is highly probable that the locality Pleš belongs to the Borinka Succession, as well.

The chert balls mostly have a diameter of 3-5 mm. Intercalations with a greater concentration of them occur in places (Pl. I: Fig. 2). Their spherulitic structure is indistinct or only preserved in relicts. Sometimes, they also possess a concentric structure with one or more rings visible in the section; the neighbouring balls may join into the form of the figure eight (Pl. I: Fig. 6).

Several balls are formed only by one peripheric ring of silica in the section (like a small contour chert nodule); such a peripheric ring consists of radially arranged mostly xenomor-

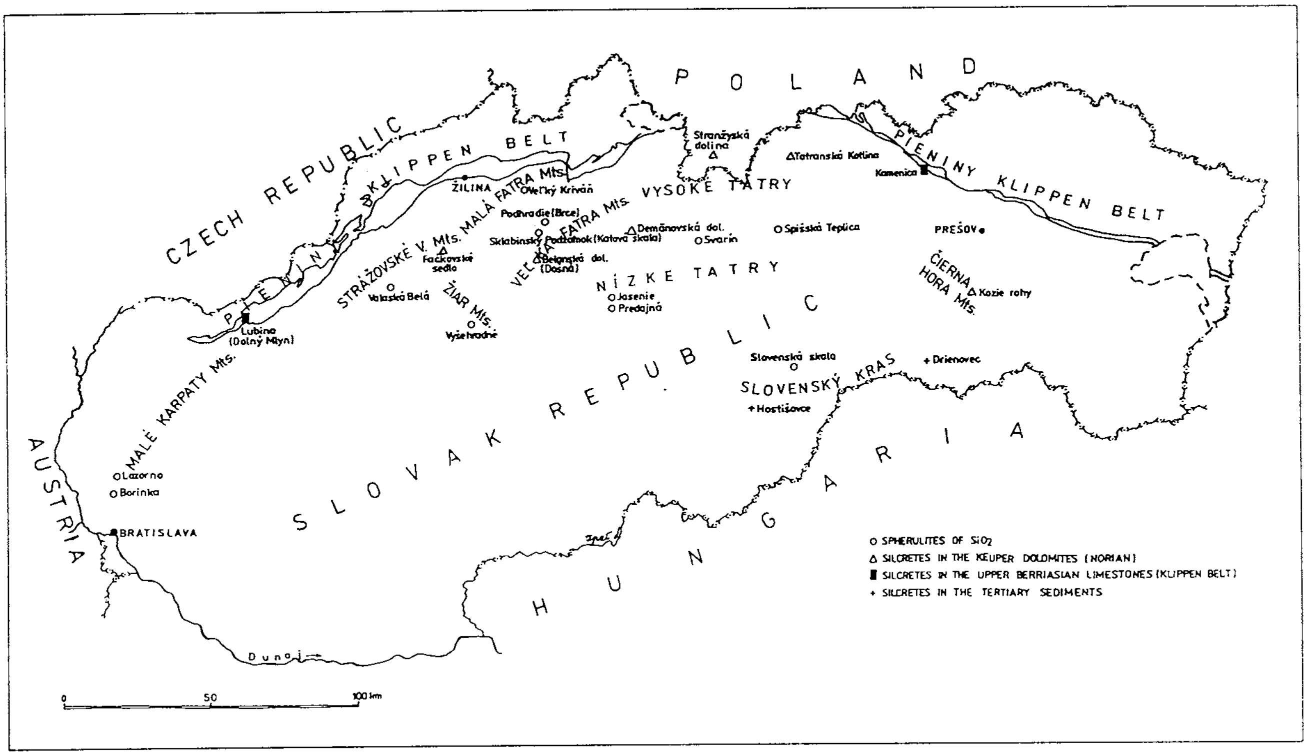


Fig. 1. Situation of the mentioned localities.

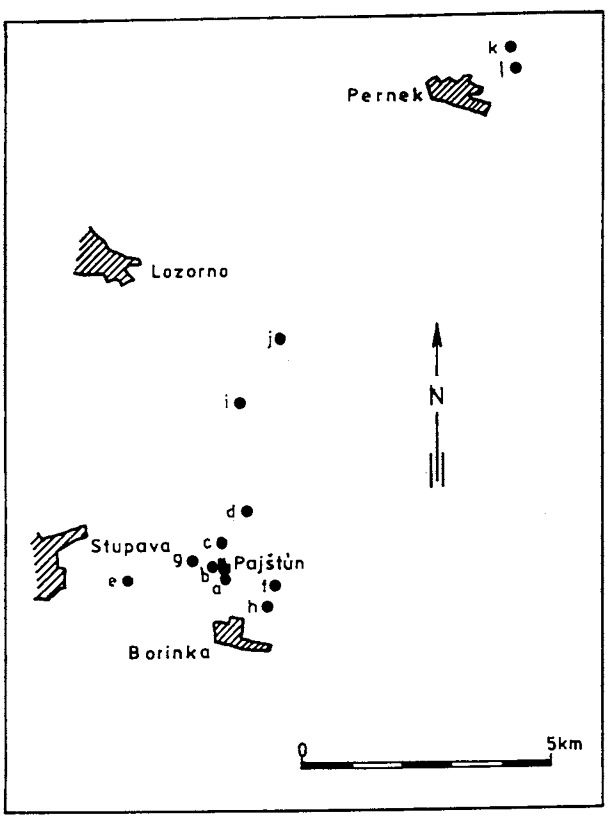
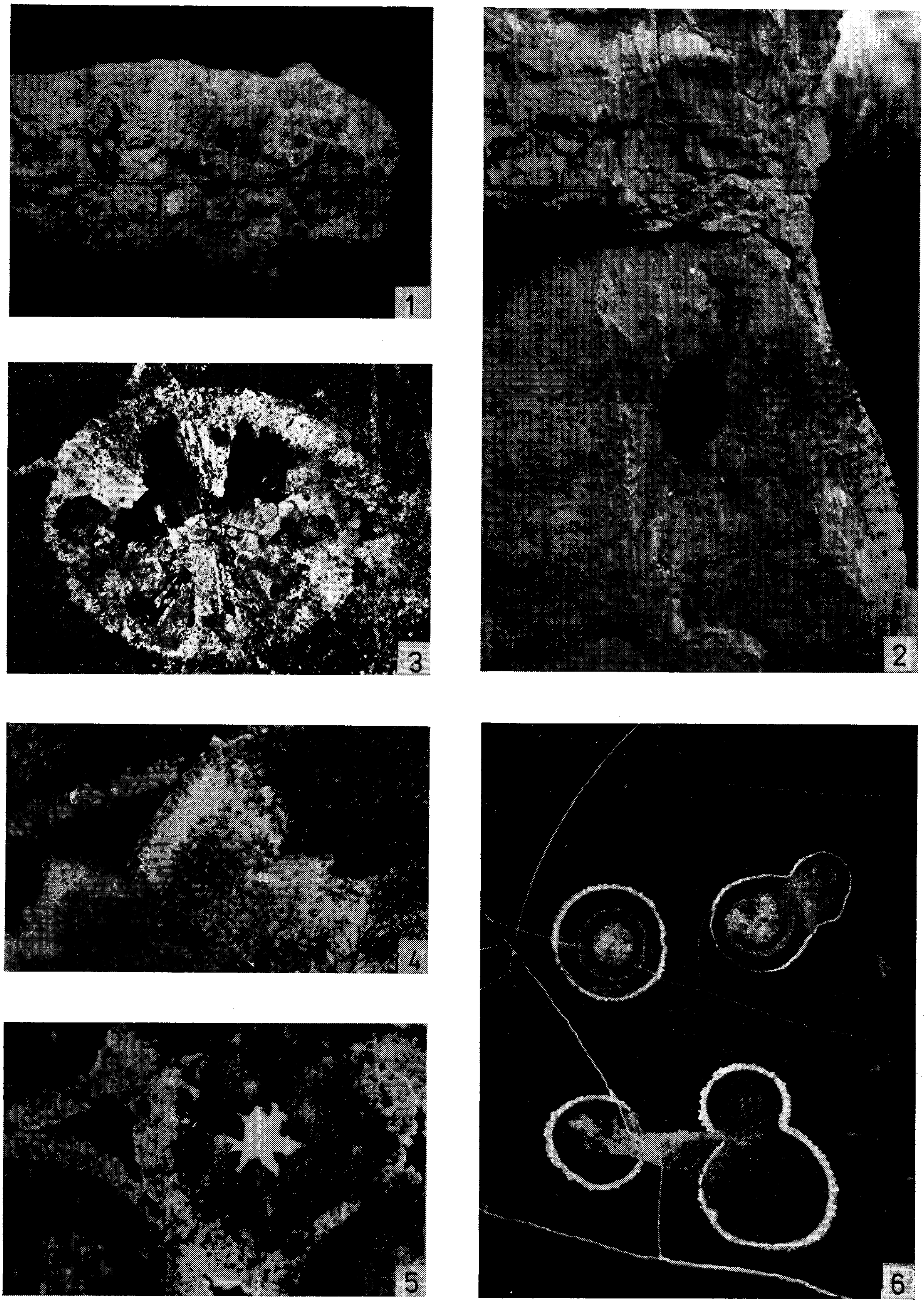


Fig. 2. Localities with tiny chert balls — silica spherulites in the Middle Triassic micrites of Borinka Unit, Malé Karpaty Mts. (N from Bratislava).

phic crystals of authigenic megaquartz. Their inner margin is filled by calcite inclusions of micritic or tiny oval grains of a diameter 0.005–0.010 mm (their calcitic nature was verified by alizarine staining). In their external parts the quartz crystals are clear.

The spherulites replaced by calcite crystals represent another type; their centre is sometimes filled by microquartz or by a mixture of fine-grained calcite and microquartz. These spherulites consist partly of wedge-like calcite individuals; relicts of microquartz ("chalcedony") with tiny calcite rhombohedra to 0.03 mm may be observed between them (Pl. II: Fig. 1). The formation of calcite rhombohedra in cherts is a common feature and no primary calcite rhombohedra occur in the marine limestones (Mišík 1992a). As such tiny rhombohedra are also sometimes enclosed in the radially arranged cal-

Plate I: Tiny chert balls ("Hornsteinkugelchen") — silica spherulites in the Middle Triassic micrite limestones of the Borinka Succession, Malé Karpaty Mts. **Fig. 1** — Weathering out of chert balls; a clast from the Liassic breccia. Borinka, old quarry of the cement works, natural size. **Fig. 2** — Horizon with the dense concentration of chert balls. Entrance to the ruins of Pajštún castle. **Fig. 3** — Substantial part of the spherulites was replaced by wedge-like calcite grains, the residual part is of microquartz. Clast from the Liassic breccia. Borinka, old quarry of the cement works. Enlarged 24×. **Fig. 4** — Euhedral quartz crystals grown along the periphery of spherulites, one of them disturbing the veinlet. Kozlisko. Enlarged 48×. **Fig. 5** — Imperfect peripheric silica spherulites (white borders). Their central part was frequently dissolved and filled by calcite crystals with points sticking inward (grey). In the case of incomplete filling the residual void is filled by microquartz (white). The black spot between the spherulites ("balls") is the original unreplaced micrite. As above. Thin section stained by alizarine. Enlarged 30×. **Fig. 6** — Tiny chert balls — imperfect spherulites with annular structure, sometimes joined in 8-like forms. As above. Enlarged 6×. Photo.: L. Osvald.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cite individuals, it indicates, that the calcite spherulites originated by the replacement of the silica spherulites.

If the chert balls occur within the pelmicrite, the phantoms of pellets are discernible in the aggregate of silica or replacing calcite. This is the evidence that chert balls originated by the metasomatic replacement of the original micrite and not by the filling of an empty space.

The specimens from the locality of Kozlisko show that a small part of the spherulites was formed by the replacement of microoncoids with a diameter of 3-4 mm. In their centres cores formed by fossils of globular outline with a diameter of 0.7 mm were observed several times. The voids after their dissolution were filled by the medium-grained calcite. Cyanophyte oncoids were formed around these cores, the relicts of their concentric structure are still visible (Pl. II: Fig. 2). Along the periphery of the calcitic microoncoid an aggregate of xenomorphic quartz was formed. In rarely cases some inner concentric rings were also partly silificied.

In connection with this phenomenon it is noteworthy that Flügel & Kirchmayer (1963, p. 122-123, Pl. IX: Fig.3) have described from the type locality of the Gutenstein Limestone in the Alps similar bodies as "verkieselte Ooiden" (silicified ooids) with a size of 15-20 mm (min. 10 mm, max. 30 mm), that is much larger than our occurrences. They mostly have a radial-fibrous calcitic core and only thin chalcedony margin. The authors mentioned that von Hauer (1853) named these tiny chert balls from Gutenstein Limestone "Hornsteinkugelchen". Summesberger & Wagner (1971, p. 349-350, Pl. 3: Fig. 2) revised the lithostratotype of Anisian Gutenstein Limestone. They rejected the opinion of Flügel & Kirchmayer (1963) about the origin of the "Hornsteinkugelchen" from the ooids and pseudooids. In the case of our occurrences, the replacement of ooids is certainly not involved, since as no ooids occur in this formation. Microoncoids (max. 5 mm) were found at two localities; at one of them they were partly silicified (Pl. II: Fig. 2). Therefore, the origin of tiny chert balls in this way may be considered as exceptional.

Borinka Unit was affected by anchimetamorphism (Plašienka et al. 1993), best observable in the continuous layers of Borinka limestones in the Propadlé quarry. However in the olistolites and clasts within the Liassic breccias the pressure affects were smoothered by the matrix. But at the locality of Kozlisko (loc. "f") the metamorphic affection is clear. The original micrite was recrystallized, the calcite grains are elongated in the plane of the metamorphic foliation. The chert balls (up to 10 mm in diameter) were deformed into ellipsoids. In the centres, they contain a fine-grained mixture of calcite and quartz which grades into radially arranged columns of authigenic quartz filled by calcite inclusions (Pl. I: Fig. 4). Quartz crystals were partly replaced by fibrous calcite in pressure shadows. The redistribution of silica into the pressure shadows in connection with the formation of pressure fringes (Pl. II: Fig. 3) was also registered at the locality "b".

Summary of the occurrences in Malé Karpaty Mts. The tiny chert balls (spherulites) were formed during diagenesis in the Middle-Upper Triassic, before the Liassic. The source of silica is unknown. In the course of anchimetamorphism (most probably during the Upper Cretaceous) their silica was partly redistributed. In spite of the fact that no direct proofs for the origin of silica spherulites by the replacement of gypsum or anhydrite micronodules were found, this process cannot be excluded. The psudomorphs after the gypsum crystals are known from the area (Mišík 1972, p. 80-84), but they were not found in the immediate neighbourhood of silica spherulites and the pseudomorphs after gypsum crystals were never formed by quartz. The cores of spherulites are sometimes formed by legth-slow chaledony (quartzine) which should, according to Folk & Pittman (1980), indicate the "vanished evaporites". Our tiny chert bodies are very similar to those described by Siedlecka (1972) from the Carboniferous limestones. She mentioned relicts of quartzine spherulites (diameter od 1-3 mm) grading outwards to the megaquartz crystals and considered them as sulphate replacement.

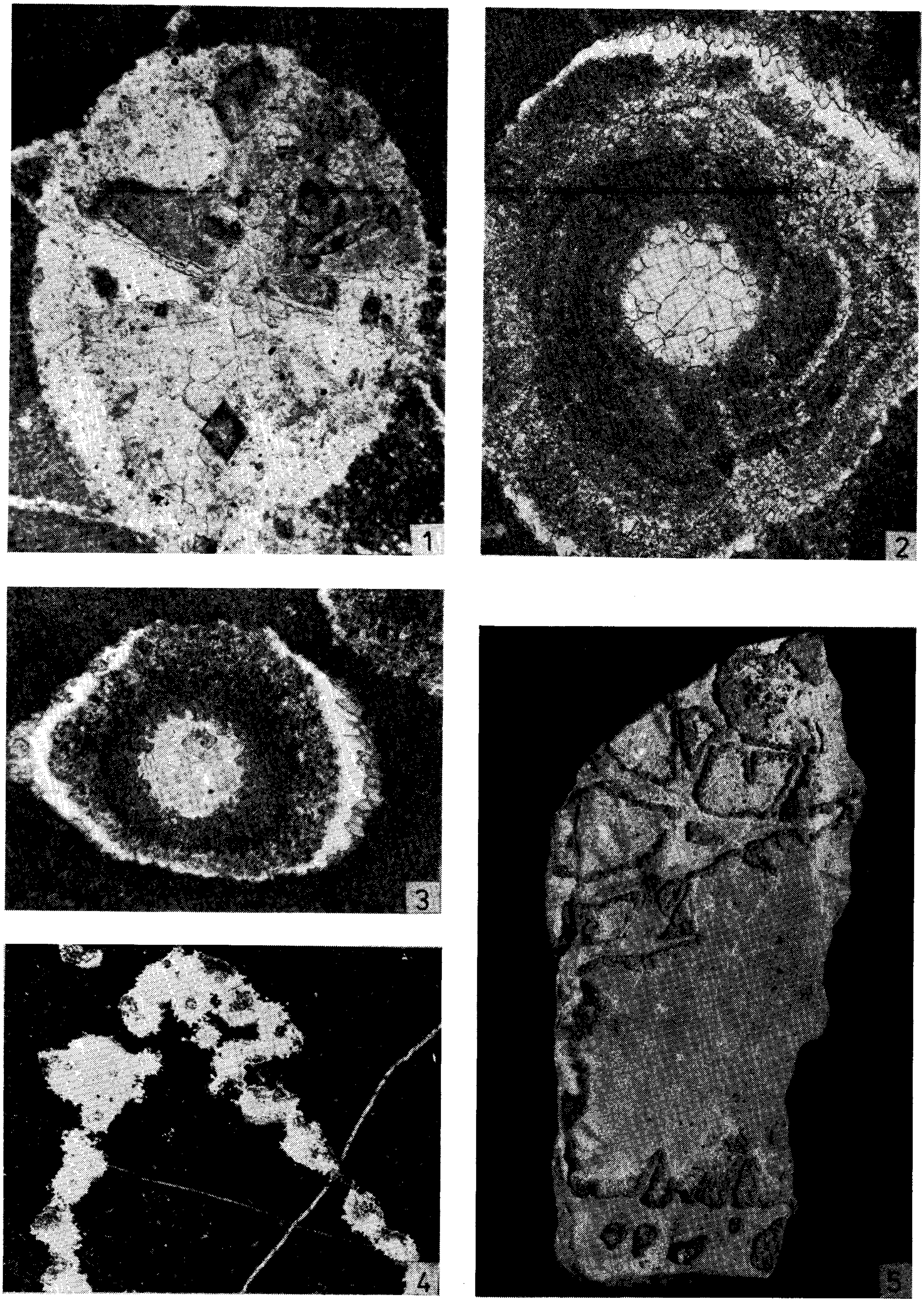
Veľká Fatra Mts., Gutenstein Limestone of the Krížna Nappe (collected by M. Sýkora).

a — East of the village of Podhradie, below the elevation point 1126.1 Brce. Dark-grey, slightly dolomitized micrite with tiny spherulites joined in chains. On the weathered surfaces, it can be observed, that the connected tiny chert balls (max. diameter of 1 mm) are arranged like the frames of polygons, mostly rectangles or rhomboids, with the sides about 1-2 cm long, similar to the further described locality (Pl. II: Fig. 5). Such patterns were probably conditioned by the formation of spherulites along the mostly rectangular network of clefts. The traces of those hair-like clefts were rarely observed in thin sections.

Most spherulites range in size from 0.6 to 0.8 mm. They consist of fibrous aggregates of quartzine and lutecite and frequently grade towards the periphery in the thin columns of euhedral quartz giving them a hedgehog-like appearance (Pl. II: Fig. 4). The columns of quartz crystallized from the last portions of strongly diluted silica solutions. Mostly, they rim only the inner part of the spherulites with regard to the polyhedra which is evidence of the inward flow from the hair-like clefts. This also agrees with the asymmetry of spherulites. The central parts of spherulites are filled by calcite inclusions. An aggregate of coarser calcite grains limited by the crystal faces along the outline of the core sometimes occurs in the centres. Several spherulites are rimmed by a fibrous calcite aggregate, but only on one side, at the difference from the pressure shadows. Exceptionally, doubled frames occur; the spherulites are better developed in the inner of the two rows. Pyrite crystals up to 0.08 mm are always limited on silica spherulites and absent in the other parts of limestone.

The surrounding rock is micrite with rare echinoderm plates, ostracods, gastropods, juvenile pelecypods, a fragment of a brachiopod and the foraminifera *Frondicularia woodwardi* (evaluated from 9 thin sections). The irregular spongy

Plate II: Tiny chert balls — silica spherulites from the Middle Triassic limestones of Malé Karpaty Mts. and Veľká Fatra Mts. **Fig. 1** — Carbonate rhombohedra have grown on the silica substratum and the spherulites was partly replaced by radially oriented calcite grains. Clast from the Liassic breccia Borinka, old quarry of the cement works. Enlarged 30×. **Fig. 2** — Tiny chert ball formed by slight silicification of a microoncoid. Kozlisko. Enlarged 30×. **Fig. 3** — Chert balls (imperfect spherulites) elongated in the sense of extension during a slight metamorphism. Fibrous borders in the pressure shadows consist of quartz and calcite. Crest W of Pajštún castle, Borinka. Enlarged 30×. **Fig. 4** — Silica spherulites connected in chains; Middle Triassic Gutenstein Limestone of the Krížna Nappe. E from the village of Podhradie, underneath elevation point 1126.1 Brce, Veľká Fatra Mts. Enlarged 11×. **Fig. 5** — Polyhedric "frames" formed by outweathering of tiny spherulites arranged in chains. As above. Underneath the Katova skala near the village Sklabinský Podzámok, Veľká Fatra Mts., slightly diminished. Photo.: L. Osvald.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dolomitization in the form of coarse-grained aggregates of the yellowish dolomite grains took place during the late diagenesis; it follows partly the veinlets. The growth of one spherulite was stopped on a dolomite veinlet showing that silicification is younger than the epigenetic dolomitization.

b — Slope of the hill Katova Skala near the village of Sklabinský Podzámok (Fig. 1); the distance from the previous locality is 5 km. This second occurrence of continuous frames of polyhedra with a thickness of 1-2 mm (Pl. II: Fig 5) contains a small chert balls formed by fine-grained quartz with calcite inclusions instead of fibrous silica spherulites. The tiny balls grade on the inner side of frames into the isolated columns of euhedral quartz with points on both ends. They are likewise filled by calcite inclusions frequently in zonal arrangement. Several frames are formed exclusively by the crowds of euhedral quartz. The pyrite crystals up to 0.1 mm occur once more only within the silica aggregates.

The tiny chert balls occur in the pelmicrites with very rare echinoderm plates, ostracods, micritic intraclasts and rare aggregates of anhedral dolomite grains. The tiny silica balls from the frames of polyhedra are younger than the dolomite aggregates corroded by them and even younger than several calcite veinlets penetrated by them.

Summary of the occurrences in the Veľká Fatra Mts. In the Gutenstein Limestone of the Krížna Nappe the tiny chert balls — spherulites are arranged along the edges of polyhedra, due to the network of hair-like cracks originated by an early tectonic event. The silicification is younger than the late diagenetic dolomitization. It took place in an anoxic environment. The pyrite crystals are linked only to the silica aggregates; they are absent in the surrounding micrite, or only the pyrite pigment occurs there. From the last and most diluted solutions the euhedral quartz columns were formed along the periphery of the tiny balls. The source of the silica remains unknown. No signs of eventual gypsum-anhydrite precursors were found.

Nízke Tatry Mts. *a* — Jasenie Limestone (Kochanová & Michalík 1986), the lower part of the Zámostie Formation, formerly considered as lower part of the Reifling Limestone; Anisian (Upper Pelsonian) of the Choč Nappe, locality Jasenie. Besides the nodular cherts, selectively silicified macrofossils and small chert balls ranging in size from 2 to 5 mm occur. They consist of quartzine spherulites (Pl. III: Fig. 1). The silica originates from sponge spicules. Two more localities can be attributed to the Reifling Limestone in the broader sense; *b* — Svarín — imperfect quartzine spherulites with the diameter about 2 mm; *c* — Predajná (found by M. Demian) — the same. No gypsum-anhydrite precursors are supposed for these tiny chert balls in the Middle Triassic in the Nízke Tatry Mts.

Upper Triassic limestones

Slovak Karst. Carnian limestone of the Turňa Nappe, hill Slovenská Skala, S of the town Jelšava. Light-grey fine-grained limestone with tiny chert balls (collected by R. Mock) bears traces of initial metamorphic recrystallization. The calcite grains are elongated along the foliation plane; they contain frequent pressure twins. The organic remains are absent.

Tiny chert balls with the diameter of 3-4 mm (Pl. III: Fig. 2) consist of microquartz; their peripheral parts are stained brown by organic matter. Relicts of fibrous spherulitic structure (quartzine) can be observed in the polarized light. In the central part of balls larger, irregular, cloudy calcite grains occur. Chert balls are filled by tiny grains and minute brownish carbonate rhombohedra. The balls are partly bordered by limonite.

It is noteworthy that the tiny chert balls were formed after the slight metamorphism, so not earlier than after the Upper Jurrassic-Lower Cretaceous. This is shown by the following facts: xenomorphic quartz grains from the periphery of balls corroded already recrystallized calcite grains; no metamorphic flow around the more rigid chert balls was observed, no fringes in pressure shadows formed; no cracks caused by the different plasticity of limestone and chert during the tectonic pressure are present.

Dolomites of the Middle Triassic age

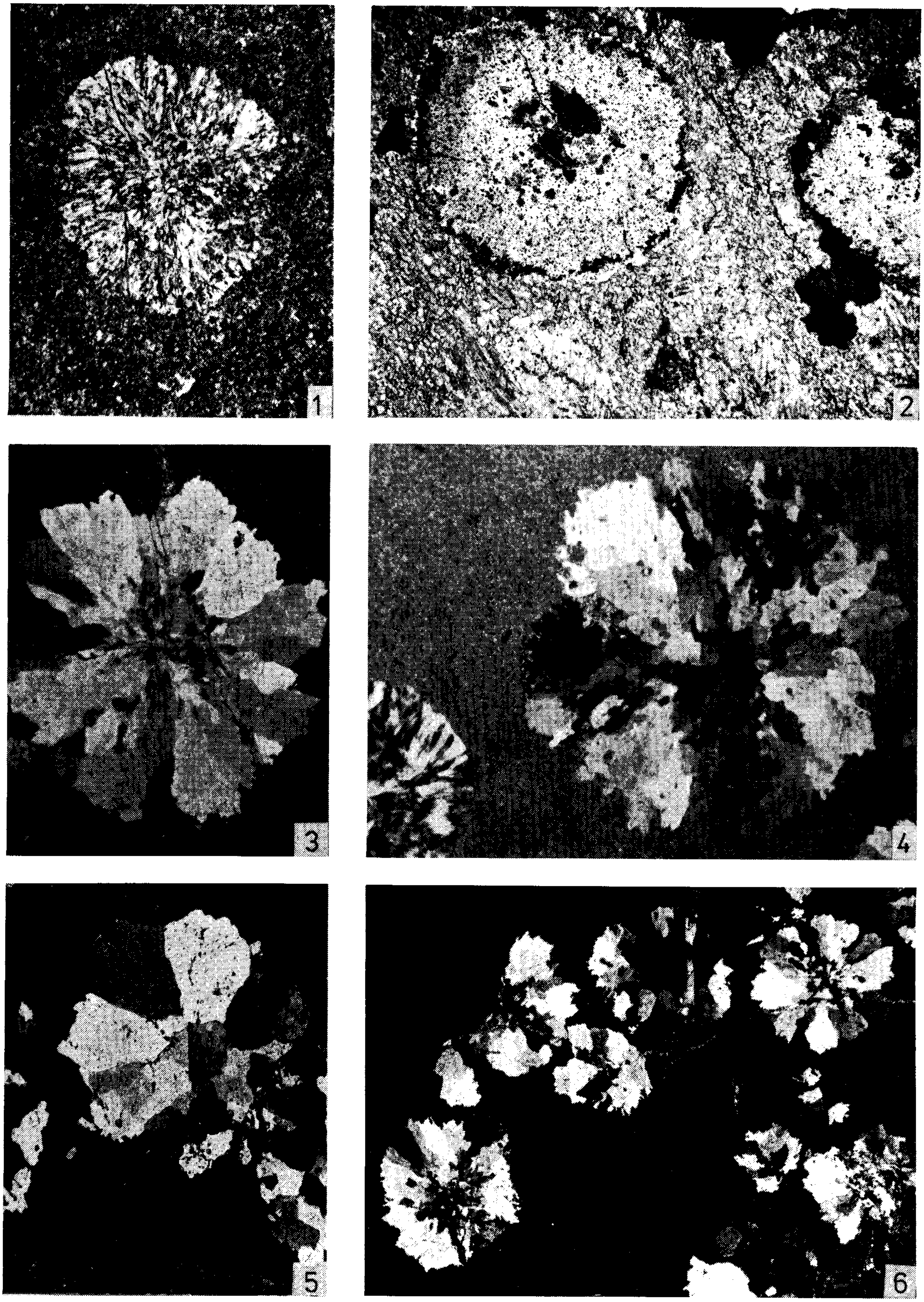
1. Veľká Fatra Mts., Došná Valley (lateral part of the Belanská dolina Valley — Fig. 1), Tatric Unit. Dolomicrites with average grain size 0.015 mm contain chert balls with a diameter of 2-3 mm (Pl. III: Fig. 4). The cores of most spherulites consist of radial-fibrous aggregates of quartzine and lutecite which grade outwards into the irregular, wedge-like "supergrains" of quartz (they are composed of several optical individuals with slight differences in extinction). Smaller spherulites used to be only from the fibrous silica and a part of chert balls is formed by coarse-grained quartz without the relicts of spherulitic structure. Corroded rhombohedra or aggregates of dolomite grains can be seen in several spherulites. Among the inclusions minute individuals of the rectangular shape with higher index of refraction and higher birefringence were observed; they could belong to anhydrite.

2. Malá Fatra Mts., hill Veľký Kriváň, Tatric Unit. Fine-grained dolomite with weathered-out balls of a diameter about 2 mm. They consist of megaquartz aggregate possessing an imperfect spherulitic structure (Pl. III: Fig. 5).

3. Žiar Mts., near the village Vyšehradné, Krížna Nappe. Dolomicrite with weathered-out balls with a diameter of 2-3 mm. The radial fibers of quartzine (length-slow chalcedony) coalesce sometimes in megaquartz grains with undulatory extinction (Pl. III: Figs. 3, 6). Dolomicrite inclusions in the core are frequent; tiny rectangular inclusions probably of anhydrite occur.

Summary of the tiny chert balls from dolomites. Spherulitic balls occur in the penecontemporaneous dolomites; the silicification is younger then the dolomitization (relicts of dolomicrite in silica spherulites are common). The dolomites do not contain any organic remains; they originated in the schizohaline environment (Kantor & Mišík 1992, p. 13, 14). The replacement of

Plate III: Small chert balls — silica spherulites in the Triassic limestones and dolomites. **Fig. 1** — Quartzine spherulite (length-slow chalcedony) in the Anisian Jasenie Limestone, near the village of Jasenie, Nízke Tatry Mts. Enlarged 25×; crossed polars. **Fig. 2** — Silica spherulites in the slightly metamorphosed Carnian Limestones of the Turňa Nappe, Slovak Karst, hill Slovenská skala near Jelšava. Enlarged 13×. **Fig. 3** — Quartz spherulite in the Ladinian dolomites of the Krížna Nappe. Roadcut E of the village of Vyšehradné, Žiar Mts. Enlarged 25×; crossed polars. **Fig. 4** — Quartz spherulite and a part of the quartzine spherulite in the Middle Triassic dolomite of the Tatric Unit. Došná Valley (lateral valley of Belanská dolina), Veľká Fatra Mts. Enlarged 30×; crossed polars. **Fig. 5** — Imperfect quartz spherulite in the Ladinian dolomites of the Tatric Unit. Hill Veľký Kriváň, Malá Fatra Mts. Enlarged 14×; crossed polars. **Fig. 6** — Quartz spherulites in dolomite; as in Fig. 3. Enlarged 11×; crossed polars. Photo.: L. Osvald.



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micronodules or stellate aggregates of gypsum is probable; such cases were frequently described (Folk & Pittman 1971; Siedlecka 1972; Milliken 1979; Konta 1955; Skoček 1988). But it was not performed by the dissolution of gypsum or anhydrite micronodules and precipitation of silica into the empty space as was the case with white "eyes" in grey micritic limestones filled by drusy dolomite with the grain size increasing inwards (Mišík 1972, p. 84–86).

Silcretes — climatic silicification in the carbonate rocks of Western Carpathians

Recent and subrecent silicification can be observed in the semiarid regions. For instance, near the northern margin of Sahara the top part of outcrops of limestones and sandstones are frequently silicified. I collected the silcrete samples for comparative purposes S of Tebessa and N of Biskra in Algeria. Chert nodules of irregular form may be found in limestones; sandstones grade into quartzites; cauliflower geodes with quartz crystals originated after the dissolution of subsurficial hypergenetic gypsum concretions. Silcretes also originated under the conditions of the alternation of strongly contrasting dry and humid seasons (Thiry & Millot 1987; Thiry & Milnes 1989).

Upper Triassic (Norian)-Carpathian Keuper

Red and light-grey chert nodules in white dolomites are suspected as the products of climatic silicification. They were found only at a few localities but their analogy with so-called "Karneoldolomit" from the German Triassic, generally linked with pedogenesis, compels us to consider them as silcretes formed near the surface. The "Karneol" silicites from the Lower Triassic were mentioned by Füchtbauer & Müller (1970, p. 497), who attribute their origin to ascendant solutions under an arid climate. Tröger (1984, p. 331) described the "Karneoldolomit" also from the Lower Triassic (Middle "Buntsandstein") as a fossil pedogenetic horizon. In the "Buntsandstein" as well as in the Carpathian Keuper continental facies are dominant. It is noteworthy that in the area of the German Triassic (platform development), as well as in the areas of the Carpathian Keuper, no volcanic activity took place. The following localities with silcretes in Keuper dolomites have been found up to now:

a — Abandoned quarry near the road between the villages Tatranská Kotlina and Ždiar; Krížna Nappe (partial nappe Bujačí). The following microscopic description was compiled from 8 thin sections. The host rock of red chert nodules (up to some dm) are dolomicrites and rare dolointramicrites, fine-grained breccias originated by drying of sediment. Intraclasts possess expressive dessication cracks (Pl. IV: Fig 1) which is evidence of temporary emersion and drying up of lagoons leading to a pedogenetic process.

Red and light-grey chert nodules consist of microquartz, sometimes with phantoms of small intraclasts. The silica aggregate is pure, and carbonate grains are almost always only in the veinlets. The outlines of chert nodules are sharp, a transition zone of strainer-like type rims sometimes forms the inner margin (Pl. IV: Fig. 2). The red colouring is irregularly distributed, its intensity is usually concentrated in two or three irregularly undulated rings; the most expressive ring follows the outline of the nodule in a distance of 1-2 mm. The inward boundary of red rings is sharp. The red rings are formed by a dense concentration of minute grains of Fe-pigment which becomes more diluted going outwards with the increasing size of pigment grains. They acquire an aspect of short tiny rods arranged parallely to the ring (Pl. IV: Fig. 3) or in fluid whirls. Such a structure was never found in about two hundred thin sections from various diagenetic chert nodules from the carbonate rocks in the Western Carpathians. The replacement of dolomicrite by silica was accompanied by local dissolution; the dissolution voids were filled by sheaf and spherulites (0.1-0.25 mm of diameter) of fibrous chalcedony (length-fast chalcedony), exceptionally by fine-grained quartz with undulatory extinction. Red colloform patterns are not rare (Pl. IV: Fig. 4). Dark coloured portions of chert consist of the finest microquartz grains of all.

Rare isolated dolomite rhombohedra up to 0.25 mm are filled with inclusions; they cut the colloform bodies. One tiny column (length of 0.03 mm) of authigenic tourmaline was found. Both chert and surrouding dolomicrite lack fossil remains. Several crowds of very fine unidentified needles (Pl. IV: Fig. 5) were found in one thin section.

Syneretic veinlets — filling of the syngenetic cracks formed by dehydratation, are common in chert nodules. The oldest of them possess red borders and are filled by chalcedony. The further generation is represented by very thin, interrupted and corroded dolomite veinlets. The dolomite rhombohedra are attached to the third generation of syngenetic veinlets ("string-of-pearls type" — Mišík 1971) and crowds of rhombohedra with equal optic orientation in linear arrangement are linked with the submicroscopic cracks. Rare calcite veinlets are filled by radial-fibrous calcite with undulatory extinction; exceptionally, they close tiny euhedral quartz. None of the mentioned veinlets continues from the chert nodule into the surrounding dolomite as is common in the case of the tectonic veinlets.

Under the electron microscope (H. Gerthofferová) the boundaries of microquartz grains are indistinct, stylolitic; on the fracture plane accessory kaolinite crystals are present (Pl. IV: Fig. 6). X-ray analysis of the insoluble residue of dolomite (E. Šamajová) indicated a slight admixture of chlorite and halloyzite (?).

Red colour of chert nodules in white dolomites could be redistributed by ascending solutions from red marly shales alternating with dolomites. The source of the silica for the supposed climatic silicification might be represented by the

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Plate IV: Silcretes represented by chert nodules in dolomites, Carpathian Keuper (Norian) of the Krížna Nappe. **Fig. 1** — Host rock - dolointramicrite with synsedimentary cracks clearly visible within intraclasts (evidence of temporary emersion). Partial nappe Bujačí. Abandoned quarry between Tatranská kotlina and Ždiar, Belanské Tatry Mts. (Fig. 1-6 from the same locality). Enlarged 11×. **Fig. 2** — Transition zone of the strainer-like type (B) between dolomite (A) and chert nodule (C). Enlarged 40×. **Fig. 3** — Rhythmic precipitation of the Fe-pigment (Liesegang ring) and "stream structure" visualized by elongated grains of the pigment. Enlarged 136×. **Fig. 4** — Colloform patterns in a red chert nodule. **Fig. 5** — Crowd of unidentified tiny needles in the red chert. Enlarged 210×. **Fig. 6** — Replica of the fracture plain red chert nodule under electron microscope. Enlarged 6800×. **Fig. 7** — Minute silica globules, probably lepispheres, enclosed within incomplete crystals of dolomite. NW from the elevation point 665.2, settlement Zelenáci near the village Valaská Belá, Strážovské vrchy Mts. Enlarged 185×. Photo.: L. Osvald.

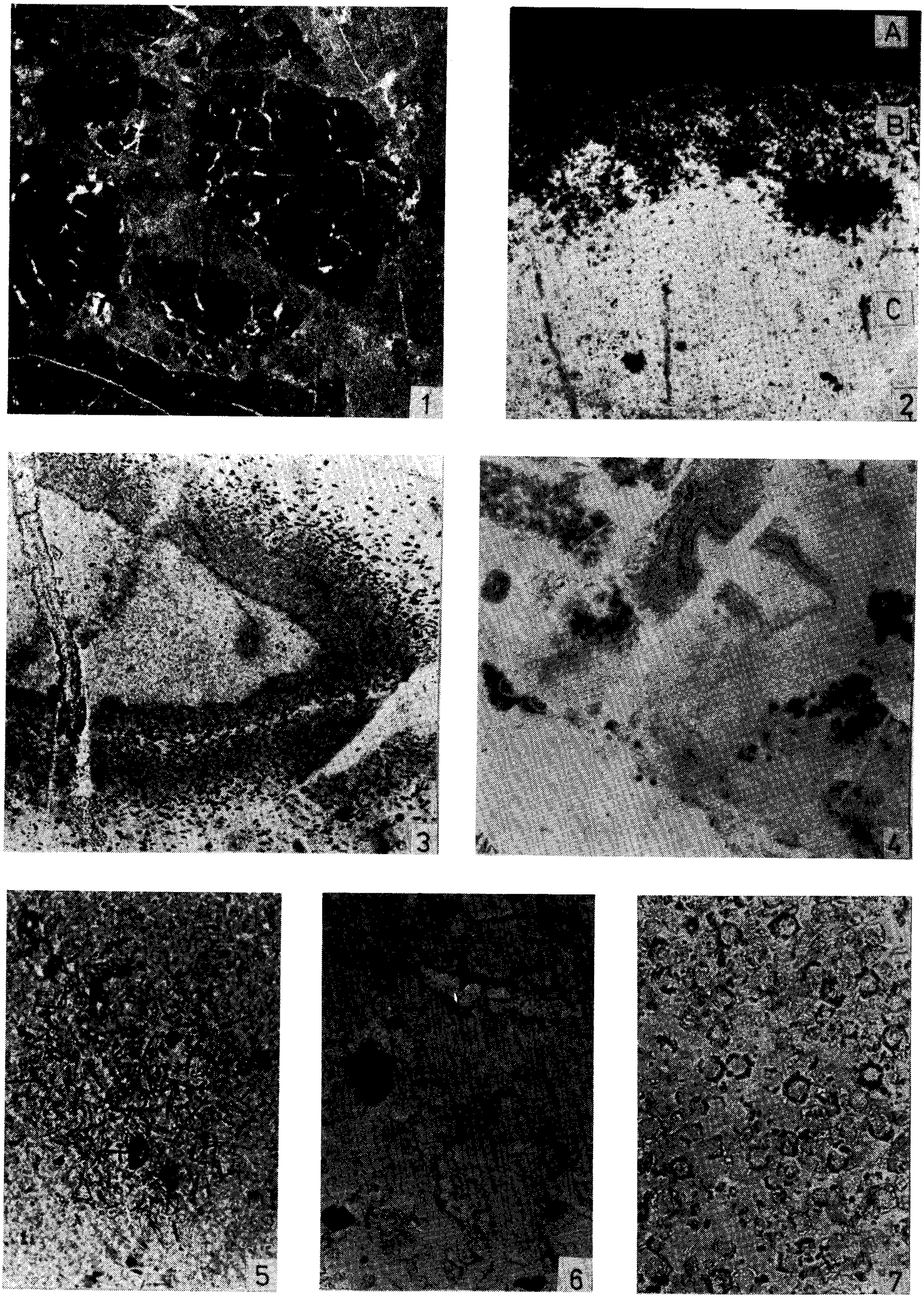
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Table 1: Chemical composition of chert nodules (silcretes) and surrounding dolomites of the Carpathian Keuper, loc. Belanská Kotlina (anal. J. Polakovičová and M. Haková).

	Dolomite		Chert nodule	
Insoluble residue	5.30%		94.60%	
SiO_2	5.18%		94.26%	
Al_2O_3	0.05%		0.10%	
Fe_2O_3	0.03%		0.24%	
K_2O	0.1%		0.1%	
	1 sample ppm	2 sample ppm	1 sample ppm	2 sample ppm
Co	traces	1	traces	-
Cr	9.3	2	28.8	5.5
Cu	1	4.3	3	8.7
Ga	-	-	traces	10
Mn	24	182	10	10.4
Ni	8.9	1	1	traces
Ti	69	26.9	41	170
V	6.9	9.3	30	11.7
W	-	-	traces	-
Be	-	-	traces	-
B	-	-	54	63
Zr	18.5	traces	10	10
Ba	10.2	11.5	20	101
Sr	129	320	62	550
Li	not done	30	not done	100
Sn	" "	-	" "	5.0

sandstone and quartzites forming other intercalations in the Carpathian Keuper.

Spectral analyses (Tab. 1) indicate the enrichment of cherts with regard to the surrounding dolomites especially in boron, less in Ba, Sn, Cr and perhaps also in Cu, Ga, W; the cherts are clearly poorer in manganese.

b — Stranžyská dolina (valley), Polish part of the High Tatra Mts. The locality is a distance of 30 km from the previous one. Fragments of red cherts ("Karneol") with similar structure occur as clasts (up to 2 cm) in a fine-grained carbonatic breccia within the Keuper sequence. Intercalations of such breccias are common in the Carpathian Keuper (situation of their localities — Mišík 1978, Fig.2). All clasts were derived from the rocks of the Keuper sequence: dolomites, red marly shales, red silicites.

c — Fačkov saddle, Strážovské vrchy Mts. (found by R. Mock), Keuper dolomites of the Krížna Nappe contain light-grey cherts. They are of heterogenous granularity, mainly of microquartz replacing dolomicrite. Small voids formed during the silicification were filled by fibrous chalcedony (length-fast chalcedony) and fine-grained quartz in their centres. Isolated dolomite rhombohedra (up to 0.10 mm) are scarce, but rhombohedra are frequently attached on the veinlets of "pearl-string type". The chert nodules are not sharply limited; silica was also dispersed in the surrounding dolomite as the in filling of small voids and cracks.

d — Settlement of Zelenáci, 250 m NW of the elevation point 665.5, near the village of Valaská Belá, Strážovské vrchy Mts. (found by J. Jablonský). Similar light-grey cherts in the Keuper dolomite of the Krížna Nappe are formed mainly by microquartz replacing dolomicrite. Small voids formed during the silicification were rimmed by concentric zones of brownish aggregate (sheafs of chalcedony in polarized light) and their centres filled by fine-grained quartz. The chert nodules enclose tiny globular grains of dolomite. They probably represent lepispheres replaced by dolomite. Such a way in which lepispheres — globular aggregates originally formed by CT-opal (e.g. Wise & Kelts 1972) have been preserved from destruction was described from the diagenetic chert nodules from the limestones of various stratigraphic horizons (Mišík 1992). Another more interesting case also occurred here. Several lepispheres were preserved from destruction without the loss of their silica composition. They were enclosed in minute dolomite crystals with a rhombic or hexagonal outline in cross section; sometimes only incomplete frames of such crystals surrounding globules are visible (Pl. IV: Fig. 2). The globules possess a constant diameter of about 0.020 mm, corresponding well to the majority of data measured in the verified lepispheres from the Recent and Neogene sediments. The lepispheres from silcretes were also quoted by Thiry & Milnes (1989). The dolomite surrounding cherts is penetrated by nests and veinlets of sheaf-like chalcedony.

e — Upper part of the lateral valley Vyvieračka, Demänovská dolina Valley, Nízke Tatry Mts. (found by M. Sýkora). Silica accumulations in the coprolitic dolomite of the Keuper sequence, Krížna Nappe. Irregular cherts of overlapping red and light-grey colours are formed by granular microcrystalline quartz, which contains colloform structures including spherulites and their fragments. The older generation of carbonate rhombohedra was corroded, even dissolved and pseudomorphosed by chalcedony. The formation of silcretes was accompanied by the cracking of dolomite; in the immediate neighbourhood of cherts the veinlets in dolomite were filled by chalcedony.

f — SE from the elevation point Kozie rohy, Čierna Hora Mts., Ružín Succession. Cherts up to 10 cm in diameter were quoted from the dolomites of the uppermost part of the Keuper sequence by Jacko (1988, p. 22). These cherts were not studied in the thin sections.

Summary of the cherts in Keuper dolomites. The penecontemporaneous Keuper dolomites do not contain any source of silica. The silica of their cherts probably originates from the dissolution of quartz grains in the underlying sandstone and quartzite layers. The signs of temporary dessication

Plate V: Thin silcrete crusts in the Neocomian limestones of the Czorsztyn Succession, Pieniny Klippen Belt. **Fig. 1** — Crust of limpide silica (A) passing downward in the silicified limestone (B) and unaffected biomicrite (C). Abandoned quarry near the village of Kamenica, Eastern Slovakia. Enlarged 11×. **Fig. 2** — The top part (A) of the same silcrete characterized by a network of syneretic cracks, later on filled by clear silica (white anastomosed veinlets). Enlarged 48×. **Fig. 3** — Profile of another analogic silcrete: A — silica crust with a network of syneretic cracks passes downward in B — silicified biomicrite and C — biomicrite (unaffected rock). The silcrete is penetrated by thicker subhorizontal veinlets with quartz infill. Settlement U Vajíčkov, Dolný Mlyn near the village of Lubina. Enlarged 13×. **Fig. 4** — Detail of the veinlet filled by quartz crystals displaying rhythmic growth. Enlarged 40×. Photo.: L. Osvald.


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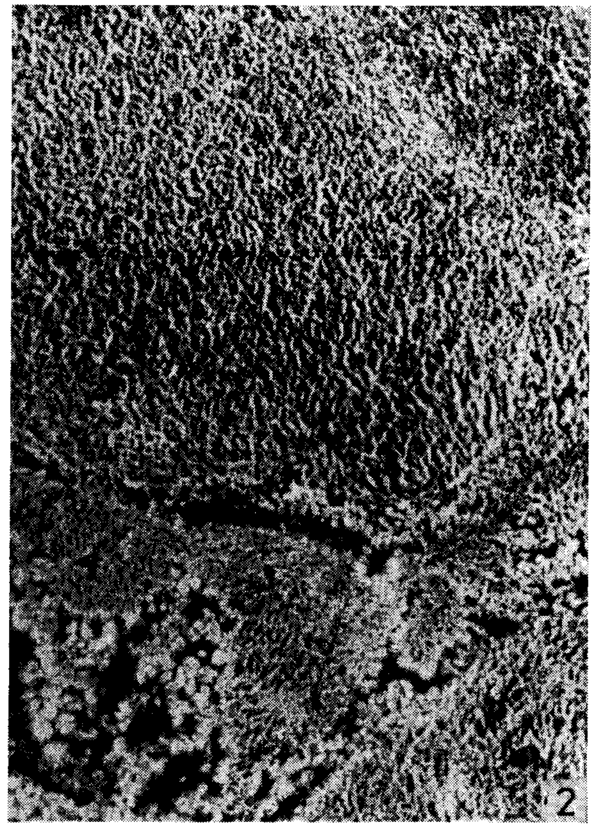
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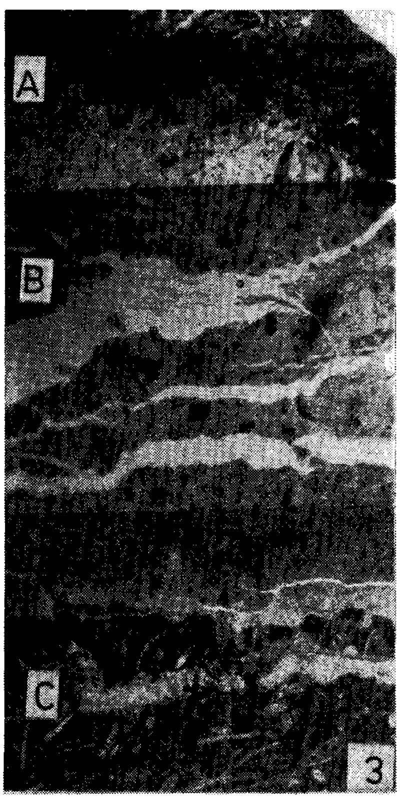
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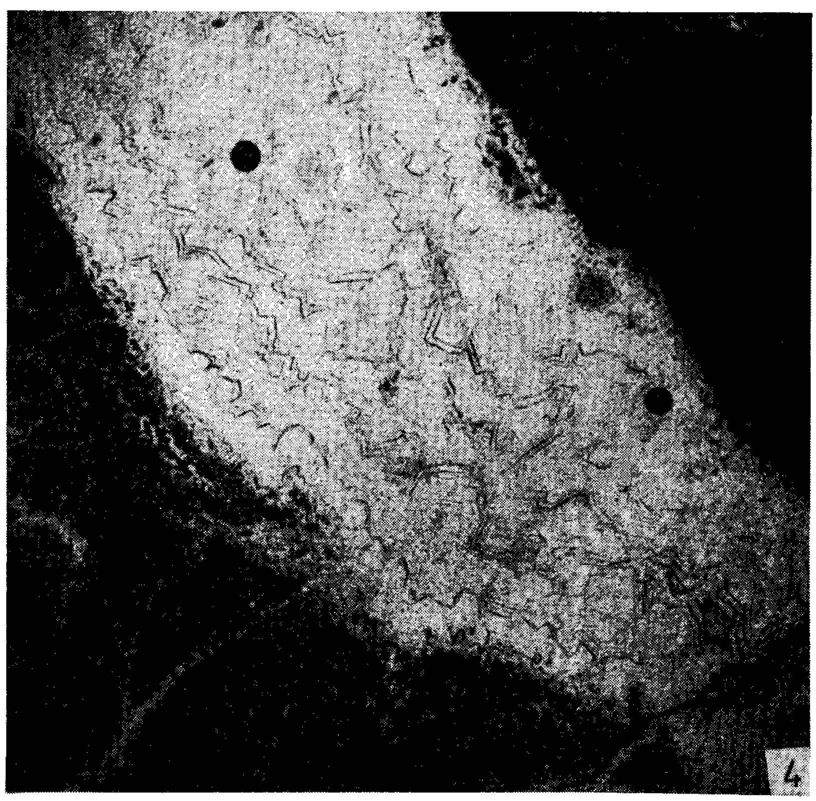
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and schizohaline environment (Kantor & Mišík 1992, p. 13–14) point to the climatic (pedogenetic) silicification, mainly as to the case of red cherts comparable to the "Karneol dolomite" of the German Triassic, interpreted in such a way. But one might be surprised about the rarity of cherts in the Keuper dolomite with regard to more than hundred studied localities of Keuper dolomite outcrops, where they were absent.

The alternative explanation should be a hydrothermal origin. However the quoted localities are very distant from the areas of neovolcanites where such postvolcanic silicification of dolomites occurred (e.g. Šály & Oružinský 1989). The silicification by thermal waters cannot be excluded even in areas far from the neovolcanic rocks. Such a case was found by us near the village of Spišská Teplica, N of the elevation point 706.8, in the marginal part of the Nízke Tatry Mts. The locality does not belong to Keuper dolomite. In the strata of Middle Triassic dolomites of the Choč Nappe an exceptional occurrence of silicification was ascertained. The dolomite breccia is formed by fragments (up to 2 cm) of middle-grained dolomite. Silica selectively replaced the clasts or the entire breccia with a mosaic of fine-grained quartz and short euhedral colums about 0.07 mm thick. Newly formed dolomite rhombohedra up to 0.4 mm occur only in the silicified portions. The breccia is of tectonic origin as is corroborated by fitting of initially separated clasts in the darker dolopseudomicrite formed by the granulation (tectonic trituration). The silicification of these Middle Triassic dolomites took place after the origin of the tectonic breccia during the Alpine orogeny (Cretaceous-Tertiary). Both climatic and hydrothermal silicification are accompanied by veinlets and voids with the infilling of the fine-grained mosaic of quartz in the surrounding rock which is never the case in the diagenetic chert nodules.

The majority of the arguments mentioned above are in favor of the silcrete interpretation for the Keuper dolomites.

Note. Our considerations concerned the most frequent penecontemporaneous Triassic dolomites of the Western Carpathians, where cherts occur only exceptionally. Diagenetic chert nodules, the SiO_2 of which comes from sponge spicules and radiolarians, frequently occur, in the rare occurrences of late diagenetic dolomites from the Western Carpathians, for example in the basement of the basinal Reifling Limestone.

Upper Berriasian

Thin silcretes were found at two localities of the Czorsztyn Succession of the Pieniny Klippen Belt. In spite of the distance of about 270 km between them, the patterns of silcretes are surprisingly similar.

1 — Kamenica, abandoned quarry near the village, Eastern Slovakia. A discontinuous silcrete only 1 cm thick was formed on a limestone bed containing *Calpionellopsis oblonga* (Cadish), *Tintinnopsella longa* (Colom) and *Cadosina fusca fusca* Wanner. The upper part of the silcrete consists of a microquartz aggregate with a brown pigment. This layer was precipitated on the empty surface, therefore is not contaminated by the carbonate inclusions (Pl. V: Fig. 1). Most probably it was formed by opal, later cracked during the dehydratation into a dense net of mostly parallel hair-like veinlets filled by clear microquartz (Pl. V: Fig. 2). The lower part of the silcrete contains some quartzine spherulites. The underlying limestone was silicified up to a depth of 6 mm (Pl. VI: Fig. 3B). The descending silicification ends with a sharp boundary (Pl. V: Fig. 1B,C). Small voids after the dissolved radiolarians and pelecypods were filled by a fine-grained drusy quartz.

2 — Settlement "U Vajičkov", near the quarry of Dolný Mlyn, at the village of Lubina near Stará Turá, Western Slovakia. Thin discontinuous silcrete with a thickness of about 1.3 mm (Pl. V: Fig. 3) contains in its upper part comparable layer of microquartz with anastomosing hair-like syneretic cracks. Thicker cracks are filled from both sides into the centre by the drusy quartz, mostly prismatic crystals displaying rhythmic growth (Pl. V: Fig. 4) and undulatory extinction (Pl. VI: Figs. 1, 2). The underlying limestone is silicified by microquartz up to the depth of 5–6 mm (Pl. V: Fig. 3B). Calcitic biodetrite like large specimens of *Globuligerina* sp. (Pl. VI: Fig. 4), pelecypod fragments and echinoderm plates resisted the silicification. The Berriassian-Neocomian age is inferred.

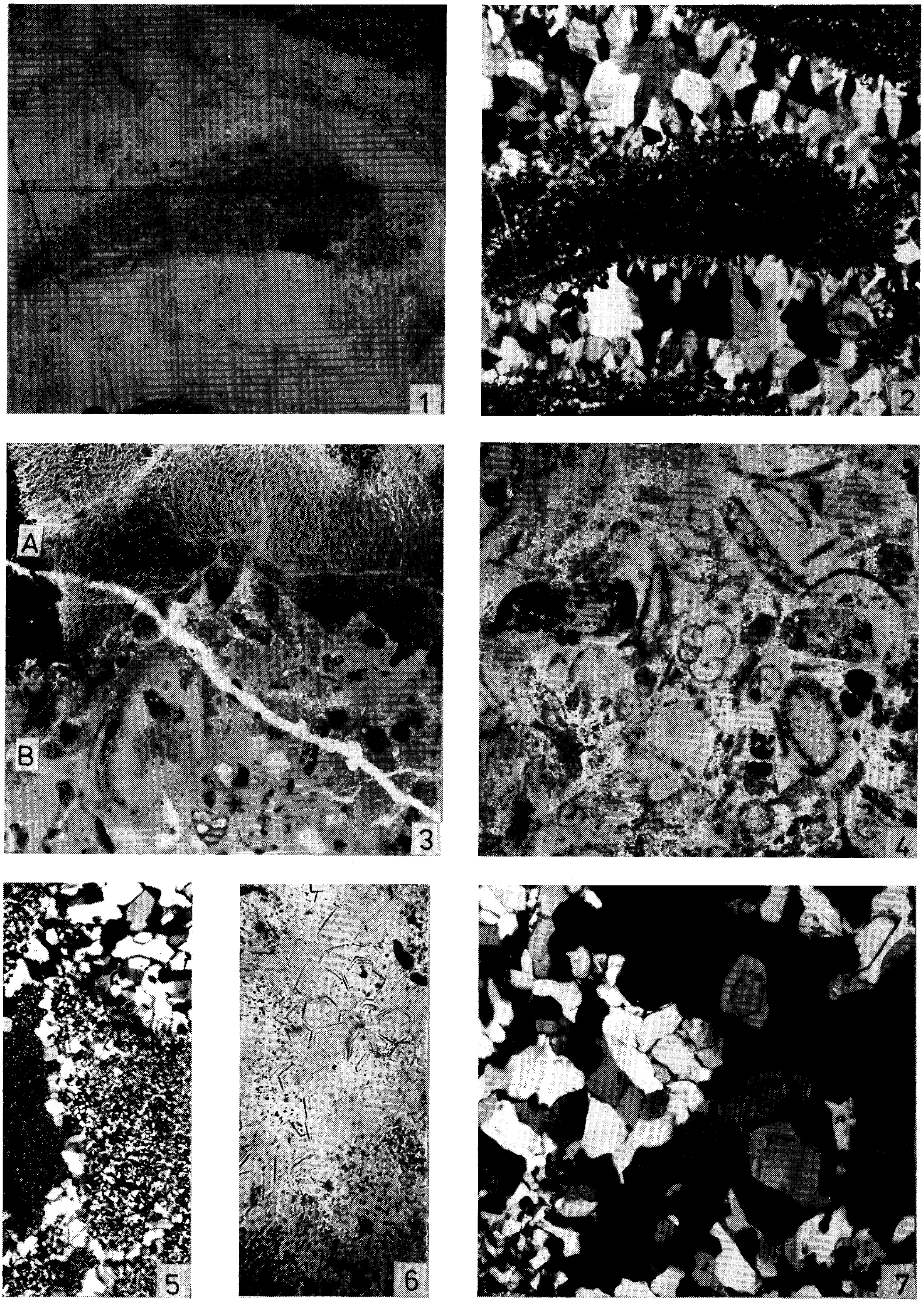
The interpretation of the mentioned thin silcretes is difficult. The first possibility is a short emersion and a seasonal humid climate. Such a silcrete was described by Namy (1974) from the Pennsylvanian limestones. But it includes only the descending silicification of limestone; contrast to our occurrences, the freely precipitated silica in the upper part of silcrete is missing. Organic remains in our localities indicate a pelagic environment but with shallow depth. The Czorsztyn Succession was deposited on a typical pelagic swell (Mišík 1993), with numerous short hiatuses during the Jurassic and Lower Cretaceous; but they are mostly considered as submarine ones.

According to the second interpretation the described silcretes should represent hardgrounds. The precipitation on the marine bottom of pure silica crusts without other sedimentary admixture and unaffected by boring organisms is improbable. Moreover no volcanic activity occurred during those times in the whole West-Carpathian area of the Czorsztyn Unit (slight manifestations are known only from the Eastern Carpathians — Mišík 1992, p. 51). I did not find any references to silica hardgrounds in the literature.

Paleocene (?)

Silcrete accompanying the bauxites near the village Drienovec, Turňa Basin (SE Slovakia). A layer about 20 cm thick of brown silicite overlies the bauxites. It displays heterogeneous granularity in thin section (Pl. VI: Fig. 5), from the microquartz to the megaquartz mosaic with grains reflecting a rhythmic growth of crystals into the void (Pl. V: Fig. 6). The

Plate VI: Figs. 1–4 — Thin silcretes in the Neocomian limestones of the Czorsztyn Succession. **Fig. 1** — Veinlets filled by quartz crystals in layers. Locality as Pl. V, Fig. 4. Enlarged 30×. **Fig. 2** — The same in polarized light; the mosaic of grains does not respect the original outlines of crystals. **Fig. 3** — Top part of the silcrete with the network of syneretic cracks was transformed into a homogeneous aggregate of microquartz; it passes downward in the silicified limestone. Locality as Pl. V, Fig. 1. Enlarged 30×. **Fig. 4** — Globigerinid foraminifer in the lower part of a silcrete (the micrite was replaced by silica, the bioclasts preserved their calcitic composition). Locality as Pl. V, Fig. 3. Enlarged 40×. **Figs. 5–7** — Silicite of the silcrete nature overlying bauxites; Paleocene, near the village Drienovec, Turňa Basin, Eastern Slovakia. **Fig. 5** — Silica with inhomogeneous granularity. Enlarged 43×, crossed polars. **Fig. 6** — Rhythmic growth of quartz crystals. Enlarged 86×. **Fig. 7** — Rhythmic growth of the quartz in the mosaic visible due to their hematite coatings. Photo.: L. Osvald.



grains in the mosaic possess an undulatory extinction like in the above mentioned silcretes from the Lower Cretaceous (Pl. V: Fig. 4). The finest microquartz aggregate bears the phantoms of layering. The silcrete contained 33 ppm Ni and 74 ppm Cr, the highest values from the 56 samples of analysed silicates from the Western Carpathians, belonging to various genetic types and numerous stratigraphic horizons, which showed its relation to the bauxite redeposited from the Senonian crusts of lateritic weathering. The stratigraphic attribution is based on the analogy with the bauxite localities Mojtín and Markušovce and on the age of the underlying Drienovec Conglomerate containing clasts with Senonian foraminifers. In contrast to other described localities, this silcrete did not originate on the carbonate substratum but on a pelitic regolite. The silcrete overlaying the bauxite indicates significant change of climate: after tropical conditions ruling during the Senonian, an alternation of humid and arid seasons took place in the Paleocene.

Egerian (Lowermost Miocene)

Borehole RK-II Hostišovce (2 km NW of the village of Budikovany), South Slovak Neogene Basin. In the interval between 111.70 m and 115.10 m the basal part of Egerian sediments overlying the grey and rosy Triassic limestone was ascertained. The weathering crust was formed immediately before the transgression of the Egerian sea. It consists of greenish argilites with the angular fragments of silicites containing "filaments" (juvenile shells of *Halobia*) in the thin sections.

As to the origin of the weathering crust, two alternative explanation might be suggested. The first one could be an analogy to the "argile a silex" from the Paleogene of the Paris Basin; by weathering and dissolving of the Senonian chalk a residual clayey sediment with flint fragments was formed there. In our case the silicite fragments would represent desintegrated nodular cherts from the dissolved Triassic limestones. According to the second interpretation the silicite clasts would represent the fragments of silcrete from the immediately underlying strata. At a depth of 113.80 m a breccia composed of bleached limestone clasts (up to 2 cm) was found. It was cemented by microquartz, and corresponds to silcrete originated by climatic silicification. In another twelve samples collected from a depth of 115.80 to the final depth of 162.20 m only one small nodular chert was found. Therefore the presence of a silcrete horizon at the base of the Egerian transgression is highly probable and should be verified at other localities.

Notes: 1. Silcretes from the clefts in the neovolcanic rocks of Slovakia, formed by descending solutions, were described by Čurlík & Forgáč (1996). Silica resulted from the alteration of volcanic glass.
2. Newly formed tiny clear quartz crystals were found in pores and small voids of Paleozoic quartzites disintegrating into sands at the locality Zlámanecká skala, near the village of Ružina near Lovinobaňa (Mišík 1956, p.96, Fig. 2). Such newly formed quartz crystals are typical for the upper part of silcretes developed on the Eocene Fontainebleau Sands (Thiry & Millot 1987). Our locality represents a fossil weathering crust with silcrete patterns at the base of the Pliocene Poltár Fm. A new study is desirable.

Summary

Silica spherulites with the diameter of 1-5 mm occurred exclusively in the Triassic micritic limestones and dolomites. The Gutenstein Limestone with spherulites in the Malé Karpaty Mts. as well as the Middle Triassic dolomites in the Veľká Fatra Mts., Malá Fatra Mts. and Žiar Mts. do not contain organic remains and display signs of a hypersaline environment. Some spherulites have centres formed by length-slow chalcedony (quartzine) grading towards the periphery into megaquartz crystals with radial undulatory extinction. Silica spherulites were sometimes replaced by calcite. In accordance with numerous authors (Folk & Pittman 1971; Siedlecka 1972; Milliken 1979; Ulmer-Scholle et al. 1993 etc.) we assume that these silica spherulites originated by the replacement of small gypsum or anhydrite nodules. The model for such a process was not formulated up to now because silicification is not known in recent evaporites (Milliken 1979, p. 251, 255). It also indicates that the silicification of evaporites was carried out in the course of late diagenesis. Ulmer-Scholle et al. (1993) concluded that silica spherulites studied by them originated at a depth of 1.3 km. Milliken (1979) found out that the temperature during the silicification was not higher than 40 °C. The source of silica for our tiny chert balls (spherulites) from the Middle Triassic limestones and dolomites remains unknown (the host rocks contain neither siliceous microorganisms nor clastic quartz and clay minerals are extremely rare); the same was ascertained by the majority of authors.

An interesting case — silica spherulites arranged along the planes of polyhedra (with the aspect of frames on the weathered surface) was found in the Gutenstein Limestone of the Veľká Fatra Mts. They followed hair-thin cracks and are younger than late diagenetic dolomite. They were formed under anoxic conditions (pyrite crystals are limited on them). The origin of silica spherulites from the Upper Triassic of Slovak Karst was initiated by the slight metamorphism; the metamorphic redistribution of silica was also registered in the spherulites in the Borinka area. Chert balls (spherulites) of the Jasenie ("Reifling") Limestone in the Nízke Tatry Mts. are of a different genesis. They accompany the normal diagenetic chert nodules and were formed at the expenses of sponge spicules and radiolarians.

Silcretes are scarce in the Western Carpathians. We include here rare occurrences of chert nodules (mostly red) from the Keuper dolomites comparable to the Karneoldolomite from the German Triassic which are considered to be pedogenetic products. The host dolomites bear traces of desication. Relicts of lepispheres preserved in tiny newly-formed dolomite crystals were found.

Silcretes only 1 cm thick were identified at two localities in the Berriasian limestones of the Czorsztyn Succession (Pieniny Klippen Belt). Their upper part consists of pure microquartz with a dense network of veinlets (former syneretic cracks); it was precipitated on the surface (into the empty space). The lower part of silcrete originated by the descending silicification, by the replacement of limestone and ends with a sharp boundary against the unaffected biomicrite. The silcrete was disturbed by veinlets infilled with quartz crystals displaying rhythmic growth. These silica crusts are product of pedogenesis; they might be eventually interpreted as hardgrounds, but such silica hardgrounds were not described up to now.

Silcrete was also found at the base of Neogene strata in a borehole near Hostišovce. Clasts in breccia from the underlying Triassic limestones are cemented by microquartz. Another silcrete of Paleocene age overlying the bauxite near Drienovec did not originate on a carbonate substratum but on a pelitic regolite. It also contains veinlets with rhythmic growth quartz crystals. High content of Ni and Cr attest the linkage with bauxite.

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