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STRUCTURES OF THE CHERT CONCRETIONS FROM THE LIMESTONES OF TITHONIAN AND NEOCOMIAN, WEST CARPATHIAN MTS.

(*Fig. 1—33*)

Abstract: Chert concretions of Tithonian-Neocomian limestones were used for comparative microscopical study as a model of the concretions originated on the micritic substratum (slightly marly biomicrite with planctonic organisms representing a pelagic facies). Attention is called to the various ways of radiolarian fossilization. The wide-spread occurrences of these limestones known as „biancone" or „majolica" in the whole Tethydian geosynclinal area offer a possibility to verify if the results of this study are valid in a large measure.

Резюме: Кремнистые конкреции титон-неокомских известняков были использованы для сравнения микроскопического изучения а также как модели конкреций возникших в микритической среде (слабо глинистые биомикриты с планктонными организмами, представляющие пелагическую фацию). Обращается внимание также на различные способы фоссилизации радиолярий. Многочисленные находки этих известняков, известных как «бианконе» и «майолика» во всей тетидной геосиклинали, представляют возможность контролирования использования результатов этой работы в широкой мере.

Introduction

The basic rock type, bearing the studied chert concretions, are light grey to dark grey slightly marly limestones, rarely mottled. They contain a radiolarian or sponge-spicules association, sometimes combined with a *Calpionella* or *Hedbergella* and/or *Nannoconus* association. The chert concretions are black, rarely light grey. Sometimes a transition zone is observable with naked eye. The investigated specimens were collected from the Kysuca and Manín Series of the Klippen Belt (Pienides), from the Envelope Series (Tatrides), and from the Krížna nappe (Subtatrides), totally from 20 localities. The size of these concretions ranges between 1—15 cm. Mostly they were elongated according to the stratification plane, spherical form was rare.

In the further text some of the ascertained facts are completed with observations of the variegated chert concretions of the Dogger-Malm, since they represent a very similar substratum of micritic limestones with a radiolarian microfacies.

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Transition zones

Several characteristic zones were discerned at the limestone-chert boundary as well as in the marginal part of the chert concretion. Not all of these zones are involved in each concretion. They are only some mm or tenths of mm thick. For their microscopic description these preliminary signs are used (Fig. 1—4):

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A — limestone (micrite) without discernible chalcedony.

AB — transition zone, limestone with dispersed chalcedony (siliceous limestone). Calcite strongly prevails over the chalcedony. In the thin section the rock of the AB zone appears lighter than A. Chalcedony is visible as a complete filling of some or all radiolarians; sometimes it is seen only in the centres of those radiolarians which were not completely filled by drusy calcite. Older calcite veinlets, passing through the AB zone, are bordered on both sides by chalcedony strips (migration of SiO_2 was stopped by the barrier of coarse-grained calcite aggregate). Zone AB is mostly 1.5—3 mm thick. In the case of imperfectly differentiated cherts (Fig. 2) the transition zone AB is macroscopically well observable attaining 1—2 cm. Sometimes it may represent the whole host rock (chert concretions in siliceous limestones).

Bo — transition zone richer in chalcedony. It is usually situated on the outer margin of the AB zone forming a strong limit against A („marginal imbibition").

Bx — transition zone formed by aggregate of coarse calcite grains (a mosaic of clouded isometric grains originated by recrystallization). It is situated on the periphery of the concretion (between AB and C). Crystals are pointing into the chert concretion. The width of the Bx zone is variable, usually between 0.3—1.5 mm. Rarely it contains ghosts of the older veinlets and phantoms of radiolarians (clear, without pigment), as well as small ankeritic (?) rhombs. Zone Bx originated in the final stages of the concretion forming process.

BC — transition zone with predominance of chalcedony over the calcite. It contains islets of the original micrite and dense pigment of the minute calcite grains. No recrytallization, no formation of the loose calcite rhombs occurs. The presence of radiolarians filled by a single calcite crystal is typical for this zone. Its width varies between 0.2—5 mm.

C — chert with absolute predominance of SiO_2, almost always with calcite rhombs originated by recrystallization of micrite relicts under the influence of silica colloids. Sometimes an external part (C_1) and internal part (C_2) may be distinguished. The external part differs by the absence of the brown bituminous pigment, or by the dimi-

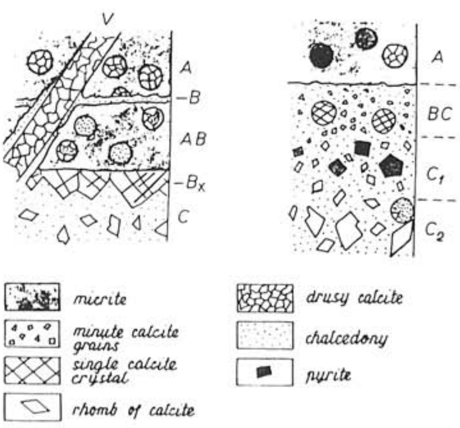


Fig. 1. Examples of the transition zones between the limestone (A) and chert concretion (C); generalized from the thin section studies. For details see the text.

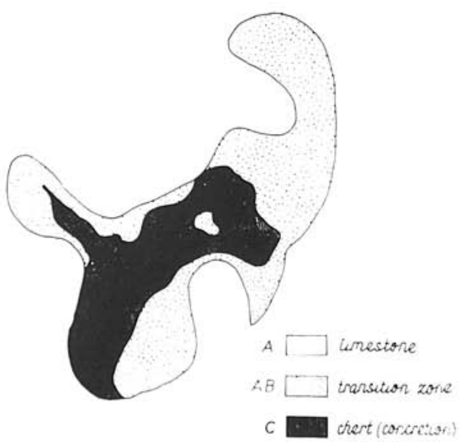


Fig. 2. Chert concretion with a distinct transition zone. Tithonian of the Kysuca Series, Klippen Belt; loc. Brodno near Žilina. $^1/_2$ of the natural size, polished section.

nution of the rhombs size (Fig. 4), by more abundant carbonate pigment, by the presence of pyrite crystals (Fig. 5). The last mentioned case was repeatedly observed; it indicates the reducing conditions during the final phase of the concretion forming process. No concentric rhytmical zonation, no ring-forming structures were found in the studied chert concretions of the Dogger-Malm and Tithonian-Neocomian rocks. Up till now such ring structures were found in the West Carpathian territory only in Reifling Limestone (Ladinian) near Turík, Chočské pohorie Mts. (M. Mišík 1972) and in the limestones of Albian age, locality Čierna Lehota, Strážovská hornatina Mts.

The transition zones are almost always discontinuous. It is not excluded that they might be more frequent in the upper or lower parts of the concretions and form geopetal structures; this problem was not yet studied.

Both limestones (A) and cherts (C) are shiny in polished sections, strongly contrasting with the dull transition zone (AB) — siliceous limestone with the scattered chalcedony (Fig. 2).

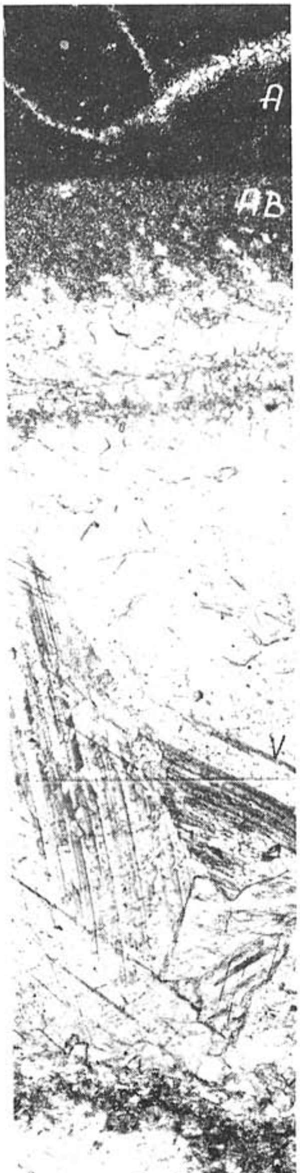
The relation between the size of the concretions and the thickness of the transition zone were not studied systematically. Preliminary it was noticed that in the smallest concretions transition zone was totally absent.

Organic remains

The chert concretions originated by replacement of the calcareous substratum with more or less uniform distribution of organic remains. But when compairing organic remains in the chert concretions and those in surrounding limestones, several differencies may be already stated. Some of the organic remains of limestone are missing in chert due to their break-down by silicification. On the contrary some microfossils like Hystrichosphaeridae may be more abundant or exclusively present in cherts, if the silicification took place early, since the silica represent the most favorable medium for their preservation.

Radiolarians. They are the most abundant fossil remains of the examined chert concretions. They were obviously the main source of the silica (radiolarian cherts). The representatives of the group *Spumellaria* strongly predominante, those of the group *Nasellaria* are rare (Fig. 20). Various manners of the fossilization of the radiolarian tests were found (Fig. 7):

a) Preservation in limestone. In the surrounding limestones (zone A) all radiolarian tests are calcified. Following cases are to be discerned: 1 — Infilling is formed by several calcite grains (coarse-grained mosaic). 2 — Infilling is formed by fine-grained mosaic (this type was partly derived from the previous one by degrading neomorhism — R. L. Folk 1965). In both cases the test was originally empty, filled by gas. In the thin sections its outlines are sometimes distinct but more frequent diffused. The test is not discernible from the infilling: probably the test was dissolved and the whole space filled by drusy calcite. 3 — Infilling by calcite mud (micrite). The test is well discernible since it was replased by calcite. It is but surprising that the cases with partly filling (sparite in the upper part of the radiolarian void, top-and-bottom structures) are missing. They were found exceptionally in the Tithonian limestone of the Klippen Belt near Lubina (Fig. 13). 4 — „Ghosts" of the radiolarians hardly discernible in the micritic groundmass. This type may be derived from the previous one by granulation of the calcite which replaced the test (degrading neomorhism). 5 — Infilling formed by drusy calcite with phantoms of globular structure (Fig. 20). In this rare case radiolarians were first of all filled by globular opal which was lately replaced by calcite.



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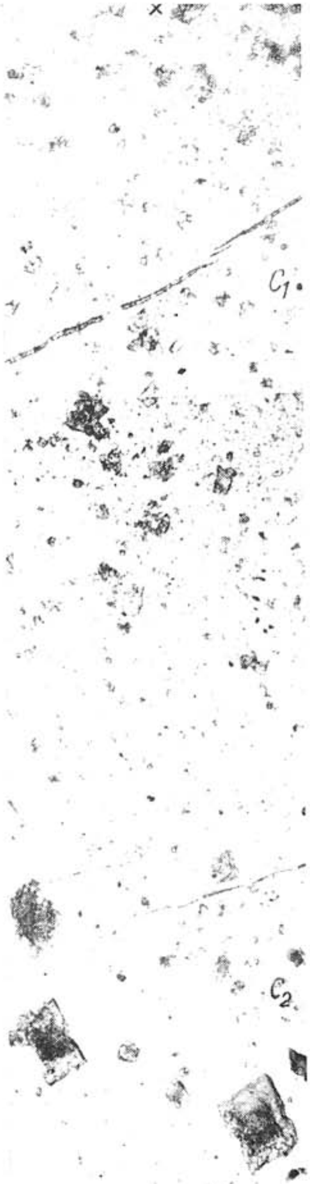

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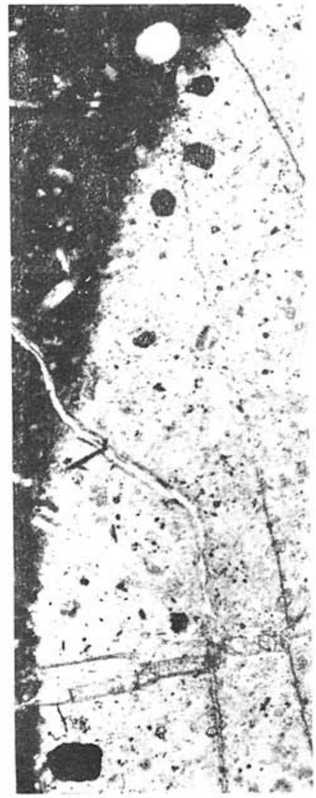

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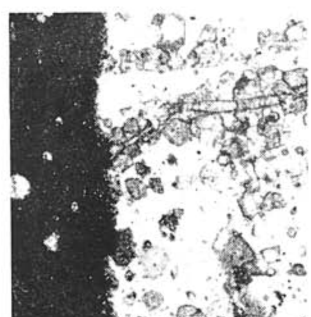

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Fig. 3—4. Zones of a chert concretion — microscopic profile; Fig. 4 is the continuation of the Fig. 3. A — surrounding rock, micritic limestone, AB — transition zone, siliceous limestone, V — veinlet of calcite along the margin of the chert, C_1 — external zone of the chert concretion with small irregular grains of calcite and tiny rhombs, C_2 — internal part of the concretion with large calcite rhombs. Neocomian of the Envelope Series, Pokraj near the gamekeeper's cottage Zabité, Malé Karpaty Mts. No. 4576, magnif. 43× — Fig. 5. Pyrite crystals bound to the external part of a chert concretion (C_1). Neocomian of the Manín Series, Klippen Belt. Quarry between Belušské Slatiny and Mojtín. No. 3551, magnif. 43× — Fig. 6. Peripheral part of o chert concretion. Phantoms of radiolarians in calcite crystals; syntaxial rims on the calcite veinlet. Loc. Brodno near Žilina, Tithonian of the Kysuca Series, Klippen Belt. No. 8b, magnif. 26×. Photo: L. O s v a l d.

These five types were found in the concretion-bearing limestones of Tithonian-Neocomian. In the red cherty limestones of Dogger-Malm another type more was noticed: 6 — Infilling by red colloidal isotropic mineral (Fe-hydroxide ?).

b) Preservation in the transition zone AB. At least some of the radiolarians are filled by chalcedony in this zone, from the immediate surroundings of the chert concretion. The transition zone is usually 1—5 mm. thick, but in the case of siliceous limestones with chert concretions the whole surrounding rock may be considered as the transition zone AB. Two kinds of preservation were found: 1 — Chalcedony forms infilling of the whole radiolaria. 2 — Chalcedony is present only in the middle of the radiolarians, the outer rim of which is formed by drusy calcite.

Obviously, when the centrifugally shifted silicification front reached this place now represented by the zone AB, the voids in radiolarians have been partly filled by drusy calcite and chalcedony filled only the rest of them.

It is to be stressed that the radiolarians in limestones never are preserved as a single crystal of calcite or as a ghost in a bigger calcite grain or rhomb, what is the frequent case in the chert concretions.

c) Preservation in the chert concretions. Following cases occur:

1 — Chalcedony infilling of the radiolarians by short-fibrous chalcedony, sometimes by sheaf aggregates, or distinct globular metacolloid structure with concentric alternation of light brown and dark brown rings (Fig. 12), rarely by very fine-grained chalcedony. The area of radiolarians differs from the groundmass by its clear appearence, by the lack of pigment. The „pigment" represents obviously various admixtures, impurities in the replaced substratum. As these are missing in the radiolarians, an empty space, a void not filled by micritic mud in the radiolarian tests must be assumed for the time of the chert concretion origine. When the pigment in the groundmass is sporadic, the radiolarians can be discerned using polarized light only, due to their content of coarser grained chalcedony aggregates in comparison with the groundmass.

2 — Radiolarians filled by a single crystal of calcite with circular outlines. Exceptionally a granulation rim is developped (Fig. 8). The growing calcite crys-

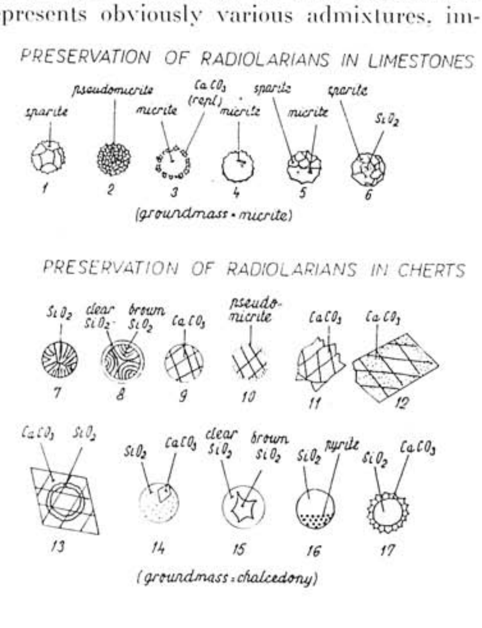

Fig. 7. Various types of the radiolarian preservation in chert concretions and surrounding limestones. Generalized from the thin section studies (see text).

tal often crossed the barrier of the test surface and formed teeth like protuberancies on the outline of the radiolarians. The further growth led to the next type.

3 — Radiolarian „ghost" in the calcite rhomb (Fig. 6 and 9). The calcite rhomb is usually light brown; it contains a white circle, a trace of the original radiolarian test. The clear phantom proves the existence of a previous void in the radiolarian test. The phantom is not always in the middle of the rhomb, sometimes it has an excentrical position. Exceptionally two phantoms were found in one rhomb. These cases suggest that sometimes the germ of the calcite rhomb was situated outside the radiolarians and these were only seized during its growth. The same is obvious in the case of radiolarians formed by single crystals which are in the contact with some calcite veinlets. Sometimes still the test formed by chalcedony is preserved in the calcite rhomb. Such a case suggests communication through the pores or damaged places of the test, as the calcite crystal formed the overgrowth on the external part of the test, syntaxial with its filling. This way of fossilization of radiolarians with a single calcite crystal is characteristic for the peripheral zone of the concretion (BC) and for the immediate neighbourhood of syngenetic calcite veinlets in chert concretions.

4 — Chalcedony infilling with 1—2 minute rhombs of calcite growing inward from the outline of the test (Fig. 8). Rarely several tiny calcite grains are in the chalcedony infilling.

5 — Radiolarians are partly filled by clear birefringent chalcedony aggregates with globular or hemiglobular outlines; the centre of the test is filled by brown almost isotropic silica („passive globular structure").

6 — Pyrite infilling with geopetal structure was rarely found. The lower part of the radiolarians contains an aggregate of globular pyrite, the upper one is filled by chalcedony (Fig. 14). Sometimes pyrite filled the whole radiolarian test.

7 — Calcite pseudomorphs after the radiolarian tests are seldom present. The originally silica test was replaced by carbonate with the preservation of all details; the infilling of the radiolarians as well as the groundmass is formed by fine-grained chalcedony (Fig. 11). This way of preservation is the most favorable one for the micropaleontological purposes. It was found also in the bedded radiolarians of the Malm sequence near Myjava (Klippen Belt) and in the Ptáva valley (Humenské pohorie Mts.).

S p o n g e s p i c u l e s. The ways of their preservation and the types of their replacement by calcite correspond well with the types of radiolarian fossilization described above; they will not be commented here in detail. Spicules of *Silicispongia* are the second important source of silica for the chert concretions. They even predominate

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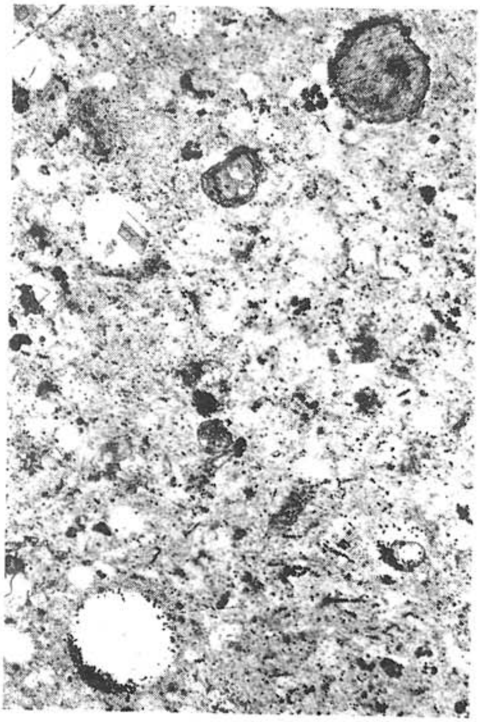
Fig. 8. Various kinds of the radiolarian fossilization in chert. Upper right — radiolaria filled with a single calcite crystal with granulated margins; near the left margin another one filled by chalcedony with a minute calcite rhomb. Neocomian of the Envelope Series, Podhradie, Veľká Fatra Mts. No. 5159, stained with alizarin, magnif. 43×. — Fig. 9. Phantoms of radiolarians within the calcite rhombs in a chert concretion. The same locality. No. 3709, magnif. 55×. Fig. 10. Chert with the syngenetic calcite veinlets partly of metasomatic nature. nature. Only in them or at their contact the radiolarians are filled by a single calcite crystal. Chert concretion from the Tithonian limestones, klippen Brodno near Žilina. No. 3992, magnif. 43×. — Fig. 11. Fragment of a radiolarian test perfectly replaced by carbonate. Chert concretion from the Neocomian of the Kysuca Series; loc. Kozinec near Zázrivá, Klippen Belt. No. 8b, magnif. 410×. — Fig. 12. Radiolarian test formed by clear chalcedony with the void filled by brown metacolloidal silica aggregate (concentric structure due to the rings coloured with variable intensity) with a minute rhomb of calcite. Chert concretion from the Neocomian limestones, Manin Series, Klippen Belt; quarry between Belušské Slatiny and Mojtín. No. 3641, magnif. 136×. Photo: L. O s v a l d.



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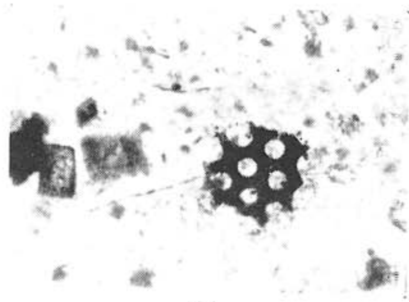

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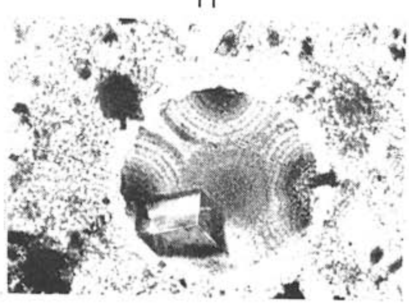

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in some cherts of the Upper Neocomian. Such sponge spicules concretions were found at the localities Belušské Slatiny and Zbýňov (Strážovská hornatina Mts.), Brložnica (Veľká Fatra Mts.). *Monactinellida* are most frequent, *Tetractinellida* and *Hexactinelida* less frequent; exceptionally some forms of the rhax type were found (Fig. 18). Sometimes the spicules display subparallel orientation.

Calpionellidae. Genera like *Calpionella, Crassicolaria, Tintinnopsella* characterize the rocks of Upper Tithonian and Valanginian. They are present in the surrounding limestones only and were never found in the chert concretions. Therefore it may be concluded that they were destroyed by the silicification process. It supports the opinion of F. Bonet (1956) who claimed that the tests of *Tintinnidae* from the Mesozoic seas were formed by $CaCO_3$ and not by chitinous matter as recent genera do. In the case of their chitinous loricae, they would be as well preserved in cherts as other chitinous organisms (see further).

Foraminifera. Several thin sections of the surrounding limestones contain characteristic *Hedbergella* microfacies (Upper Hauterivian-Barremian). *Spirillina, Textularia* and other arenaceous forms are sporadic. Phantoms of silicified foraminifera were found only exceptionally in cherts.

Dinoflagellata. Acritarcha, Spores. Surprisingly perfectly preserved specimens of these originally chitinous remains were identified in the this sections of chert concretions proceeding from numerous localities of Neocomian age — e. g. *Oligosphaeridium complex* (White i) — Fig. 16 and Tithonian age — e. g. *Cannosphaeropsis* sp. — Fig. 17 (determined by O. Čorná). In the thin section of the surrounding limestones they were found only exceptionally. Probably they were strongly affected by diagenesis in the limestones, and well preserved in the colloidal silica medium.

Globochaets. They are present only in the surrounding limestones, namely of Tithonian age. In the concretions they were evidently destroyed and could not be found. Exceptionally a phantom of *Globochaete alpina* Lombard was identified due to the strong pigmentation of silica matrix in a Dogger-Malm chert (Fig. 19).

Nannoconus. Chert concretions from the *Nannoconus* bearing limestones did not contain reliable traces of *Nannoconus*. It is necessary to suppose that these tiny remains were totally destroyed by the silicification process.

Aptychi. In the chert concretion from the locality Brodno syntaxial overgrowths of calcite with the rhomb edges on an aptychus was found (fig. 30).

Echinoderms. Similar case of overgrowths on the crinoid ossicles are present in the chert concretions.

Other remains. In the surrounding limestones *Cadosina*, ostracods and phosphatic fish scales are seldom preserved. None of them was found in chert concretions. Rare fragments of carbonized plant tissues were found in limestone and chert.

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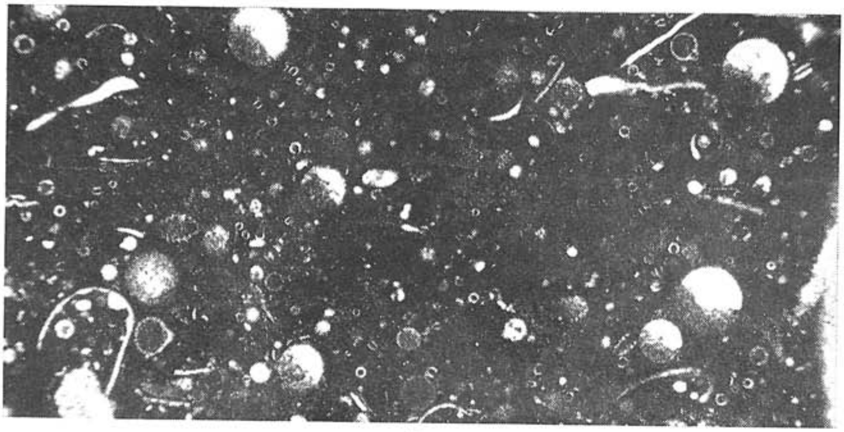
Fig. 13. Geopetal (top-and-bottom) structure. The voids in radiolarians were partly filled with limy mud. Then the drusy calcite crystallized into the upper empty part. Limestone with Calpionella-Radiolaria microfacies. Tithonian of the Kysuca Series, Klippen Belt; loc. Lubina, Myjavská pahorkatina Mts. No. 3—30, magnif. 22 ×. Fig. 14. Geopetal structure in a chert. The floors of the radiolarian voids ocvered with globular pyrite, the rest filled by chalcedony. Chert concretion from the Neocomian limestones of the Envelope Series; loc. Podhradie, Veľká Fatra Mts. No. 5159, magnif. 24 ×. — Fig. 15. Rhombs of two carbonates in a chert. Dark rhombs (Fe-dolomite) seem to be older than calcite ones. Concretion from the Dogger-Malm limestones of the Križná nappe; loc. Čeitach near Smolenice, Malé Karpaty Mts. No. 9, magnif. 55 ×. Photo: L. Osvald.



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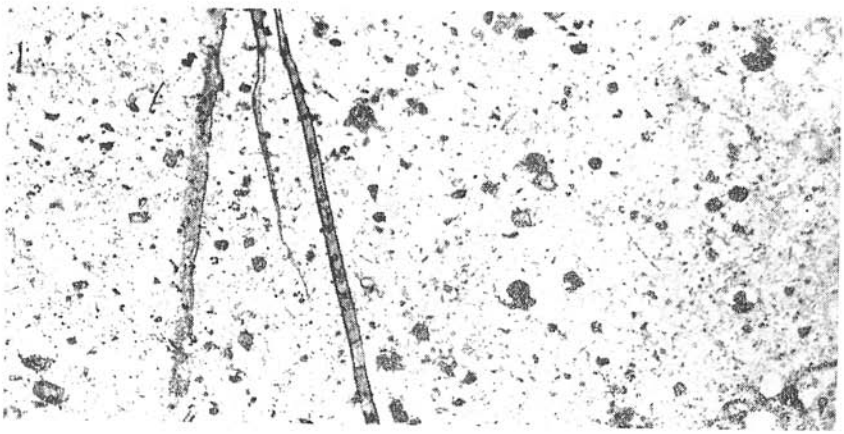

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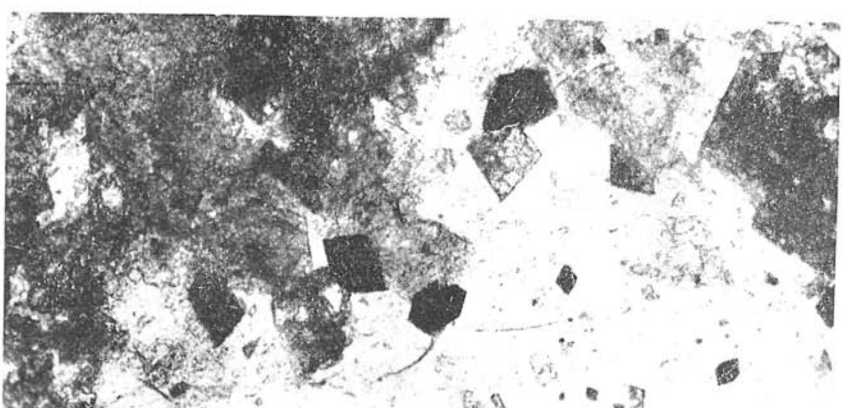

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Mineral components

Groundmass of the chert concretions. Is is formed by microcrystalline, short-fibrous aggregate, for which a conventional name „chalcedony" is used here. By the X-ray analysis (J. Babčan) from the silica minerals only the presence of quartz was confirmed. Two structural types of the groundmass may be recognized on the base of the electron microcropic photos made from the fracture plane replicas (H. Gerthofffferová): a) Blocky, polyedric structure corresponding to the novaculite type of R. L. Folk — Ch. E. Weaver (1952), to the smooth-blocky type of I. V. Chvorova — A. L. Dmitrik (1969), to the „granular" type of A. E. Oldershaw (1968) or to the microcrystalline type of M. Harman — K. Borza (1970); e. g. chert concretion of Neocomian, loc. Pokraj (Malé Karpaty Mts.) with average grain size about 1,5 μ (Fig. 25). b) Spongy type (R. L. Folk — Ch. E. Weaver 1952), with abundant liquid inclusions: e. g. chert concretion of Tithonian of the Envelope Series, loc. Zázrivianska valley (Malá Fatra Mts.) — Fig. 26. M. Harman — K. Borza (1970) have published electron microscopic photos from the Tithonian chert concretion from the locality Brodno. They described its structure as fine-grained type corresponding to spongy type of R. L. Folk — Ch. E. Weaver.

As to the thin section study abundant inclusions (microlites, „pigment") are conspicuous in the groundmass. Using higher magnifications following minerals were found: minute grains of carbonates predominate, further clay minerals, apatite, rutile, pyrite, turmalin. Only organic remains (radiolarians, sponge spicules) and veinlets are devoided of the inclusions or these are there substantially less numerous. This is just the criterion of the void infilling of previously empty space. On the other hand, pigmented groundmass evidences the metasomatic replacement. Besides the previous voids within the organic remains or after the dissolution of organic remains and formerly open cracks, larger parts formed by clear sheafy chalcedony aggregates were found only as exceptions (concretion from the locality Brložnica 4597). It may be supposed, that the last mentioned case also represents filling of voids after the dissolution of some larger organic remains. Clastic quartz grains of the sand category were found exceptionally in a chert concretion (Brložnica 5497); no syntaxial rims over those clastic grains are present. The fact, that silica do not overgrow syntaxially the clastic quartz grains was repeteadly proved in our thin sections studies of Liassic arenaceous limestone with cherts from the Envelope Series of High Tatras.

Rhombs of carbonates. They occur almost in all studied chert concretions and are missing in the surrounding limestones. They were formed by the recrystallization of micrite under the influence of migration silica colloids (M. Mišík 1968). It was proved by staining that in several concretions the rhombs belong exclusively to calcite. In other cases (approximately a third of examined thin sections) the simultaneous presence of two carbonate minerals was ascertained: calcite predominates over Fe-dolomite (ankerite ?). The rhombs of the latter are always somewhat smaller, darker, brownish to cloudy and with more perfect outlines. At the mutual contacts the Fe-dolomite rhombs seem to be older (Fig. 15) but contrary cases were found too. Their origin should be then placed in a succesion between the older and the younger calcite rhombs. The calcite rhombs are often corroded and overfilled by inclusions (probably by the liquide ones). No preferred orientation of rhombs was observed. Sometimes calcite rhombs contain phantoms after radiolarians (Fig. 9), originated either by syntaxial overgrowth on the radiolarians filled by a single calcite crystal, or were seized by a growing calcite rhomb (excentrically situated phantoms, two radiolarian phantoms in one rhomb, half of the radiolaria forming part of the rhomb and other half formed by chalcedony). Some kind of relation appears to be existing between the size of calcite rhombs scattered loose in the matrix and the size of chert concretions. Rare cases of big concretions with minute rhombs or without calcite rhombs may be probably explained by slight recrystallization, imperfect „assimilation" of calcite relicts. The corrosion of calcite rhombs is frequent; the conditions of precipitation and dissolution of calcite seem to have oscillated. In some cases distinct enlargement of the rhomb size towards the centre of the concretion was observed (Fig. 4). Rarely a decreasing of the size towards the centre was registered (loc. Kozinec — 8b, Brložnica — 5520). Seldom a group of rhombs with the equal optical orientation was found (loc. Podhradie, loc. Jatky); no veinlet connecting such rhombs are visible. Besides the isometric rhombs, strongly elongated to columnar forms are sometimes common (loc. Jatky). Maximum size of rhombs in concretions generally varies between 0,1—0,7 mm, the maximum size about 0.3 mm is the most frequent.

C l a y m i n e r a l s. They are a constant component of all substratum rocks of the studied concretions. Due to their minute size it is difficult to estimate their content. Distinct larger individuals (probably illite) were found approximately in a quarter of all thin sections. In the concretion of the locality Pokraj (Malé Karpaty Mts.) they have a disposition subparallel to the bedding plane and are larger than in the surrounding limestone. Their diagenetic enlargement in the silica environment may be suggested. In the insoluble residues of limestones illite, kaolinite and chlorite were clearly identified (E. Š a m a j o v á). Due to the impossibility of their extraction and concentration from cherts, no unambiguous results were obtained by X-ray analysis of cherts. Some indications about the nature of clay minerals and their possible authigenesis in cherts were obtained by microprobe (see p. 152).

A p a t i t e. The occurence of tiny idiomorphic crystals of apatite in three quarters of thin sections from the Tithonian cherts is noteworthy. Approximately the same frequency was found in Dogger-Malm cherts. The maximum size was 0,06 mm. (Fig. 22 and 23). In some cases a preferential forming of apatite around the fragments of organic matter was observed.

R u t i l e. Fine needles with high refractive index in Tithonian-Neocomian black cherts probably pertain to rutile; in one case a typical knee-like twins were found. In the red chert concretions of Dogger-Malm rutile is more frequent accompanying chlorite.

T u r m a l i n. Single minute columnar crystals of authigenic turmalin were found twice in the black chert concretions of Tithonian-Neocomian age (loc. Podhradie — 5250 max. dimensions $40 \times 8\,\mu$ and loc. Pokraj — 4581 $40 \times 10\,\mu$). They have a greenish-brown pleochroism. In the red chert concretions of Dogger-Malm the tiny turmalin crystals are somewhat more frequent (Fig. 24); they display a green pleochroism. In the thin sections of the surrounding limestones no turmalin was found. It appears that it is at least more frequent in chert concretions and that the formation of authigenic turmalin is favorized by the diagenetic concentration of the silica colloids. The higher content of boron in cherts that in surrounding limestones supports this assumption (Tab. 1).

P y r i t e. It is a common constituent as pigment, small globules and irregular grains; idiomorfic crystals and rod-like aggregates (probably replacing plant tissue fragments) are less frequent. Pyrite is realively more abundant in the chert concretions, namely near their periphery (C_1). The idiomorphic crystals to 0.2 mm, may be found there (Fig. 5); they are missing in the surrounding limestone. Rarely a contrary case was found (loc. Brložnica — 5497), where larger crystals of pyrite to 0.12 mm, were present only in the central part of the concretion (C_2). Radiolarians are seldom filled with globular pyrite; the cases of partly filling with geopetal structure are noteworthy (Fig. 14). Pyrite related to the immediate neighbourhood of the calcite veinlets in cherts was exceptionally found (loc. Dlhá).

Brown colouring organic matter. No discrete colour-bearing particles were found even using the highest magnifications of the light microscope. Probably the organic matter is closely connected with colloidal silica. It adds brown colour to the groundmass in the thin sections and black colour to the macroscopic samples of cherts. Sometimes the colouring matter is irregularly distributes like in the Neocomian of the Envelope Series loc. Brložnica — 3709 (Veľká Fatra Mts.). As the surrounding rock there is a spotty marly limestone, the irregular distribution of the organic matter can be considered as inherited. Rarely the colouring is limited to the centre of the concretion (C_2), meanwhile the periphery is clear.

Spectral analysis. Tab. 1 contains results of three pairs of the studied cherts and corresponding limestones; further three pair analysis from the other horizons of the Carpathian Mesozoic are added for comparative purposes. These semiquantitative analysis show, that by the migration process during the diagenesis, following elements are preferentially concentrated in chert concretions: Mo, W, Ga, Li, Ti, V, B. Among them Mo, W, Ga were detected in chert concretions only, in the surrounding rocks they could not be registered. Li was found only in cherts and from the surrounding rocks once in dolomite. Cherts are also enriched in Ti, V and B; these elements display substantially lower concentrations in the surrounding carbonate rocks. On the other hand, chert concretions have a lower content of Pb, Mn, Sr with regard to the host limestones.

Microprobe analysis. First specimens of chert concretions with their transition zones were preliminary studied by J. Krištín, concerning the content of Ca, Mg, Si, Al, K, Na, Fe (Fig. 29). The sample from the Neocomian of the Envelope

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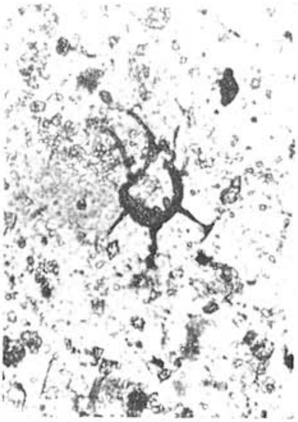
Fig. 16. *Oligosphaeridium complex* (White) in a chert concretion from the Neocomian limestones, Manín Series, Klippen Belt: quarry above Dobrá near Trenčianske Teplice (identification by O. Čorná). No. 2752, magnif. 210×. — Fig. 17. *Cannosphaeropsis* sp. (Dinoflagellata) in a chert concretion from the Tithonian limestones of the Envelope Series, Malá Fatra Mts.; quarry in Zázrivá valley. No. 4006, stained with alizarin, magnif. 410×. — Fig. 18. Rhax in a chert from the Neocomian limestones of the Križná nappe; Zbýňov, NO part of Strážovská hornatina Mts. No. 121, magnif. 210×. — Fig. 19. *Globochaete alpina* Lombard („forme bipartite") entirely replaced by chalcedony, visible as a ghost due to the pigmented outlines. Some „filaments" — juvenile pelecypods also entirely silicified are present. Chert concretion from the Dogger-Malm limestones of the Križná nappe; loc. Čejtach near Smolenice, Malá Karpaty Mts. No. 5b, magnif. 136×. — Fig. 20. Metasomatic replacement of the chalcedony by calcite. Phantoms of the metacolloidal structure in the calcite of the radiolarian filling. Chert concretion from Tithonian limestones of the Kysuca Series: klippen Kozinec near Zázrivá. No. 8b, magnif. 136×. — Fig. 21. Replacement of the chalcedony by calcite. In a calcite aggregate some phantoms of colloidal structure may be seen (previously a radiolaria filled by silica colloids). Chert concretion from the Dogger-Malm limestones of Križná nappe: loc. Jatky, Belanské Tatry Mts. No. 10, magnif. 136×. — Fig. 22. Tiny crystal of authigenic apatite in a chert concretion. Dogger-Malm limestones of the Križná nappe: loc. Sklabiňský Podzámok, Veľká Fatra Mts. No. 4640, magnif. 410×. — Fig. 23. Crystals of apatite formed along the margins of a fragment of organic matter. In the centre and below is calcite partly of rhombic form. Chert concretion from the Tithonian limestones of the Envelope Series, Malá Fatra Mts.: quarry in Zázrivá valley. No. 4006, magniff. 210 ×. — Fig. 24. Columnar authigenic turmalin in a chert concretion from the Dogger-Malm limestones of the Križná nappe; Zázrivá valley, Malá Fatra Mts. No. 5160, magnif. 210×. Photo: L. Osvald.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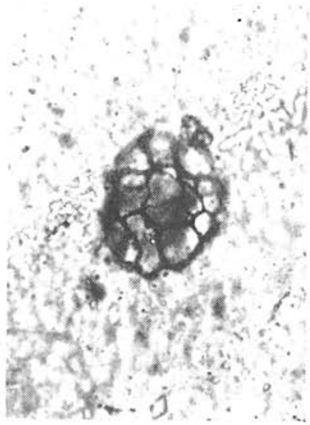
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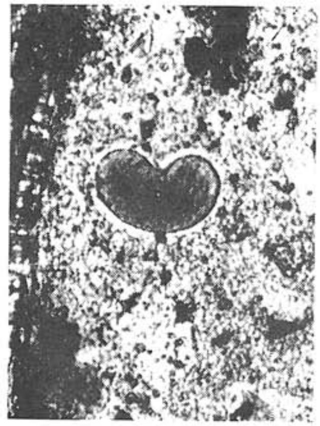
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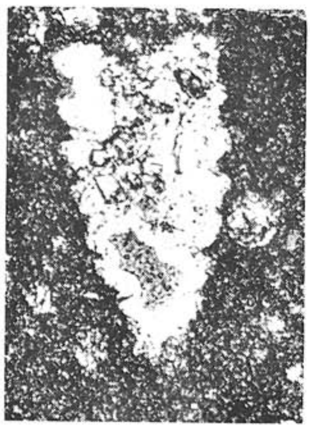
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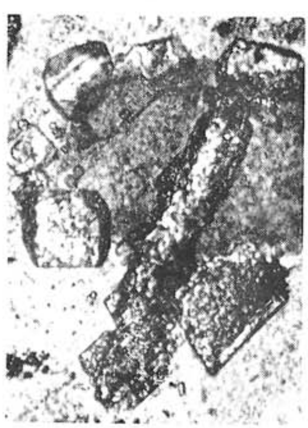
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Table 1. Semiquantitative spectral analysis of the chert concretions and surrounding rocks from the West Carpathian Mesozoic

	1	1–2	2	2–3	3	3–4	4	4–5	5
1A	Ca, Si, Mg, Al, Fe, Na, Sr	—	K	Ba, Mn	Cu	Cr, Ti	In, Ag, Ni	—	Pb, Co
1B	Si, Ca, Mg, Al, Fe, Na	—	Sr	—	Mn, Ti, Cu, Cr, Ba	Ni	Pb, In, Ag, Co, B	—	K
1C	Si, Al, Fe, Ca	Mg, Na	—	Ba, Ti	Mn, Cu, Cr, Sr	Ni	In, Ag, Co, B	—	Pb, Ga, Li
2A	Ca, Mg, Si, Al, Fe	—	Na, K	Sr, Mn, Ba	Cu	—	Pb, In, Ag, Ni, Cr	Ti	—
2C	Si, Al, Ca, Fe	Mg	—	Sr, Ba, Na, Mn, Ti	Cu, K, Cr	Ni	In, Ag, Co	V	Pb, Ga, Mo, B
3A	Ca, Mg, Fe, Na	Si, Al, K	Sr	Ba	Mn, Ti, Cu	Ag, Pb, Cr	In, Ni	Co	—
3C	Si, Al, Fe, Ca	Mg, Na	—	Ba, Ti	Mn, Cu, Cr, Sr	Ni	V, In, Ag, Co	K	Pb, W, Ga, Mo, Li
4A	Ca, Mg, Si, Al, Fe, Na	K	Sr	Mn	Ti, Cu, Cr, Ba	In, Pb, Ni	Ag, Co	V	B
4C	Si, Ca, Al, Fe	Mg, Na	Ba	Sr, Ti, Mn	Cu, Cr	Ni	In, Ag, Co	V, Pb, B	W, Ga, K, Li
5A	Ca, Mg, Fe	Si, Al, Na	—	—	Mn, Cu, Sr	Pb, Ti, V, Cr	In, Ag, Ni, Co, Ba	Li	—
5C	Si, Fe	Mg, Ca, Na	Al	—	Ti, V, Cu, Ba, Sr	Cr, Mn, B	Ag, Ni	—	Pb, Ga, Mo, In, Li
6A	Ca, Si, Mg, Fe	Al	Na	Sr	Mn, Cu, Cr	—	Ni, In, Ag, Ti, Ba	V	—
6C	Si, Ca, Mg	Al, Na	—	Sr	Mn, Cu	Cr	Ti, In, Ag, Ni, Ba, B	V	W, Ga, Li

Series of Malá Fatra Mts., loc. Podhradie gave the following results. Total length of the line — 0.85 mm. Si-Ca are in the complementary relations. The curves of Si and Al show that Al is not in any correlation with chalcedony: all peaks of Al correspond to the peaks of K, resp. Na, Mg, Fe. The course of the Mg curve is in the direct relation to the content of Ca, indicating its slight isomorphic admixture in calcite. Only one common peak corresponding to a dolomite grain of 0.03 mm diameter was found in the chalcedony mass. All other Mg-peaks are obviously independent on Ca and directly connected with the Al-peaks, probably representing clay minerals. Low content of Fe roughly corresponds to Mg, representing another isomorphic admixture in calcite. Only one Fe-peak is independent on Mg, obviously a pyrite grain of 0.02 mm diameter. K—Al are clearly connected forming the same sharp peaks mainly of clay minerals. Low backround content of Na display an indistinct dependance on K; from three Na-peaks two coincide with K—Al peaks, one only with Al-peak. At the whole on the 0.85 mm long trajectory following alumosilicate peaks were found: 10 peaks of K—Al (illite), 2 peaks of K max.—Mg max.—Fe—Al (? mineral), 2 peaks of Na—K—Al (feldspar ? mica ?), 1 peak of Fe max.—Mg—Al (chlorite), 1 peak of Na max.—Al (albite ? Na—mica ?).

Veinlets in chert concretions

The absolute majority of veinlets in the studied chert concretions is formed by calcite. Several types of veinlets according their structure and relative age may be discerned.

a) Older syngenetic calcite veinlets. They correspond to the contraction cracks originated in the early stage by dehydratation of the silica gels (syneresis). Characteristic sings are: they do not go out from the outlines of the concretions, they often are interrupted (the interruptions are represented by hair veinlets of fibrous chalcedony, or they were completely healed by still plastic silica groundmass), the parts of the veinlets were shifted by invisible dislocations (Fig. 31), their margins are corroded by the chalcedony groundmass. Some of these syngenetic veinlets with diffused borders must be at least partly of metasomatic origin as they include radiolarians. Very often all radiolarians in the immediate contact with the older veinlets are filled with a single calcite crystal. As such calcite filling of radiolarians are missing in the surrounding chert, this fact suggests an early origin of these veinlets. Their drusy calcite contains abundant inclusions what is likely related with their metasomatic nature. The carbonate-bearing solutions were introduced into the submicroscopical con-

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1A. Slightly marly limestone, Tithonian of the Kysuca Series; klippen Brodno near Žilina. — 1B. Transitional zone from the limestone into the concretion; the same specimen. — 1C. Chert concretion; the same specimen. — 2A. Slightly marly limestone, Neocomian of the Envelope Series; Pokraj near gamekeeper's cottage Zabité, Malé Karpaty Mts. — 2C. Chert concretion (grey); the same specimen. — 3A. Marly limestone, Neocomian of the Envelope Series; Podhradie, Veľká Fatra Mts. — 3C. Chert concretion (black); the same specimen. — 4A. Red marly limestone, Dogger-Malm of the Krížna nappe; Zázrivianska valley, Malá Fatra Mts. — 4C. Chert concretion (red); the same specimen. — 5A. Dolomite, Keuper (Norian) of the Krížna nappe; quarry near Belanská Kotlina, High Tatra Mts. — 5C. Chert concretion (red); the same specimen. — 6A. Reifling Limestone (grey), Ladinian of the Choč nappe; quarry near Turík, Chočské pohorie Mts. — 6C. Chert concretion (black, with concentric structure); the same specimen. Anal. J. Chudý.

traction cracks and from there they replaced the silica groundmass. The oscillation of the conditions during the early stage of concretion-forming process was responsible for the disruption and partial replacement of the calcite veinlets by the silica colloids.

b) Bordered calcite veinlets. They are also partly of metasomatic nature. Their clear central part represents the drusy-calcite filling of an open crack. Cloudy borders of the veinlets were formed by syntaxial growth, by metasomatic enlargement. Sometimes optically identical overgrowths are on the both sides of the same calcite grain of the crack infilling (Fig. 32). Besides inclusions, some *Hystrichosphaera*, involved in the calcite rims, testify their metasomatic nature.

c) Veinlets of string-pearl type (M. Mišík 1971). Some of the calcite veinlets as well as of fine hair ones with calcite or chalcedony display idiomorphic calcite crystals which grew beyond the margins of the veinlet. The rhomb points are facing into the chert. Some rhombs represent syntaxial overgrowths on the calcite grains from the veinlet filling; they are pigmented and then probably metasomatic. Such cases indicate the transition between the bordered type and pearl-string type of the calcite veinlets. Pearl-string structure was commonly formed on the syngenetic veinlets, but it was observed also on some veinlets running out of the chert and thus something younger ones.

d) Calcite veinlets with chalcedony rims. They belong to the older epigenetic veinlets running out of the chert concretions. At first a calcite filling was quickly precipitated into the open crack. The migration of the silica was not finished yet in those times. Since the coarse-grained calcite of veinlet represented a barrier for the colloid migration, they concentrated themselves on its border and in a slight measure replaced the calcite of the veinlet. Typical structures of this type can be seen in the transition zone (AB). in siliceous limestones. By the slow opening of the crack the calcite filling can have a prismatic structure; by the simulataneous lateral movement the calcite individuals acquired an „S" forming shape.

e) Young calcite veinlets. They are filled by clear drusy calcite without chalcedony rims as they were formed after the last migration of SiO_2. Sometimes they taper out not far from the outlines of the chert concretion. These veinlets were formed by tectonic pressure and conditioned by the different rigidity (competition) of the brittle chert and more plastic limestone (M. Mišík 1971).

f) Dashed veinlets (M. Mišík 1971). They are typical for the „Biancone" limestones. Probably they originated by the recrystallization, by the coalescence of several parallel submicroscopic veinlets. It was observed that the dashed veinlets entering the chert lose their dashed aspect. The different rigidity was responsible that a swarm of parallel hair cracks was formed in the marly limestone and an open crack in the chert.

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Fig. 25. Blocky polyedric structure of a chert concretion from the Neocomian limestone of the Envelope Series; loc. Pokraj near the gamekeeper's cottage Zabité, Malé Karpaty Mts. Replica of the fracture plane, magnif. 5000×. Photo: H. Gerthofferová. — Fig. 26. Spongy structure of a chert concretion from the Neocomian limestones of the Envelope Series; quarry in Zázrivá valley, Malá Fatra Mts. Replica of the fracture plane, magnif. 5000×. Photo: H. Gertrofferová. — Fig. 27. Distribution of silicon in the chert. Dark areas represent calcite rhombs in a chalcedony groundmass. Inclusions of SiO_2 in calcite are very rare. Locality as in fig. 25. Microprobe analysis, SiKα, magnif. 536×. Photo: J. Krištín. — Fig. 28. The same part — composition, showing two mineral phases: calcite rhombs and chalcedony groundmass. The ray trail is visible. Photo: J. Krištín.

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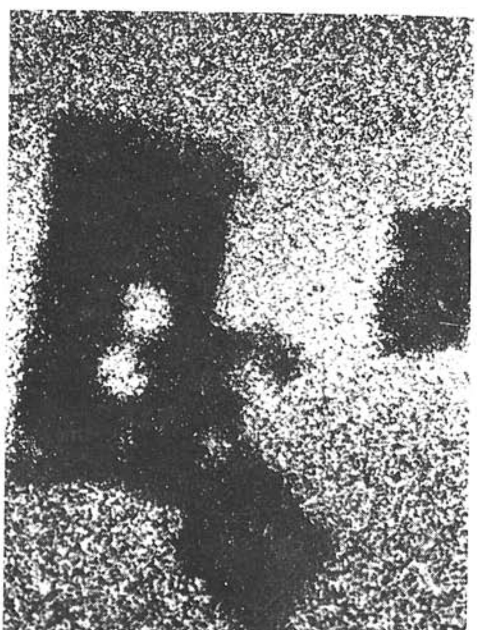

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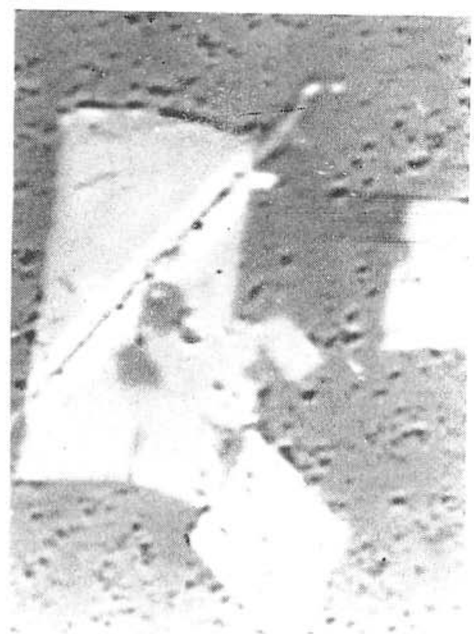

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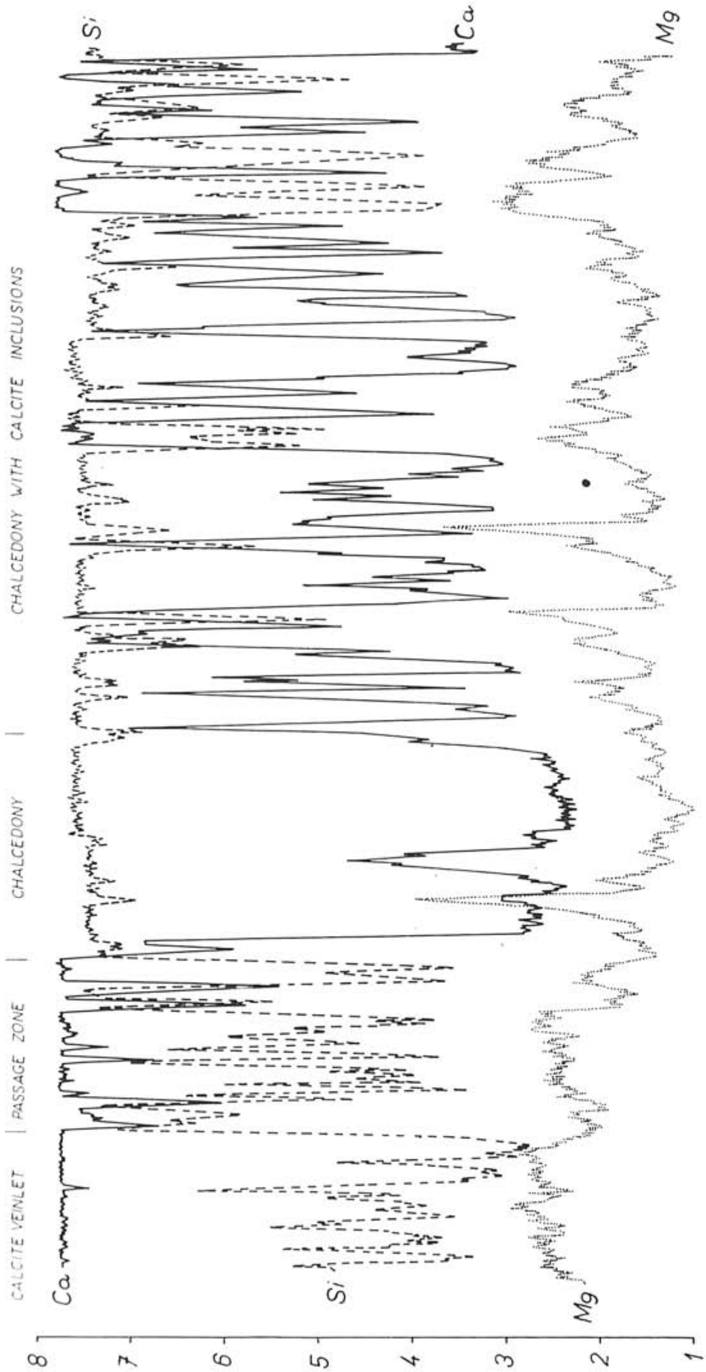
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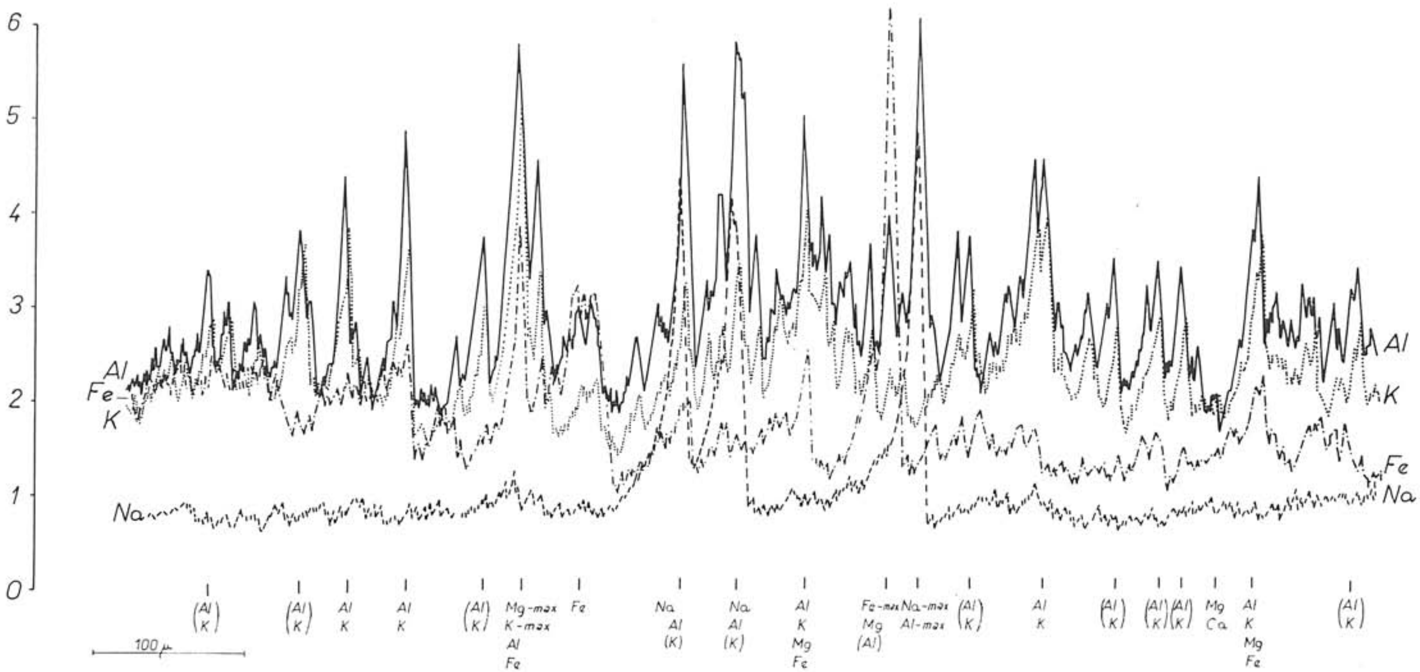

Fig. 29. Microprobe analysis of a chert concretion (external part) from the Neocomian of the Envelope Series; loc. Podhradie, Veľká Fatra Mts. (anal. J. Krištín).

g) Chalcedony veinlets. Hair veinlets with short fibrous chalcedony may be considered as syngenetic contraction cracks.

The majority of veinlets, namely of younger ones, is oriented roughly normal to the elongation of the chert concretions, to the bedding plane. Exceptionally veinlets were found which followed a certain sector of the concretion outline. They were formed in the transition zone on the dishomogeneity plane.

Conclusions

Microscopical structures of the chert concretions, their transition zones, various kinds of the radiolarian preservation as well as the veinlets of various structure and age gave many facts about the possible process of chert concretion forming.

Following transition zones were discerned: AB — limestone with dispersed chalcedony (siliceous limestone), B_0 — „marginal imbibition" by chalcedony, B_x — zone formed by coarse calcite grains at the outlines of the concretion, BC — peripheral zone of the concretion with the amount of not recrystallized micrite. In some concretions there was possible to distinguished an external part (C_1) which differs from the internal one (C_2) by abrupt change in size of rhombs, eventually by presence of pyrite crystals etc.

Tests of the radiolarians within the limy mud were originally empty (void with gas), or filled by mud. The silica test was dissolved or replaced by calcite. Later the drusy calcite filled the radiolarian voids. Combined filling with micrite and sparite displaying polarity structures is exceptional. The concretion forming process should have been a very early one, older than the crystallization of drusy calcite (calcite cement) into the radiolarian voids. Only in the transition zone AB the last centripetally migrating colloids found the voids already rimmed by drusy calcite and they filled only their rest in the centre. By the concentration of silica in the concretion area the microcrystalline calcite was gradually replaced by chalcedony. Not „digested" micrite recrystallized under the influence of silica colloids, forming rhombs. Sometimes two carbonates are present: calcite and Fe-dolomite (?). In the area of the concretion the voids in radiolarians were filled by silica with a globular structure. Exceptionally they contain floor-rims of globular pyrite. Sometimes the silica tests of radiolarians were replaced by carbonate conserving all details of their structure. It is difficult to explaine the characteristic filling of radiolarians with a single calcite crystal in cherts (BC zone and immediate neighbourhood of the syngenetic veinlets).

Syneretic cracks in chert concretions were filled by chalcedony and more frequent by calcite. The thickness of these veinlets often grew by metasomatic replacement. For

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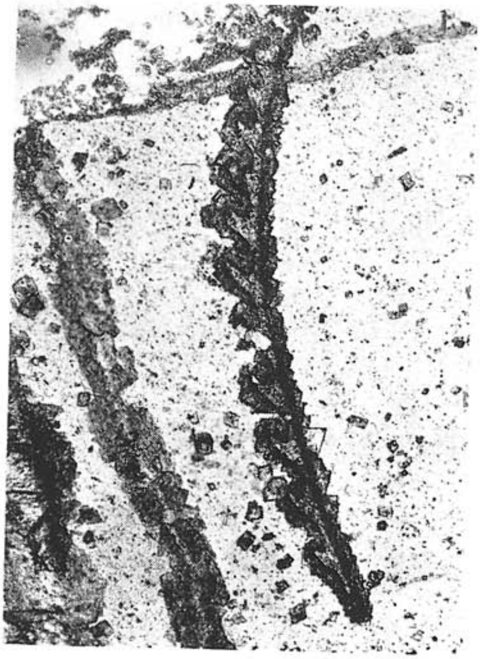
Fig. 30. Aptychus with syntaxial overgrowth of calcite, delimited by rhombic planes. Chert concretion from the Tithonian limestones of the Kysuca Series. Klippen Brodno near Žilina. No. 5715, magnif. 55×. — Fig. 31. Network of syngenetic contraction veinlets in chert (several of them display pearl-string structure). The veinlets are disrupted, theirs segments mutually shifted along the invisible cracks healed by colloidal silica. The same locality. No. 5669, magnif. 20×. — Fig. 32. Bordered veinlets in the chert. On the clear calcite grains from the drusy aggregate of the normal veinlet (filling of an open crack) the syntaxial overgrowths were formed. These cloudy overgrowths with inclusions originated by replacement of the chalcedony groundmass. The same locality. No. 3992, magnif. 55×. — Fig. 33. Dashed veinlet (originated by coalescence of parallel hair veinlets) passing into the normal veinlet in chert. Neocomian of the Envelope Series: Brložnica, Veľká Fatra Mts. No. 5497, magnif. 24×. Photo: L. Osvald.



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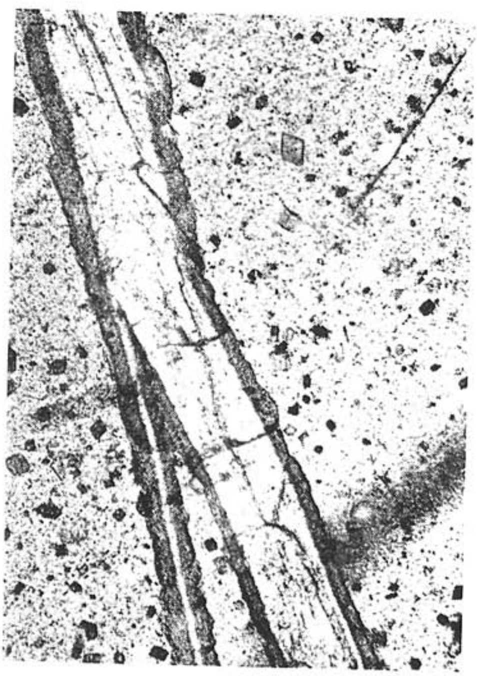

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syngenetic veinlets the „string-pearl" aspect is typical. Younger calcite veinlets in cherts originated already after the last migration of colloidal silica. They were conditioned by the higher competence of chert and therefore the calcite veinlets in the chert concretions are more abundant than in the surrounding limestones.

From the preliminary studies it may be concluded that during the concretion forming process within the chert space the conditions changed several times, that the precipitation of silica alternated with the precipitation of calcite. This is proved by the corrosion of carbonate rhombs and calcite veins, as well as by the relics of globular structure in the calcite aggregates, by the calcite replacement of radiolarian tests in cherts, by metasomatic calcite veinlets in cherts on the other and.

Some organic remains as *Calpionellidae, Cadosina, Nannoconus,* which are abundant in the surrounding limestones, were not identified in chert concretions. These tiny microorganisms are entirely destroyed by silicification. On the contrary *Hystrichosphaeridae* and *Acritarcha* are more frequent or exclusively present in the chert concretions. Early silica concretions protected them against the unfavorable diagenetic influences.

As to the mineralogy, the presence of tiny crystals of authigenic apatite and rarely also of turmalin in the cherts is noteworthy. Microprobe and X-ray analysis have shown the admixture of illite, chlorite and other alumosilicates. Chert concretions are enriched in Mo, W, Ga, Li, Ti, V, B and impoverished in Pb, Mn, Sr.

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