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RELICT OPAL-CT LEPISPHERES IN LOWER CRETACEOUS NODULAR CHERTS (KLIPPEN BELT AND CENTRAL WESTERN CARPATHIANS)

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Abstract: Nodular cherts from four stratigrafic profiles of Lower Cretaceous limestones: Rochovica, Krivá, Butkov and Bralo, were studied. The cherts from biomicritic pelagic limestones contain tests of radiolarians mostly replaced by calcite. The cherts are formed microcrystalline quartz (grain size range from 0.1 to 6 μm) with a low crystallinity index (CI = 1.7 to 3 relative units: Murata & Norman 1976). This range of grain size of quartz is the main condition for the identification of lepisphere textures of mikroquartz precursor - opal-CT. The opal-CT relict textures indicated chert formation by maturation process of silica mineral. We can also present (chert from locality Butkov) a bladed form of the original opal-CT microcrystals, forming the lepispheres. The presence of silica tests in host limestones or also in cherts, suggest biogenic source of chert silica.

Key words: nodular chert, silicification, Lower Cretaceous limestones, opal-CT lepispheres, relict textures, grain size, quartz crystallinity index.

Introduction

Most authors assume that Mesozoic deep-sea cherts contain opal-CT relict textures indicative of chert formation by maturation process of silica (Heath & Moberly 1971; Kastner et al. 1977; Gao & Land 1991; Maliva & Siever 1988, 1989a, 1989b; Oehler 1975; Land 1979; Milliken 1979). This process has been proved and experimentally verified (Kastner et al. 1977; Williams et al. 1985; Williams 1985; Gao & Land 1991) for example on material from boreholes of the DSDP project. Gradual recrystallization of silica in limestones was proved in older cherts, for example Paleozoic ones (Knaugth & Epstein 1975; Kolodny & Epstein 1976; Gao & Land 1991). It is often possible to trace these changes by means of relict textures preserved in the cherts, which directly document the presence of preceding mineral phases.

The problem of silicification and the formation of cherts, as results of the diagenetic process in limestones, has appeared only sporadically in literature from the Western Carpathian region. An exception is the work of Mišík (1973), in which the author gave a detailed petrographic study of Tithonian and Neocomian nodular cherts from the Western Carpathians. On the basis of external signs and microscopic observations he solved their relation to the surrounding rock, and the conditions of their formation. We also selected four our study material from Lower Cretaceous (Neocomian) limestones and we can indirectly continue the earlier studies.

Samples of cherts from limestone beds of three units were investigated: the Kysuca Klippen Belt (Rochovica, Krivá), the Manín Unit (Butkov), and Tatric (Bralo) (Fig. 1). The samples come from known outcrops or profiles, with published results, mostly from stratigraphical and paleontological observations (Andrusov 1945; Michalík et al. 1990; Vašíček et al. 1990; Peterčáková 1990; Ožvoldová & Peterčáková 1992).

The aim of this study is to show how it is possible to obtain further information from studies of cherts, and according to them to judge the diagenetic development of the rock.

Description of the localities and samples

These four profiles, from which samples of chert were chosen, document the Upper Jurassic - Lower Cretaceous development of sedimentation in the three above mentioned units. The nodular cherts are associated with pelagic biomicritic limestones (mostly wackestones to mudstones), which sedimented below the level of reach the waves. The presence of calcified, originally silica tests indicate the biogenic resources of the chert silica.

The Rochovica profile (Fig. 1) is one of the most fully developed and preserved Pieniny limestone formations of the Lower Cretaceous of the Kysuca Unit of the Klippen Belt (Vašíček et al. 1992). Cherts were studied from the upper part of the profile (Rochovica 380 - Vašíček et al. 1992), which is formed by dark grey, spotted, mostly biomicritic limestones (wackestone to packestone) with nannocones and radiolarians. The radiolarians in the limestones are mostly calcified. The Hedbergella microfacies indicates probable Barremian age. In this part silicification is not very intensive, but nodular cherts of a dark grey colour, and very fine-grained (porcelain appearence on broken surfaces), with sharp contact with carbonate, are also present.

Andrusov (1945) described the characteristic development of the Pieniny series in the Orava part of the Klippen Belt between the villages of Krivá and Dlhá (locality Krivá, Fig. 1). We studied cherts from the Neocomian Biancone limestones which reach a considerable thickness in the profile (100 - 150 m). The occurrence of cherts in the limestone beds is irregular, forming more regular bands only in places. Apart from calpionelides, relatively abundant radiolarians in the biomicritic limestones (wacke-

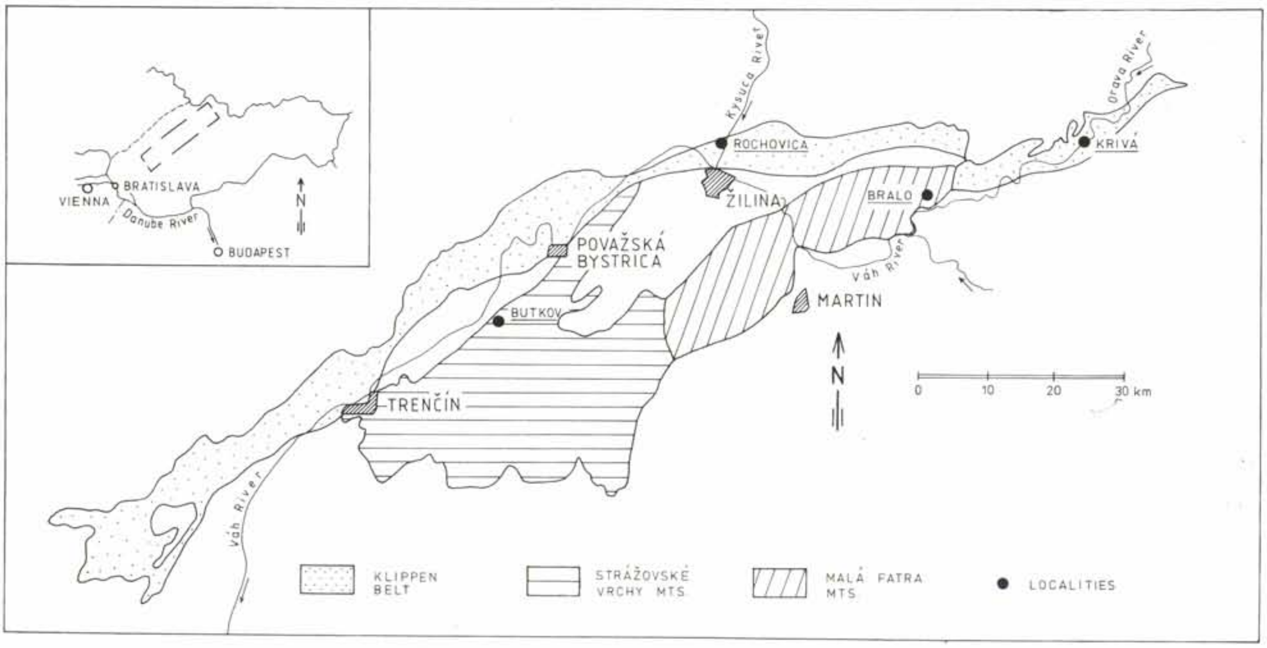


Fig. 1. Regional geological setting of the region, with the location of the profiles from which samples were studied.

stone) were also described. However, their test sections in microscope are mostly calcified, or filled with secondary grains of quartz. The limestones also contain ammonites and their aptychies, and also belemnites. Most forms in this quite monotonous fauna point to a Hauterivian age (Andrusov 1945).

The profile in the Bralo quarry exposes on a relatively large surface a significant part of the Lower Cretaceous sequence of the Tatrid Malá Fatra Unit (Polák & Bujnovský 1979, Michalík et al. 1990;). We studied cherts from heavy bedded grey micritic limestones (Lučivná Formation). Here, cherts are developed as large nodules, which in places merge into irregular stratiform horizons. The nannocone biomicritic limestone contains accumulations of framboidal pyrite, authigenic quartz and Fe hydroxide coats. There is partial silicification of calcite tests and calcification of silica (radiolarian) tests (Michalík et al. 1990). According to work cited, the limestones belong to the sequences of uppermost Hauterivian age.

Research on the Upper Jurassic and Lower Cretaceous formations of the Manín Unit, from the exploited quarry of Butkov, brought many new bio- and litho-stratigraphic results (overview in Michalík et al. 1990). The measure of silicification in the formations is extensive and heterogeneous and the size, shape and colour of the cherts are very different. We selected samples of Hauterivian limestone with cherts (Kališčo Formation) from the survey main of the quarry (Michalík et al. 1990, Peterčáková 1990, Ožvoldová & Peterčáková 1992). The occurrence of abundant chert concretions (nodules), with different resistence towards compaction in comparison with limestones, are the reason for the resulting nodularity of the limestone. It occured mostly in the lower part of the formation, and also actually restricts it. The limestone is biomicritic, light grey, the cherts are darker light brown and of porcelain appearence. The limestones contain abundant nannocones, sponge spicules, ostracods, foraminifers and radiolarians. In the upper part of the formation, the content of cherts is much lower, the limestones are coarsely heavy-bedded, weakly marly. The samples are from the lower part. We also took samples from chert, which filled the core of a large cephalopod (diameter about 35 - 40 cm), with sharp contact with the surrounding limestone.

Methods

We used the X-ray diffraction record of powder samples of chert in comparison with records of quartz standard (Fig. 2) to obtain crystallinity index of quartz - CI: the method of Murat & Norman (1976). Highly ordered crystalline quartz standard has a value of 10. We relate the quartz crystallinity index to the grain size of the quartz in the chert. The grain-size composition of cherts was evaluated from scanning electron microscope (SEM) photographs. The relationship between the fossils preserved in the surrounding chert, and the presence of relict morphological traces in them were also studied by the SEM-method. We used samples with etched surfaces for this study. We etched the broken surfaces of chert and polished slabs for 10 minutes with concentrated HF (Gao & Land 1991). We also etched thin sections with concentrated HF, but for a shorter period of time - only 30 seconds. Chemical analyses of the powdered limestone samples were done by the X-ray flourescence method. Microelements in the cherts and in the limestones rock samples were analysed spectrochemically.

Results

1 - Grain-size composition and quartz crystallinity index (CI)

The size of the silica crystals in the cherts, as their porcelain appearence also indicated, is very small, and it does not vary more significantly in the studied samples. The grain size of the chert matrix varies from less than 0.1 to 6 μm, but the prevailing part of the grains were in the range 0.8 to 2.5 μm (Pl. I, Pl. II).

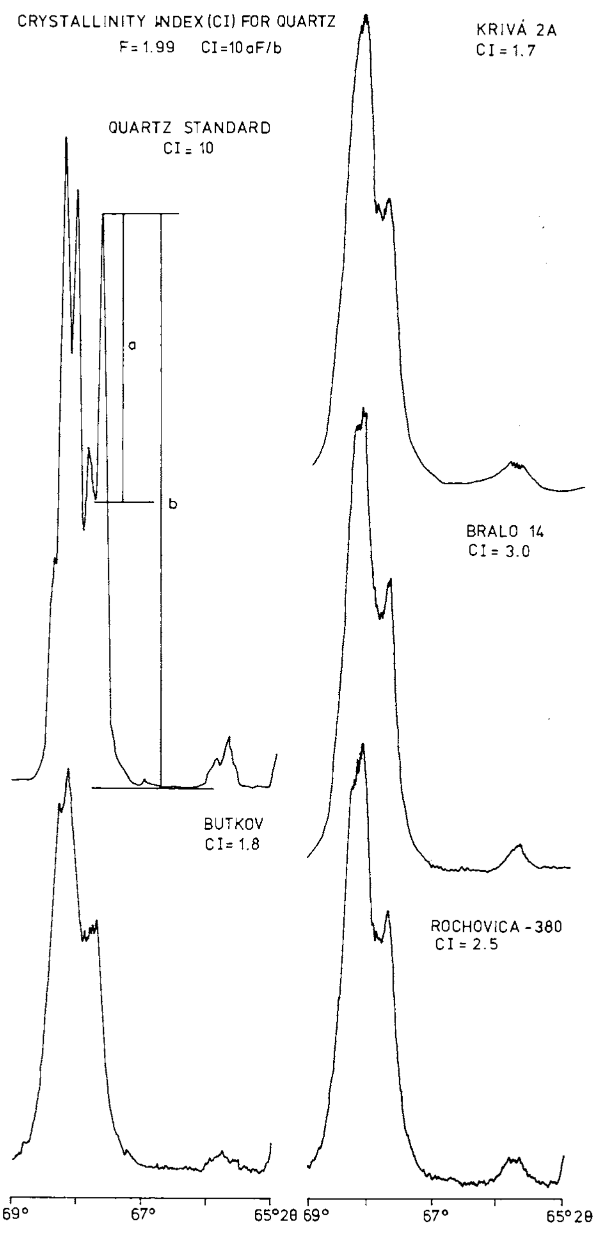


Fig. 2. The X-ray diffraction records of the cherts and the quartz standard document the differentiation in Crystallinity index of quartz (CI).

Chert matrix is formed by mostly irregular to isometric grains, less by pyramidally ending elongated crystals of rim cement in cavities. Very fine-grained quartz crystals (less than 0.1 - 1 μm) were in pseudomorphosed precursor opal-CT (opal crystobalit - tridymit) and we can see in SEM lepispheres as named original concentric agregates of opal-CT. We will discuss this in greather detail (Pl. I, Pl. II). From the X-ray diffraction record of powdered samples of chert, we found that microcrystalline quartz as the only mineral phase of silica, was present in all the samples. We used the quartz crystallinity index (CI) (Murata & Norman 1976) for relative comparison of the chert silica mineral (Fig. 2). All the samples showed a relatively low CI in comparison with the quartz standard with the value 10 of CI. The CI of quartz is above all a function of the size of grains of microquartz in chert (Murata & Norman 1976). In Mesozoic organogenic cherts (the tests of organisms are the source of silica) it is usually lower and values comparable to the quartz from magmatic crystalline rocks are reached only as a result of metamorphic changes (Murata & Norman 1976; William & Crerar 1985), that is the CI is not only a reflection of the relative age of the cherts of the rock, but also of the thermodynamic history of the rock/cherts.

2 - Relict textures in SEM

The presence of fossils with originally silica tests in the host limestone, but also directly in the chert demonstrates a biogenic source of silica. We do not suppose another source of silica, although it is impossible to exclude the contribution or admixture of SiO_2 of another origin (SiO_2 from the transformation of clays, SiO_2 from solutions of volcanic origin; authigenic grain of quartz are described in the surrounding limestones).

Various preserved "tests" of radiolarians, or other fossils (foraminifers, sponge spicules, nannocones Pl. II: Figs. 8, 9, 12), emerged from the matrix of the cherts after their etching (Pl. I: Figs. 2, 3; Pl. II: Fig. 3). Mišík (1973) described the forms of preserved radiolarians in thin sections and his observations were a good guide to us in identifying the relict textures of tests in SEM. The process of dissolution the original tests, formed by opal-A, occured in stages before the compaction of the sediment. From the way the relicts of tests are preserved, we consider that after sedimentation the tests were dissolved and replaced with calcite (completely or the cavities in them Pl. I: Fig. 2; Pl. II: Fig. 3) and the "tests" were enclosed in chert. The chert formation is a result of diagenetic dissolution (replacement of the calcite sediment. Remnants of calcite in the chert, or pseudomorphs after calcite tests, document the process of dissolution) replacement of carbonate (Pl. II: Figs. 8, 12). However, new calcite grains also formed later, for example in the cavities (Pl. I: Figs. 7, 12; Pl. II: Fig. 1), or partially also in the silica matrix of the chert (Pl. II: Figs. 9, 11). It is probably recrystallized calcite from the cavities, but also of the calcified walls of radiolarians (Pl. I: Figs. 2, 7; Pl. II: Figs. 1 - 4, 10). If the calcite was high in Mg, crystals of dolomite may have formed as well (Maliva & Siever 1989b). Hydrated MgO molecules (or hydroxide), which may form nucleation cores for opal-CT, may also be another source of Mg^{2+} for dolomite "in the closed system of chert" (Kastner et al. 1977; Maliva & Siever 1988). Relict textures of the mineralogical precursor (opal-CT) of microcrystalline quartz were found in all the cherts studied. Opal-CT forms characteristic spherical aggregates of bladed microcrystals, so-called lepisheres (Pl. I: Figs. 1, 4 - 6, 9; Pl. II: Figs. 5 - 7) and also rim cements (Pl. I: Fig. 12; Pl. II: Figs. 5, 6, 9, 10) in cavities, for example of the original tests of radiolarians. Their presence also confirms the idea about the process of maturation of silica during the formation of the cherts. Williams et al. (1985) presented the following summary of this process: opal-A (biogenic, silica ooze) - opal-A' (nonbiogenic, amorphous silica secondary S = 198.3 g/m^2, AS = 60 - 130 ppm) - disordered opal-CT (disordered cristobalite - tridymite) - ordered opal-CT (S = 181.6 g/m^2, AS = 20 - 30 ppm) - cryptocrystalline quartz, chalcedon - quartz (S = 172.2 g/m^2, AS = 6 ppm; AS is water solubility, S is specific surface). As is also seen in the SEM pictures (Pl. I: Figs. 5 - 6), bladed crystals are also preserved in pseudomorphs. They were found in the sample of nautiloid cephalopod filling. In the usual nodular or stratiform cherts we partially observed the bladed form of the crystals, but by detailed examination, they broke down into more or less isometric crystals, or only oval particles of very small dimensions (under 0.1 μm). The size of the observed lepispheres was in the range 10 - 20μm. The best they were preserved in the cavities mentioned, but the matrix of the chert also has an entirely spherical texture which was enhauced after etching (Pl. I: Fig. 9; Pl. II: Figs. 1, 4, 7).

3 - Chemical composition of limestones and cherts

Chemical analyses of the rock limestone samples (Tab. 1) give information about the extent of silicification and the relative content of chert and "silicate SiO_2" (mostly bound in clay minerals). Apart from clay minerals, sulphides, mostly pyrite (also framboidal - in the cavities of tests, e.g. locality Krivá Pl. II: Fig. 9), also occur in the carbonates. Microelements were analyzed in the limestone and in the chert (Tab. 2). Apart from Sr they are associated with non-carbonate minerals. The contents of B, Ba, Pb, Cu in the cherts are higher than in the limestones, contents of other elements apparently decreased. However, there are certain differences for samples from different localities, but these results have only a rough orientational value. In the SEM study we also distinguished particles of detritic clay minerals in the chert (Pl. I: Fig. 8). It is evident that they may bears trace elements. The presence of clay minerals makes impossible to find differences in the distribution of such elements as Mg, Al, Fe, or Na and K, which appear significant for the kinetic of opal-CT crystallization (Kastner et al. 1977; Maliva & Siever 1988), or other sources of silica. On the other hand, presence of clay material may significantly influence the rate of transformation of silica mineral phases in the diagenetic process (Hurd 1973; Kastner et al. 1977; Williams et al. 1985; Siever & Woodford 1973).

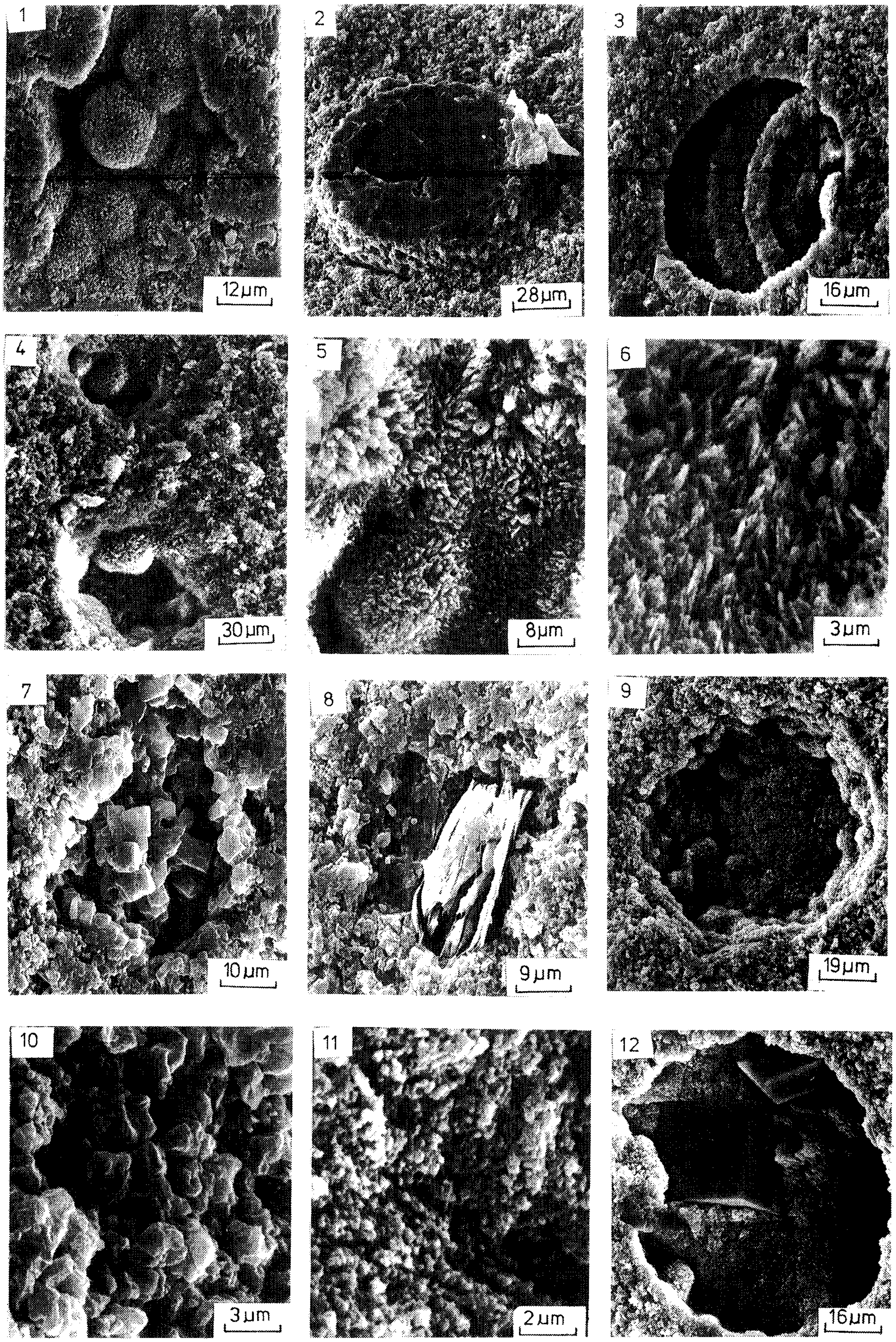
Discussion

Silicification may occur in carbonate, at different time periods after sedimentation (Hein et al. 1978; McBride & Folk 1979). Many authors consider the dissolution of calcite, and its replacement by silica in carbonate rock, to be a diagenetic process, which occurs as a result of changes in the mixture of marine/meteoric solutions (mixing model - Knauth 1979), oxidation of organic substances (change in the partial pressure of CO_2, formation of complexes: Williams et al. 1985; Bennett & Siegel 1987) or H^+ ions liberated as a result of the oxidation of H_2S (Maliver & Siever 1989a, 1989b). These processes could be reflected in the presence of traces or relict of the dissolution of carbonate. A more universal explanation of the causes of the dissolution and replacement of calcite by silica in the corresponding place, is the crystallization - controlled replacement model, presented by Maliva & Siever (1989). According to the authors it applies to practically all stages and conditions of the formation of cherts. It is based on the influence of pressure on solubility of calcite, and on nonhydrostatic pressure of crystallizing minerals in the intergranular spaces. The achievement of the state of the undersaturated solutions with respect to calcite (and his dissolution), is associated with intergranular solutions, while other pore solutions in the sediment may be saturated to moderately supersaturated with respect to calcite. Calcite grains, matrix and cements close to the silicified part of the rock need not bear traces of dissolution, which is connected with silicification (Maliver & Siever 1989). The properties of the host rocks, such as the content of organic matter, porosity and permeability, concentration of biogenic opal-A are factors, which direct and influence the actual form of the creation of chert nodules, and also the progress of recrystallization of the unstable forms of silica (nucleation of opal-CT) to the final quartz. The main cause of this stabilization, is the burial of the sediment, and the changes of temperature/pressure conditions associated with this. The progress of this maturing process was confirmed in the studied cherts, on the basis by identification of relict textures (lepisphere, rim cements opal-CT) of the intermediate silica phases. The form of preservation of fossils indicated a certain process of silicification in the diagenetic development of the rock. The dissolution of silica tests, and their replacement with calcite, occurred soon after sedimentation, and we consider that tests were the source of the silica for the formation of chert. We did not suppose another source of silica, but we cannot exclude anyone (solutions of volcanic origin, transformation of clay minerals etc.: Kastner et al. 1977; Pollock 1987).

The grain size composition of the cherts gives information about the process of recrystallization of silica-phases, and is a limiting factor for the preservation of relict textures of the original calcite, the precursors of the final quartz, and also relicts of the tests of fossils. The grain size range of microquartz found in the studied Lower Cretaceous cherts, falls into the grain size range described for Mesozoic cherts (Maliva & Siever 1988). According to the work mentioned, this shows the growth of crystals according to Ostwald ripening (Williams et al. 1985; Maliva & Siever 1988; Morse & Casey 1988).

Coarse quartz crystals (in cement) are formed by direct precipitation from solutions supersarturated with regard to quartz, but undersaturated with regard to opal-CT (Maliva & Siever 1988). After the dissolution of opal-A, silica may be precipitated, for example in the cavities of fossils or open spaces and cracks, and form quartz or chalcedony. Such quartz fillings and cements are described from Neocomian limestones (Mišík 1973), and we also find them in thin sections from our samples, as we mentioned in the descriptions of the samples. They may be formed at different stages of diagenesis, also in early stages of diagenesis before lithification, before the cherts formation and also later, after the burial of the sediments.

Plate I: Figs. 1 to 8 Butkov: 1 - polished surface, other broken surfaces of samples etched for 10 minutes with concentrated HF. **Fig. 1** - Matrix of the chert - microcrystalline quartz - with relict opal-CT lepispheres textures. **Fig. 2** - Calcified test of a radiolarian surrounded by microcrystalline quartz. On the outer surface, the texture of the test is partly preserved, formed by fine grained calcite. The central part is filled by coarse calcite. **Fig. 3** - Relict of recrystallized radiolarian. The test was not calcified, opal-A was recrystallized on microquartz. **Fig. 4** - Chert matrix, which fills the test of a large cephalopod. Lepispheres are easily visible in the cavities. **Figs. 5, 6** - Detail from Fig. 4. The size of the lepispheres is about 10μm. The quartz microcrystals have a flat - bladed form, well visible on **Figs. 6, 7** - A rhombohedral grain of calcite is formed in a cavity, probably in the calcified test of a radiolarian. The newly formed fresh like calcite evidently originated by recrystallization of the walls of the test. If the calcite was high - Mg, microcrystals of dolomite may also be formed in the cavities. **Fig. 8** - Clastic clayey material (illite) in a chert matrix. **Figs. 9 - 12** - Bralo, broken surface, etched with HF for 10 minutes. **Fig. 9** - Nicely preserved lepispheres of intermediate opal-CT in the cavity of a radiolarian test. The surroundings are formed by microquartz with signs of lepisphere structure. **Fig. 10** - The size of the microcrystals in the chert matrix varies in the range 0.1 to 6.0 μm. **Fig. 11** - The grain size of the crystals of the lepispheres is under 0.5 μm. **Fig. 12** - Cavity of a calcified test filled with microcrystalline, needle-like material and lepispheres, which are replaced by fresh rhombohedra of carbonate. There also may be found dolomite - compare with Fig. 7 and Figs. 1 and 11 from Plate II.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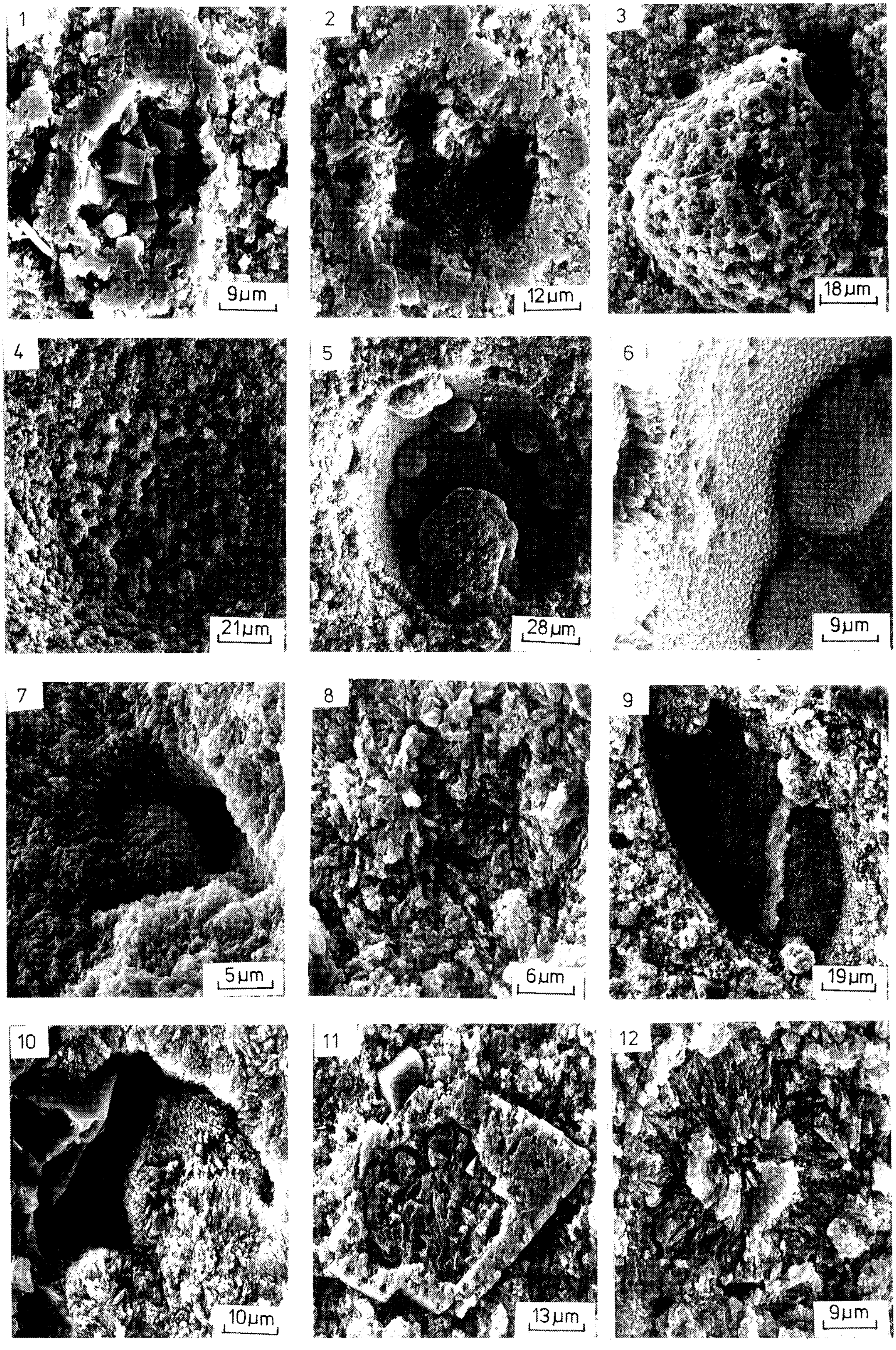
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Table 1: Chemical analyses of the limestones. The values are given in weight %, H_2O^- – H_2O lost by drying, H_2O^+ – H_2O loss by burning (corresponding to carbonate CO_2).

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	H_2O^-	H_2O^+
Butkov M	8.09	0.07	1.65	1.05	0.06	48.84	0.82	0.39	0.08	0.39	38.32
Bralo 14	38.28	0.04	0.96	0.45	0.10	33.56	0.29	0.21	0.04	0.22	25.79
Krivá 2a	5.59	0.02	0.88	0.40	0.04	51.29	0.58	0.22	0.04	0.28	40.42
Rochovica 380	18.92	0.03	0.85	0.52	0.06	44.81	0.41	0.20	0.07	0.31	33.60

Table 2: Contents of microelements in the limestones (Tab. 1) and cherts. The values are in ppm, the determination limit of the elements is 3 ppm.

Sample	Ba	B	Pb	V	Cu	Ni	Co	Cr	Sr
Limestones									
Butkov M	182	56	8.1	26.3	26	44.6	6.5	25.7	300
Bralo 14	49	71	3.0	3.0	22	3.0	3.0	3.0	275
Krivá 2a	56	31	4.8	19.5	13	16.2	3.0	4.2	300
Rochovica 380	38	50	3.2	5.4	30	8.3	4.4	3.6	389
Cherts									
Butkov M	102	63	12.3	3.0	21	14.8	3.0	9.8	36
Bralo 14	63	45	5.5	3.0	30	3.3	3.3	4.2	45
Krivá 2a	74	83	10.0	4.3	10	7.6	3.0	6.8	54
Rochovica 380	38	49	6.3	3.3	13	6.3	3.0	5.8	78

Conclusion

By studying of the cherts from Lower Cretaceous limestones, we attempted to obtain results about the origin and development of the cherts.

The biogenic origin of the silica material was confirmed by the presence of mainly radiolarian tests, and the way in which they were dissolved and replaced in the cherts in the limestone.

The presence of relict opal-CT lepispheres confirm existence of precursor (intermediate phase) of the observed microcrystalline quartz, confirms the process of recrystallization and ripening of silica in carbonate rocks. Lepispheres of the precursor opal-CT are very well identified in samples from all the Hauterivian to Barremian limestones studied. The microcrystals which form the lepispheres, also partly preserve their typical bladed morphology.

The grain size composition and quartz crystallinity index (CI) may also documented the progress or the degree of maturation of the silica mineral phases. The similarity of the properties of quartz studied in the cherts, seems to exclude more essential differences in the post-sedimentary temperature and pressure development of the rocks of equal age, in the three tectonic units we studied.

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Plate II: Figs. 1 - 6 - Krivá: 1,2 - thin section etched in HF for 20 seconds, the other broken surface etched for 10 minutes with HF. **Fig. 1** - Cavity of a calcified test, filled with recrystallized calcite. The matrix bears lepisphere textures. **Fig. 2** - Cavity of a calcified test filled with microcrystalline, needle-like to bladed crystals forming lepispheres. **Fig. 3** - Calcified radiolarian test, with only very weakly preserved textures of the test. Rhombohedral grains of calcite on the surface are quite clearly visible. The central part is evidently also filled with coarse calcite. **Fig. 4** - Fragment of a test of a calcified radiolarian in microcrystalline chert. **Fig. 5** - Cavity with clearly visible rim cement, with characteristic morphology of quartz grains and lepisphere textures. **Fig. 6** - Detailed view of the rim cement. Lepispheres are also formed by collumnar crystals of quartz. **Figs. 7 - 12** - Rochovica: all thin sections, etched for 20 seconds with concentrated HF. Matrix with easily distinguishable lepispheres and collumnar quartz crystals. **Fig. 8** - Accumulation of silicified and recrystallized nanocones. Cavity of a test filled with lepispheres formed by needle like crystals. In the upper part, a typical lepisphere, below framboidal pyrite. There were also rhombohedra of carbonate mineral in the matrix. 10. Cavity with lepispheres and etched calcite crystals. **Fig. 11** - Corroded (replaced) calcite rhombohedron in the chert matrix (surroundings) and a newly formed rhombohedron. We can see here several phases of dissolution and recrystallization. Originally the rhombohedron could have formed by growth from a calcified test of, for example, a radiolarian - a partly circular cross section of the corroded part. This was dissolved, and a new generation of calcite was precipitated from the solution. **Fig. 12** - A silicified nanocone in chert. Silicification occurred before the chert formed.

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