GEOLOGICA CARPATHICA, 46, 4, BRATISLAVA, AUGUST 1995
227 - 239

AUTHIGENIC QUARTZ CRYSTALS IN THE MESOZOIC AND PALEOGENE CARBONATE ROCKS OF THE WESTERN CARPATHIANS

MILAN MIŠÍK

Department of Geology and Paleontology, Faculty of Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovak Republic

(Manuscript received June 13, 1994; accepted in revised form March 16, 1995)

Abstract: The frequency of authigenic megaquartz in thin sections of Mesozoic carbonate rocks makes it possible to estimate the relative degree of thermal exposition of the compared tectonic units. The following groups were distinguished in the Western Carpathians: *1* - unaffected complexes (Pieninicum, Silicicum), 2 - affected by intensive diagenesis (premetamorphic stage - e.g. Krížna Nappe), *3* - anchimetamorphosed (part of Tatricum) and epimetamorphosed complexes (e.g. Borinka Unit). Dating of the origin of authigenic megaquartz was derived from its relation to compaction, cementation, lithification, dolomitization, microstylolites, veinlets and metamorphism. The regional distribution of a special authigenic quartz type with zonally arranged inclusions proceeding from an exotic source was traced in the younger sediments.

Key words: Western Carpathians, Mesozoic, Paleogene, anchimetamorphism, limestone diagenesis, authigenic quartz.

Introduction and aims

During thin-section studies of Carpathian limestones the hypothesis emerged, that the abundance of authigenic quartz crystals is proportional to the degree of thermal and dynamic effects on the investigated units. Therefore sets of thin sections were systematically evaluated with regard to the presence of authigenic quartz grains. Simultaneously the dating of their origin to various diagenetic processes was studied.

The following conditions are needed for the formation of authigenic quartz in limestones:

1 - Presence of suitable source: clastic quartz, easy destructible clay minerals like smectites, and volcanic glass.

2 - Conditions for the dissolution of the clastic minerals in one place (alkaline environment, especially evaporites might play a positive role - Grim 1962) and for silica precipitation at other, usually nearby places.

3 - Suitable structure, porosity and permeability of the host rock. Silica solutions are transported essentially through the pores, not through the cracks. The fact that the abundance of idiomorphous authigenic quartz crystals are not dependent on the vicinity of veinlets is evidence of this (rare cases of authigenic quartz in the calcite veinlets will be quoted later).

The authigenic origin of quartz is usually shown by cutting of allochems or cement aggregates, calcite or anhydrite inclusions, euhedral shape, absence of cathodoluminiscence (Molenaar & de Jong 1987 and others).

This contribution is partly connected with another one concerned with the selective silicification of calcite bioclasts by microquartz (Mišík 1995) where some general processes of diagenetic silicification were described; they will not be repeated here.

Results of thin-section studies of authigenic quartz

Amount of inclusions. The crystals grow preferentially in micrite; in that case, they are filled by inclusions. However they are clear if they grow at the expense of sparite (Pl. I: Fig. 2). Tiny calcite inclusions are usually concentrated in the central part of crystals and the peripheral parts are clearer because during the last growth stage the impurities were pushed out similarly as in authigenic feldspars. Calcite inclusions sometimes show zonal arrangement which may reflect the oscillation in the concentration of solutions (Pl. I: Figs. 3, 4).

Syntaxial overgrowths. The majority of auhigenic quartz crystals do not display a core, but overgrowths on the clastic quartz grains are relatively frequent (Pl. I: Figs. 5, 7). Syntaxial overgrowths use to possess at least partly euhedral outlines. Syntaxial rims grown under the conditions of anchimetamorphism exhibit xenomorphous outlines (Pl. IV: Fig. 2). Clastic quartz grains forming the core of ooids can grow at the expense of cortex. Phantoms of concentric layers in the crystal are visible due to tiny calcite inclusions (Pl. I: Fig. 6). Prismatic planes are always significant; the fission of less perfect rhombic terminations was observed (Pl. I: Figs. 6, 7). Syntaxial overgrowths were also found within the Orbitolina tests agglutinated partly from the quartz silt (Mišík et al. 1981, p. 33). Clastic quartz in contact with bioclasts can grow preferentially into them (Mišík 1995; Pl. I: Figs. 4, 5).

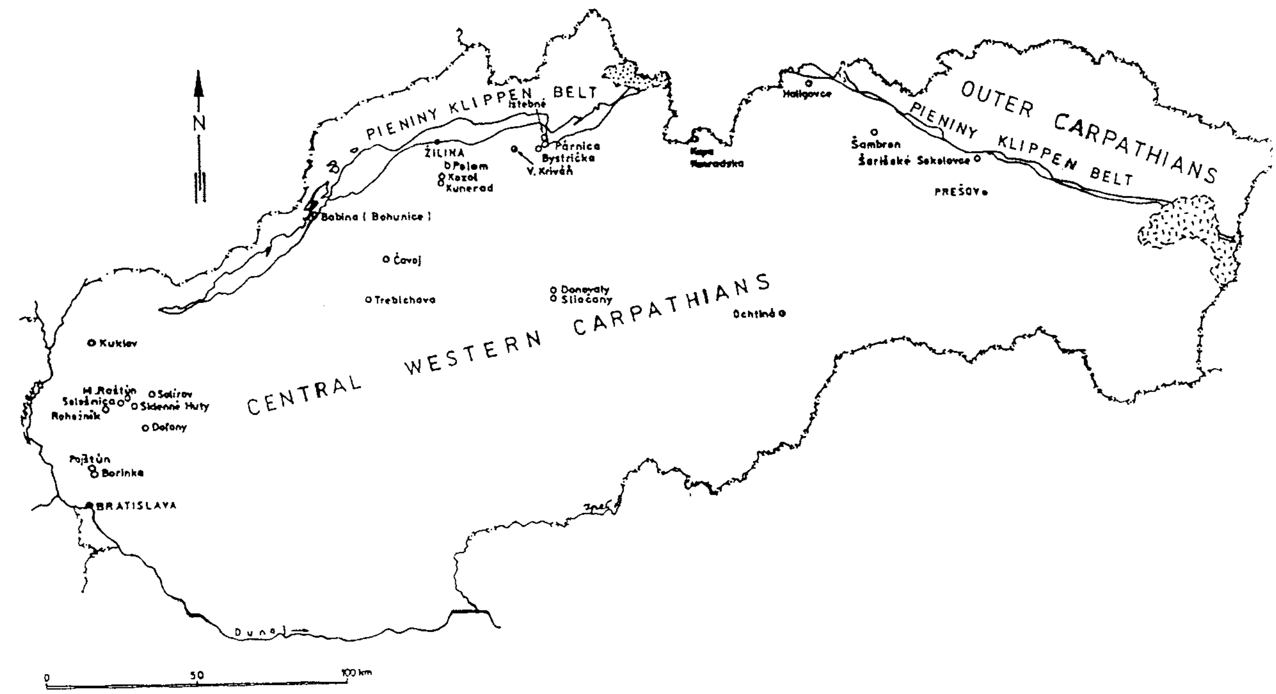


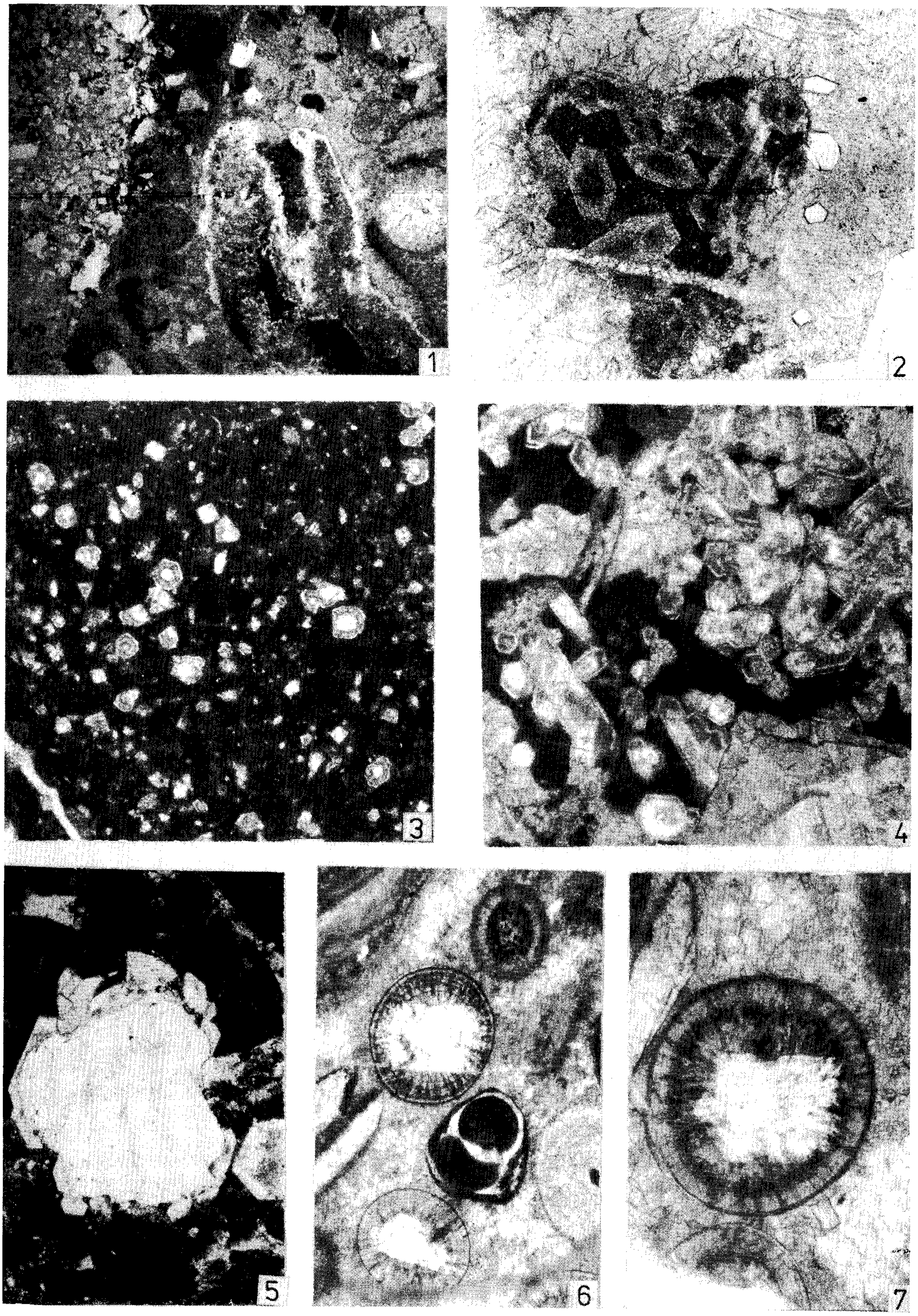
Fig. 1. Situation of localities with authigenic quartz mentioned in the text (occurrences of redeposited authigenic quartz with zonally arranged inclusions are at the Fig. 2).

Selective replacement of biodetritus by megaquartz. In a large majority of cases the silica replacing calcitic bioclasts is represented by microquartz (quartzine-lutecite). Very rarely (e.g. in Reifling Limestone) the replacement of foraminifers and ostracods by an optical individual of authigenic quartz was observed. We mentioned authomorphic quartz crystals in nummulites and coralline algae in another paper (Mišík 1995, Pl. I: Figs. 2, 3). In contrast to the early diagenetic silicification of bioclasts by quartzine-lutecite, the growth of quartz crystals in the mentioned fossils took place during late diagenesis, in the pre-metamorphic conditions (see later). Besides bioclasts the cortex of calcitic ooids can also be selectively replaced by comparable authigenic megaquartz (Pl. IV: Figs. 3-7) which will be described further.

Habitus of crystals. It is noteworthy that no interpenetration of authigenic quartz crystals was ever observed in Western Carpathian limestones. The crystal habitus was influenced by the concentration of solution. According to Konta (1954) more elongated (crystals) were formed from less concentrated solutions. The most frequent relation of lenght and width in columnar crystals is about 1 : 3. Turan & Vavro (1970) also mentioned rare pseudocubic crystals with preferential development of rhombic planes from the slightly metamorphosed Borinka Limestone (temperatures of 250–300 °C, Plašienka et al. 1993). According to McBride & Folk (1977) pseudocubic quartz is usually formed in connection with evaporites. Turan & Vavro (1970, p.170) accepted the opinion of other authors claiming that the pseudocubic quartz originated in conditions of somewhat higher themperature; they found it in places more strongly affected by metamorphism. A skeletal growth with the fission of xenomorphic quartz crystals was observed in the Middle Triassic limestones of the Göller Nappe in the borehole Kuklov-4 (Pl. II: Figs. 1, 2 and Fig. 2).

Youngest limestones with authigenic quartz crystals. The youngest authigenic euhedral quartz crystals were found in Eocene limestones from pebbles of the Šambron Zone spread along the inner border of the Pieniny Klippen Belt (Fig. 2). The Šambron Zone displays signs of the pre-metamorphic stage.

Plate I: Fig. 1 - Authigenic anhedral quartz with clear peripheral part was formed only in the neighbourhood of a tuffite clast - acid volcanic rock (local source of silica). Crinoidal limestone with admixture of clastic quartz, Bajocian, Czorsztyn Succession, Pieniny Klippen Belt. Quarry Babina, ×20. **Fig. 2** - Group of euhedral crystals of authigenic quartz; those crystallized on the micritic substratum are filled with calcite inclusions, especially in their central parts, those formed on sparite are clear. Triassic Wetterstein Limestone, a pebble from the Albian Ludrová Conglomerate, Malá Magura Succession of Tatricum, Čavoj, Strážovské Vrchy Mts., thin section No. 10662, ×48. **Fig. 3** - Zonal authigenic quartz in the Upper Triassic micrite; pebble from the Albian conglomerates, Drietoma Succession, Pieniny Klippen Belt, Bošáca, thin section No. 10470, ×48. **Fig. 4** - Group of zonal authigenic quartz crystals in the Barremian-Aptian limestone; pebble from the Albian conglomerates, Malá Magura Succession of Tatricum, Čavoj, Strážovské Vrchy Mts., thin section No. 10580, ×30. **Fig. 5** - Euhedral syntaxial overgrowths on the clastic quartz core; Těšín Limestone, Berriasian-Valanginian of the Flysch Belt, Goleszów, Poland, thin section No. 13932, ×43. **Fig. 6** - Authigenic quartz syntaxially overgrowing the clastic core; prismatic planes are expressive, a fission of rhombohedric termination during the growth may be observed. Rhaetian limestone of the Krížna Nappe, Kunerád, Malá Fatra Mts., ×31. **Fig. 7** - As previous, ×61.


1
2
3
4
5
6
7

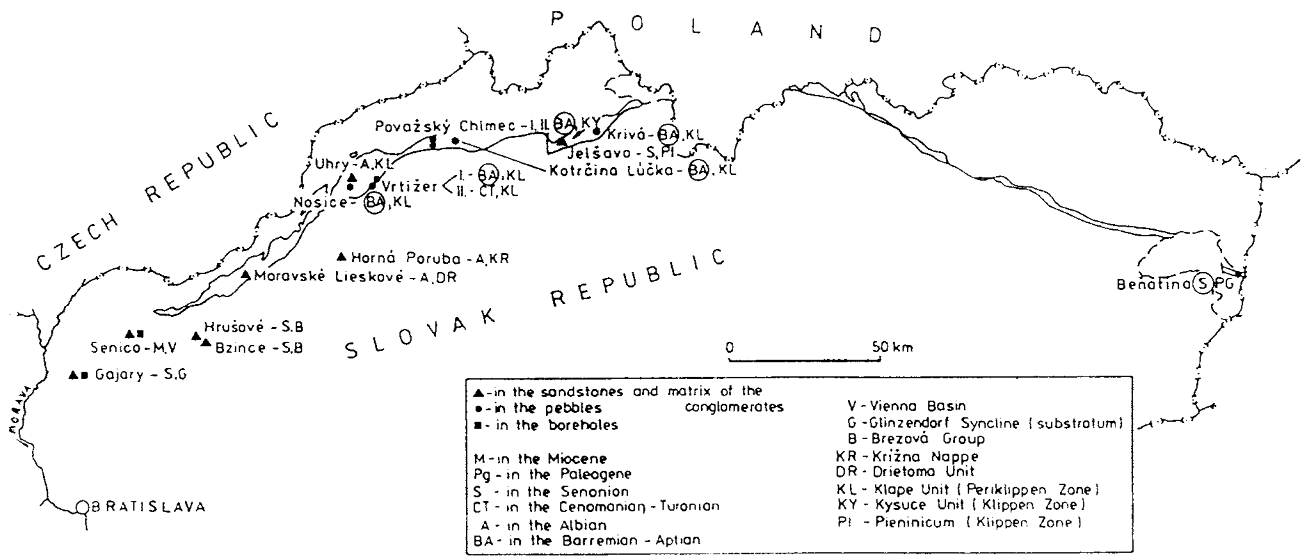


Fig. 2. Localities containing the redeposited authigenic quartz with zonally arranged micaceous inclusions derived from the Pieniny Exotic Ridge, from the inner margin of the Pieniny Klippen Belt.

The youngest authigenic feldspars in the Western Carpathians were also found in that zone, in a Páleocene limestone with *Glomalveolina* near Ježovka by Haligovce (Fig. 2; Mišík 1994a). In the Neogene marine limestones of Slovakia authigenic megaquartz is completely missing; it is also absent in the fresh-water Tertiary and Quaternary limestones.

Relationship between the intensity of diagenesis (initial metamorphism) of carbonate complexes and the frequency of authigenic quartz crystals

Several authors called attention to the correlation between the initial metamorphism and the frequency of authigenic quartz and feldspars (more in Mišík 1994a). However it is necessary to compare equal lithotypes (lithofacies) of different tectonic units, because the formation of authigenic quartz is influenced not only by factors such as temperature, pressure and time factors, but its frequency also depends on the chemical composition of solutions (especially evaporitic ones - Grim 1962; Fabricius 1984) and on the quantity and quality of the clastic admixture.

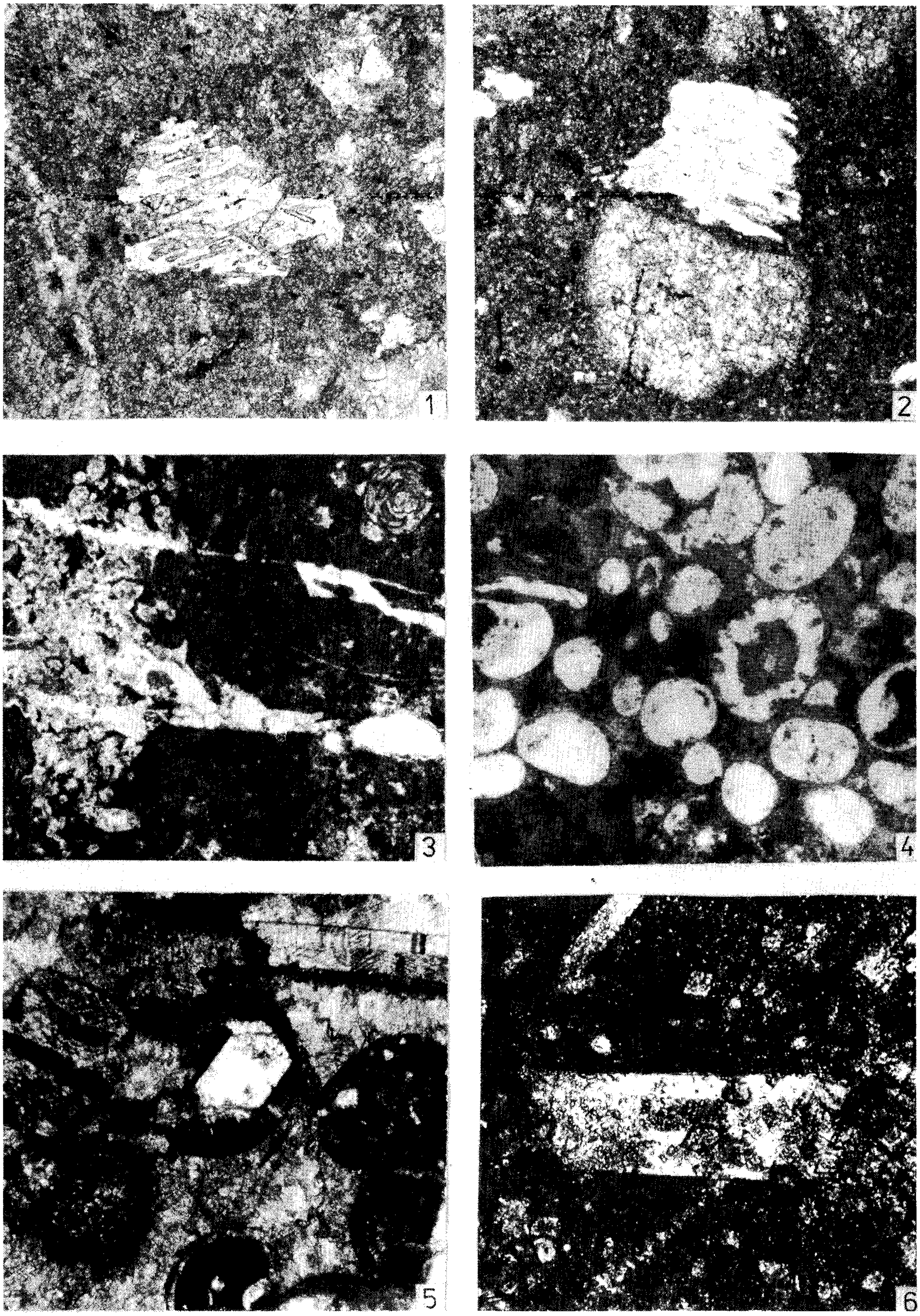
The frequency of authigenic quartz in carbonate rocks (thin sections from 1098 samples - Tab. 1) enable us to identify a degree of thermal effects on certain complexes which still cannot be defined as anchimetamorphism. We suggest distinguishing three stages:

1 - Non-affected complexes (in the Western Carpathians e.g. Pieninicum, Silicicum, post-tectonic Paleogene, Neogene; Jurassic limestones of the platform cover in the Alpine and Carpathian foreland). 2 - Pre-metamorphic stage (e.g. Križna Nappe). 3 - Anchimetamorphic to epimetamorphic stage (e.g. Donovaly Succession of the Tatricum, Borinka Unit in the Malé Karpaty Mts.).

The present author tried to obtain some preliminary results by comparing the frequencies of authigenic quartz and feldspars in the thin sections of comparable limestone types. The effects observable on echinoderm plates can provide another auxiliary criterion: 1 - echinoderm plates without twinning lamellae or with rare thick twins (non-affected complexes), 2 - all plates contain dense thin twilling lamellae (pre-metamorphic stage), 3 - twins are bent or disintegrated up to total loss of homogeneous optic orientation of plate (pre-metamorphic to anchimetamorphic stage). According to Ferril (1991), at temperatures below 150–170 °C the intensity (number of twins per mm) grows with temperature; between 150–200 °C the transition from thin to thick lamellae takes place. Further indicators are transformation of orthomicrite into pseudosparite, the origin of metamorphic foliation, reflectance of vitrinite, colour alternation index (CAI) of conodonts and pollen grains. The most promising samples will be investigated by means of gas-liquid inclusions, oxygen isotopes and illite crystallinity to precisely determine the temperatures of quartz formation.

The quantity of authigenic quartz could be evaluated from insoluble residues or from thin sections. It is obvious that the authigenic quartz can be lacking in a random thin section and at the same time present in the insoluble residue from the same sample. The plate of rock used for a thin section has a very small volume about 20 × 20 × 0.005 mm, meanwhile the volume of

Plate II: Fig. 1 - Authigenic anhedral quartz with skeletal growth and elongated inclusions. Middle Triassic limestone, Göller Nappe, basement of the Vienna Basin, borehole Kuklov-4, 3730-3731 m, ×95. **Fig. 2** - As Fig. 1. **Fig. 3** - Cluster of authigenic quartz grains in a Triassic dolomite with *Glomospirella* sp.; Križna Nappe, Lysica digitation, Istebná Valley, Malá Fatra Mts., ×40. **Fig. 4** - Selective silicification of ooids in the Middle Triassic limestone of Veterník Nappe, Mt. Malý Roštún (Vápenná), Sološnica, Malé Karpaty Mts., thin section No. 2621, ×26. **Fig. 5** - Authigenic euhedral quartz was formed at the same time as the microstylolite which stopped its growth. Rhaetian fine-grained coquina limestone with ooids, Križna Nappe. Rybná Dolina Valey near Rajec, Malá Fatra Mts., ×43. **Fig. 6** - Columnar authigenic quartz closing a dolomite rhomb shows that the dispersed dolomitization was older than the crystallization of authigenic quartz. Gutenstein Limestone, Anisian; a pebble from Paleogene Šambron Conglomerate, Šarišské Sokolovce, thin section No. 1236, ×210.


1
2
3
4
5
6

a cube of rock with the edge of 20 mm used for the extraction of insoluble residue is 4000× larger and the probability of catching the authigenic quartz (if any) is much higher. For the comparison purposes it is sufficient to evaluate only the presence or absence of authigenic quartz in a set of thin sections from a certain lithotype (lithostratigraphical unit). Limestones with an approximately similar composition of bioclasts and share of clastic quartz were compared.

The frequencies of authigenic feldspars were compared in another place (Mišík 1994a). Supplementary data concerning the same sets of lithostratigraphic units for authigenic megaquartz are quoted in the following Tab. 1 (the number of thin sections studied is in the denominator, the number of those with authigenic quartz in the numerator; the frequency in %).

Table 1: Frequencies of authigenic quartz in thin sections.

Jurassic limestones of the Krížna Nappe from Veľká Fatra Mts. and Nízke Tatry Mts.	88/196 = 45%
Jurassic limestones of the Tatricum Donovaly Succession (Nízke Tatry Mts.)	12/14 = 86%
Liassic limestones of the Nižná Succession, Pieniny Klippen Belt	0/25 = 0%
Jurassic limestones of the Czorsztyn Succession, Pieniny Klippen Belt	1/216 = 0.5%
Jurassic limestones of the Kostelec Succession, Pieniny Klippen Belt	0/52 = 0%
Pebbles of Barremian-Aptian limestones from the Albian Ludrová Conglomerate, Central Western Carpathians	16/50 = 30.2%
Pebbles of Barremian-Aptian limestones from the "Upohlav" Conglomerate, Klippen and Peri-Klippen Belt	14/152 = 9.25%
Oxfordian-Berriasian limestones of Krížna Nappe, Malé Karpaty Mts.(Borza & Michalík 1987, Figs. 8,11,12)	50/102 = 49%
Jurassic-Lower Cretaceous limestones of the Manín Unit (Borza & Michalík 1987, Fig. 2).	2/59 = 3%
Norian Hallstatt Limestone, Silicicum	1/25 = 4%
Upper Jurassic Barmstein limestones with shallow-water biodetritus, Čachtické Karpaty Mts. (equivalent to Silicicum)	0/96 = 0%
Pebbles of Upper Jurassic limestones with shallow-water biodetritus, proceeding from the Silicicum, in the Senonian and Egerian conglomerates	1/60 = 0%
Senonian fresh-water post-tectonic limestones	0/44 = 0%

The comparison of the frequencies of authigenic megaquartz in the thin sections gives a clear result: Jurassic limestones of the Klippen Belt (Pieninicum) and Silicicum were not thermally affected in contrast to those of the Krížna Nappe and Tatricum which reflect a pre-metamorphic stage, and some of Tatric successions (e.g. Donovaly Succession) which are even anchimetamorphosed. The Manín Unit is almost unaffected in contrast to the Krížna Nappe. In the post-tectonic (Upper Cretaceous and Cenozoic) limestones of the Central Western Carpathians authigenic megaquartz is entirely missing.

A comparison with the Jurassic limestones of the platform cover in the foreland and beneath the Carpathian foredeep would be interesting. No occurrences of authigenic quartz were quoted from the surface (from the outcrops), but from the deeply buried Jurassic limestones under the foredeep in Moravia (SE slopes of the Czech Massif) Řehánek (1977) quoted euhedral crystals of authigenic quartz up to 0.3 mm long (borehole Němčičky-2, depth 2038 m) from the Kurdějov Limestone.

The differences cannot be explain by the lack of silica source, since the Lower and Middle Jurassic crinoidal limestones of Pieniny Klippen Belt contain approximately the same amount of clastic quartz as Jurassic crinoidal limestones of the Central Carpathian units. It is interesting that the unique case of authigenic megaquartz found among 206 thin sections of Jurassic limestones of the Czorsztyn Unit, is formed by xenomorphic grains in the immediate vicinity of a clast of acid tuffite (Pl. I: Fig. 1) which served as an anomalous silica source.

In the Middle Triassic limestones and dolomites of the Tatricum and Krížna Nappe clastic quartz is almost entirely missing. However it is noteworthy that in spite of the absence of an obvious silica source (the limestones also lack sponge spicules) authigenic quartz does occur (Pl. II: Fig. 3). Single grains of authigenic quartz occurred in the Anisian Gutenstein Limestone in 30 % of thin sections (in only 6 % they possess euhedral form). From the 110 samples of Triassic dolomites (Keuper dolomites not included) authigenic quartz was present in 16 % of the thin sections (euhedral crystals in 6 % – Mišík 1972). Silica spherulites ("Hornsteinkugelchen") in Triassic carbonate rocks which probably originated by the replacement of evaporitic minerals, will be treated in an other place.

Plate III: Fig. 1 - Authigenic euhedral quartz is younger than the calcite veinlet; Ladinian Reifling Limestone of the Choč Nappe; Hradkovo, Choč Mts., thin section No. 2380, ×136. **Fig. 2** - Authigenic quartz is younger than veinlet and small normal faults disturbing it. Anisian Gutenstein Limestone, Tatricum. Quarry near Párnica, Malá Fatra Mts., thin section No. 2233, ×55. **Fig. 3** - Dashed veinlet in dolomite (formed by the coalescence of a swarm of subparallel shear veinlets) partly replaced by authigenic anhedral quartz (left) with phantoms - relicts of dashed structure. Triassic dolomite, a pebble from the Albian Ludrová Conglomerate, Tatricum, Malá Magura Succession, Čavoj, Strážovské Vrchy Mts., thin section No. 2356, ×95. **Fig. 4** - Columnar authigenic quartz in the Anisian Gutenstein Limestone torn to pieces by the extension during the Upper Cretaceous or Tertiary; Tatricum, Mt. Kopa Kondratska, Western Tatra Mts., ×136. **Fig. 5** - Calcite shear veinlet partially replaced by authigenic quartz (white) with relicts of dashed structure formed by calcitic inclusions (a similar object as at the Fig. 3). Dolomites of the Upper Visean-Lower Namurian of Gemericum; abandoned magnesite quarry, Ochtiná, thin section No. 18423, ×30. **Fig. 6** - Columns of authigenic quartz oriented in the plane of foliation, synchronous with the slight metamorphism of the Upper Cretaceous or Tertiary age. Anisian Gutenstein Limestone, Tatricum, Mt. Kozol, Malá Fatra Mts., thin section No. 1076, ×46.

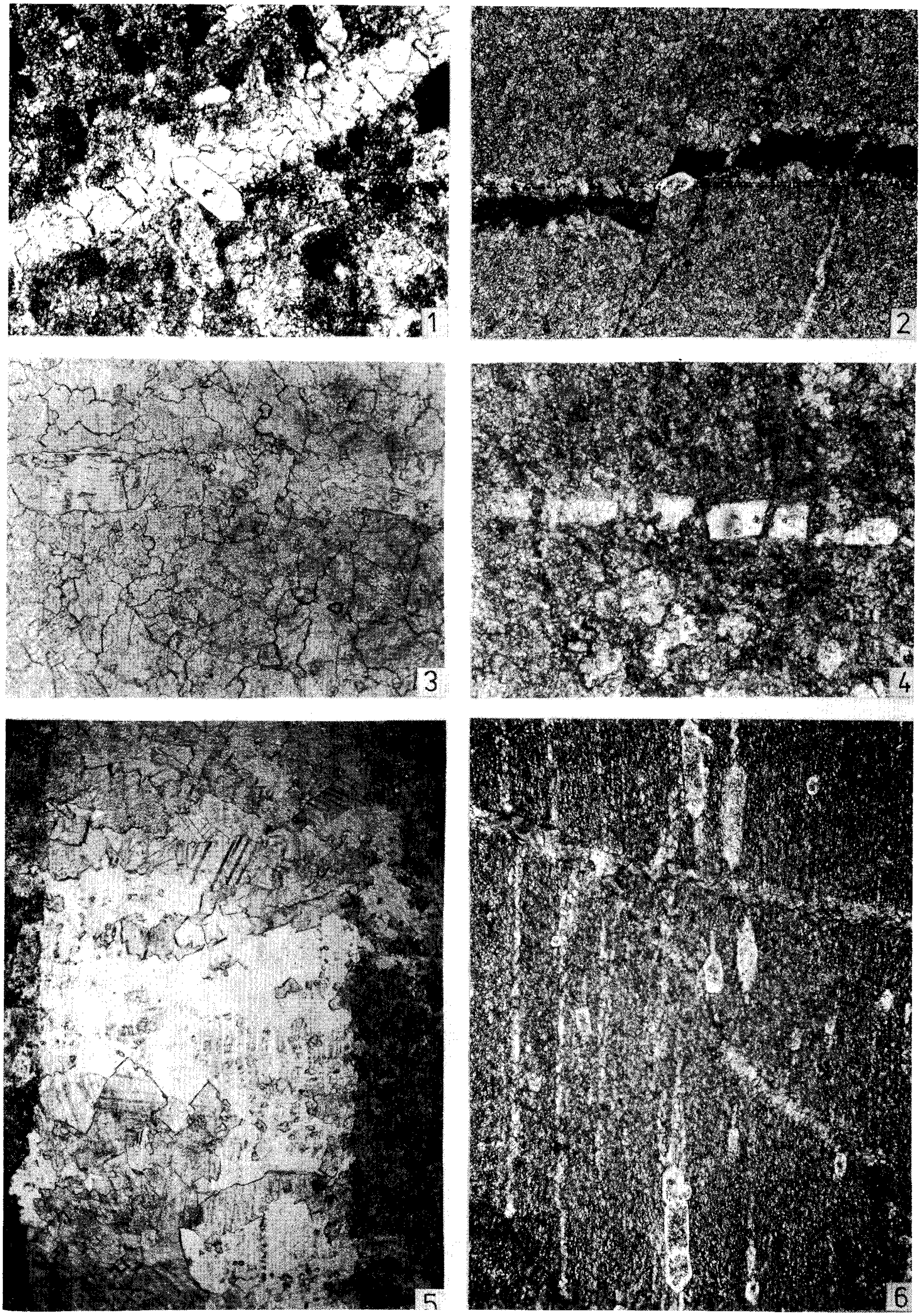
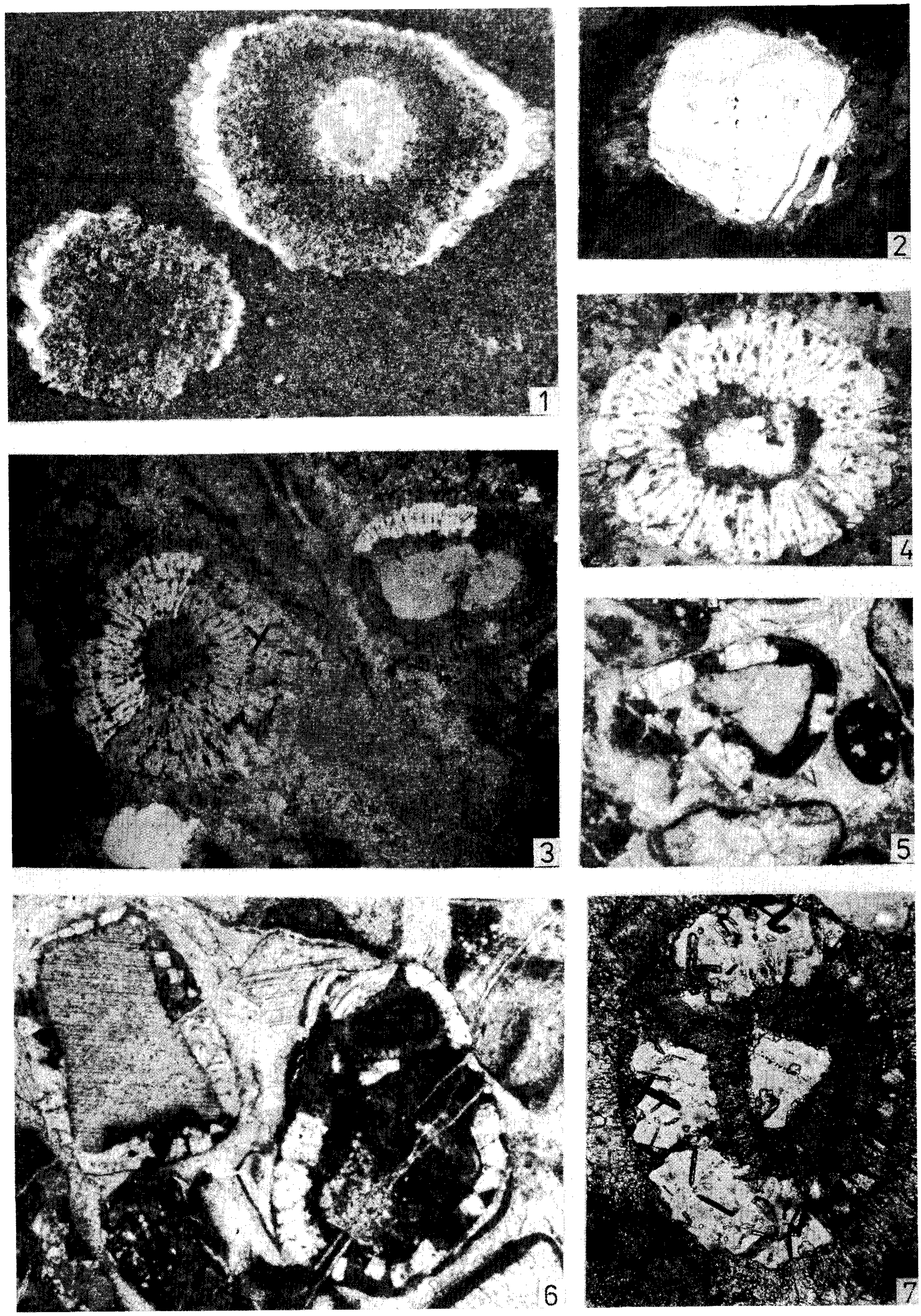

1
2
3
4
5
6

PLATE IV



Authigenic quartz was found surprisingly also in the very "pure" Ladinian Wetterstein Limestone (at the locality Trebichava crystals up to 0.4 × 0.13 mm filled by calcite inclusions). Mello (1975, Figs. 3-6) quoted them from the Wetterstein Limestone of the Silica Nappe, (Slovak Karst) as very rare. More than a hundred thin sections from the Wetterstein Limestone of the Silicicum from the Malé Karpaty Mts. (Rohožník area) were checked and none of them contained quartz. A pebble of Wetterstein Limestone from the Albian Ludrová Conglomerate of the Tatricum, from the Malé Karpaty Mts. does contain authigenic quartz crystals (Pl. I: Fig. 4), but they are thought to have originated already in the conglomerate which bears distinct signs of initial metamorphism (Mišík et al. 1981).

Dating of authigenic megaquartz in relation to other diagenetic processes and metamorphism

The following cases were observed:

Compaction. The crystals of authigenic quartz are younger than the compactional break-down of shells (Mišík 1995; Pl. I: Fig. 6).

Cementation. The authigenic quartz crystals are younger than the second generation of calcite cement (Pl. I: Fig. 2).

Lithification. Authigenic megaquartz was always formed after the lithification.

Dolomitization. In a huge majority of cases dolomitization preceded the formation of authigenic quartz which usually forms anhedral grains between dolomite rhombs. Authigenic quartz in dolomites contains tiny dolomite inclusions. A small dolomite rhomb was observed in an authigenic quartz within the slightly dolomitized Gutenstein Limestone (Pl. II: Fig. 6). The central parts of voids after the dissolved gypsum microconcretions ("birdseyes") filled by drusy dolomite used to be sealed by a mosaic of quartz grains representing the youngest filling.

Microstylolites. A case of roughly contemporaneous growth of quartz with the formation of a microstylolite was ascertained (Pl. II: Fig. 5). The course of the microstylolite was accommodated to the obstacle represented by the quartz crystal whose growth continued on the other termination until it was stopped by impermeable membrane.

Veinlets. *a* - The majority of calcitic or dolomitic veinlets are younger than the authigenic quartz, but the direct evidence, authigenic megaquartz disturbed by a veinlet, did not occur in our thin sections.

b - Authigenic quartz of microscopic size was observed several times within the calcite veinlets in the Neocomian limestones. Macroscopic quartz crystals in the calcitic veinlets (approximately synchronous filling of a crack) are very rare in the Mesozoic limestones of the Western Carpathians. They occur at the following localities (Fig.1): 1 - Liassic carbonate breccia of the Borinka Succession, Malé Karpaty Mts., near the castle of Pajštún (Turan & Vavro 1970). Euhedral crystals of 1-3 cm size are not rare. The authors estimated the temperatures of origin of quartz crystals about the 100 °C according to the decrepitation analyses. For the purpose of comparison the well-known "Maramuresh diamonds" - clear quartz crystals found in the calcite veinlets penetrating the Paleogene sandstones of the Flysch Belt in Eastern Slovakia and Transcarpathian Ukraine should be mentioned. According to Matkovskiy (1961) they were formed at a minimum temperature of 155 °-185 °C, or according to Hurai et al. (1989) at 140 °-160 °C and 50-100 MPa. Further localities are: 2 - Liassic limestones of the Vysoká Succession, Majdán near Sklenné Huty, Malé Karpaty Mts., 3 - Liassic limestones of the Orešany Succession, Tatricum, quarry NW from Doľany, Malé Karpaty Mts. The anhedral quartz grains (up to 1.5 cm) are younger than the calcite; they were precipitated into the spaces between the calcite crystals. They did not replace the calcite, and did not contain any calcitic inclusions. 4 - In a calcite vein which penetrated the Middle Liassic limestones with phosphatic clasts (Križná Nappe, 300 m W from the elevation point 937.1 in the Bystrička Valley, Malá Fatra Mts.) clear euhedral quartz crystals up to 7 mm were found. It is peculiar that all macroscopic quartz crystals in the calcite veins from the Central Western Carpathians proceeded from the Liassic carbonate rocks.

c - The younger age of the authigenic quartz compared to the calcitic or dolomitic veinlets is shown if a euhedral quartz crystal penetrated from the host rock into the veinlet (Pl. III: Fig. 1); in one case it traversed even a microscopic normal fault (Pl. III: Fig. 2).

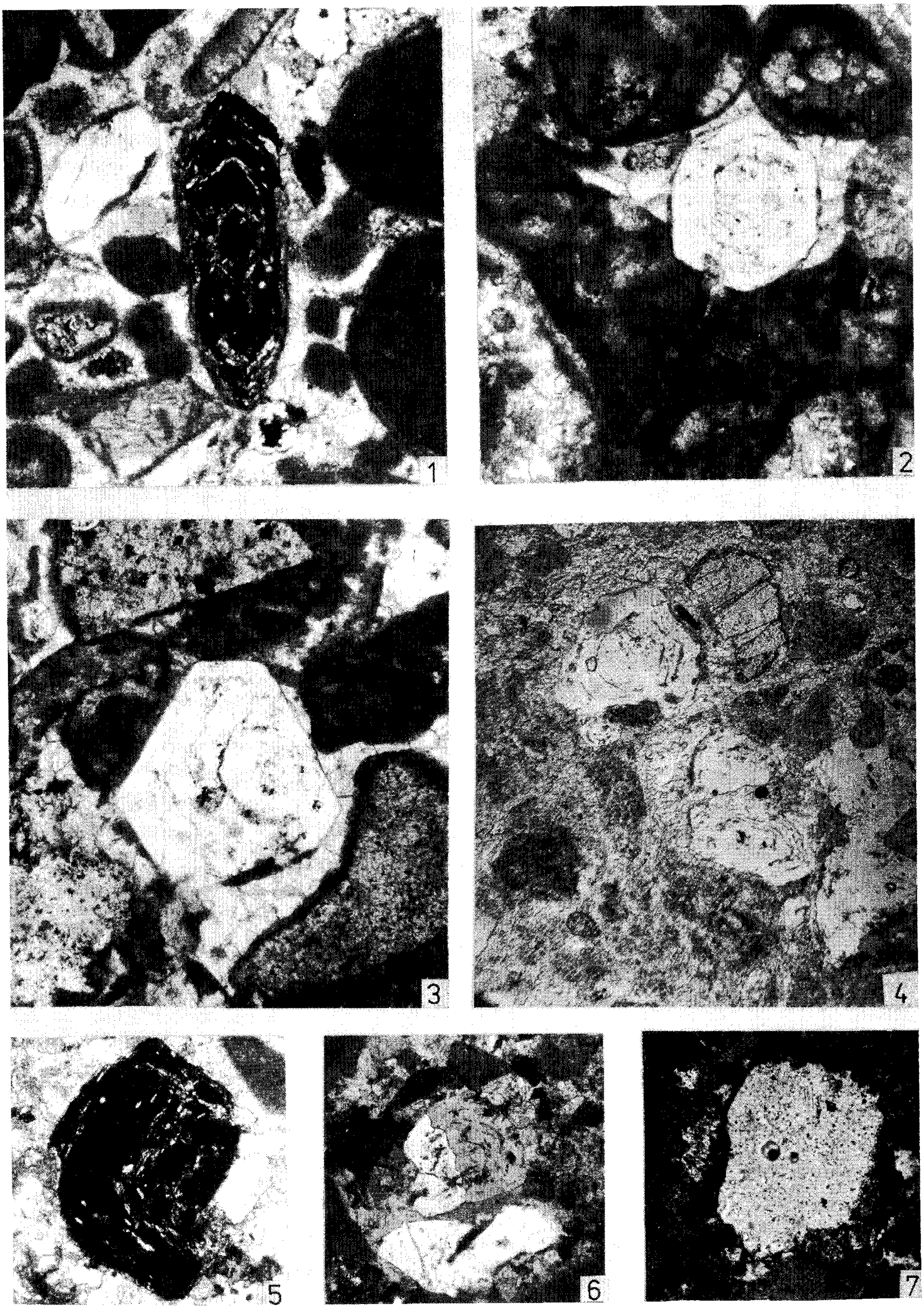
If calcite veinlets in the siliceous limestones were older than the migration of silica during the pre-metamorphic stage, a thin fibrous rim of the microquartz was formed along them. The calcite filling of veinlets is partly replaced by silica. This type of veinlet makes it possible to recognize siliceous limestones in the thin sections even in cases where the fine dispersed silica admixture could be overlooked.

If the limestone is affected by a slight metamorphism, the authigenic megaquartz can completely replace a section of the veinlet and preserve the phantoms of so-called dashed veinlets (Mišík 1971). Such veinlets originated according to Ramsay (1980) by the "crack-and-seal" mechanism. The rows of tiny carbonate inclusions betray the original thin subparallel shear veinlets. Such relicts completely disappeared from the other parts of a veinlet with later recrystallized dolomitic filling (Pl. III: Figs. 3, 5).

Metamorphism and pressure phenomena. Opal-A as well as opal-CT cannot be formed during metamorphism. Such a

Plate IV: Authigenic quartz formed during the incipient metamorphism. **Fig. 1** - Small spheroidal cherts ("Hornsteinkugelchen" - originally spherolites) elongated by the extension during a slight metamorphism; "fringing cement" from calcite and microquartz (white) was formed in the pressure shadows. Micritic limestone, Triassic, Borinka Unit; W from the Pajštún castle ruin, Borinka, Malé Karpaty Mts., thin section No. 17878, ×30. **Fig. 2** - Syntaxial overgrowth on the clastic quartz grain originated during the slight metamorphism; the narrow authigenic anhedral rim is filled by calcite inclusions, a fibrous calcite aggregate ("beard") was formed in the pressure shadows. Barremian-Aptian limestone of Tatricum, Solírov, Malé Karpaty Mts., thin section No. 20464, ×25, polarized light. **Fig. 3** - Selective replacement of calcite ooid cortex by authigenic quartz during a slight metamorphism; Lower Liassic limestone of Donovaly Succession, Sliačany, Nízke Tatry Mts., ×55, polarized light. **Fig. 4** - The same; authigenic quartz overgrown the clastic quartz core of an ooid, ×61. **Fig. 5** - Cortex of an ooid partially replaced by the authigenic quartz; Barremian-Aptian limestone, pebble in the Albian Ludrová Conglomerate, Tatricum (slight pre-metamorphic affection), Malá Magura Succession, Čavoj, Strážovské Vrchy Mts., thin section No. 11880, ×42. **Fig. 6** - The same; phantoms of the concentric structure of ooids can be locally seen in the authigenic quartz grains. **Fig. 7** - As Figs. 3, 4; Slightly pleochroic micaceous minerals (chlorite? biotite?) were formed only in the authigenic quartz during the metamorphosis; they lack in the neighboring limestone; ×136.

PLATE V



process of silica "rejuvenation" in carbonate rocks could be initiated only by thermal solutions produced by post-volcanic activity or by the solutions accompanying climatic silicification (silcretes). Initial metamorphism intensified the dissolution of megaquartz, microquartz, or other minerals containing SiO_2. The silica migrates in very diluted ionic solutions and new aggregates of SiO_2 can be precipitated as fine-grained microquartz or as megaquartz crystals.

A rare case of authigenic quartz formed before the tectonic pressure was observed at the locality Kopa Kondratska, Tatry Mts. (Fig. 1; Pl. III: Fig. 4); a columnar crystal in limestone was torn to pieces by the extension. In rare cases the formation of quartz crystals can be synchronous with the metamorphic foliation and columnar crystals are oriented in the foliation plane (Pl. III: Fig. 6).

Mostly anhedral isometric quartz grains originated during metamorphism. Their calcite inclusions are somewhat larger than the inclusions in authigenic quartz from unmetamorphosed limestones. The fact is considered as evidence that such authigenic quartz was formed after the incipient recrystallization of limestone (examples: Mišík in Marschalko et al. 1976, p. 48, 49; Mišík & Sýkora 1981, p. 16, 17). The syntaxial rims which overgrew the clastic quartz in the anchimetamorphosed limestones of the Solírov Succession (Tatricum of Malé Karpaty Mts.) also possess xenomorphic outlines (Fig. 1; Pl. IV: Fig. 2). In the Borinka Limestone displaying metamorphic lamination authigenic quartz, is concentrated in the lighter laminae.

The anhedral grains of authigenic quartz replacing parts of the veinlets in anchimetamorphosed limestones and dolomites (Pl. III: Figs. 3, 5) are also post-metamorphic.

Quartz spherulites ("Hornsteinkugelchen") in clasts of Triassic limestones from the breccias of Liassic Borinka Formation sometimes possess new-formed "beards" of fibrous SiO_2, comparable to pressure shadows (Pl. IV: Fig. 1). Quartz spherulites will be treated in an other paper (Mišík in prep.). We suppose that quartz spherulites originated from an early diagenetic replacement of gypsum in the Triassic and their "beards" during the metamorphism in the Middle Cretaceous (the temperatures of metamorphism in the Borinka Unit were estimated at 250-300 °C - Plašienka et al. 1993).

The selective replacement of calcite ooids by the authigenic quartz during the anchimetamorphism was observed in the Liassic limestones of the Donovaly Succession (Tatricum, Nízke Tatry Mts., Fig. 1). The cortex of ooids was replaced by 1-3 optic individuals of authigenic quartz containing newly-formed mica minerals (Pl. IV: Figs. 3, 4, 7). Silica penetrated into the ooids along their radial structure. The calcite cores of ooids and the calcitic matrix were not touched by replacement. If the ooid possessed a core of clastic quartz, then the syntaxial overgrowth on the core replaced the cortex and resulted in an optic individual of quartz displaying an ooid form (Pl. IV: Fig. 3). The same type of replacement was found in rare ooids within a pebble from Albian Ludrová Conglomerate (Tatricum), bearing signs of the pre-metamorphic stage (Pl. IV: Figs. 5, 6). As far as I know such a kind of ooid silicification was not described up to now; in all other cases of silicification ooids were replaced by microquartz-chalcedony s.l. (six authors were quoted by Mišík 1963, p. 297). The silicification of ooids by microquartz was also found rarely in the Western Carpathians Triassic limestones at the localities Malý Roštún (Vápenná, Malé Karpaty Mts., Fig. 1; Pl. II: Fig. 4) and in the quarry Polom near Žilina.

Redeposited authigenic quartz with zonally arranged inclusions of micaceous minerals

This typomorphic terrigenous component occurs in the Western Carpathian sedimentary rocks starting from the Barremian-Aptian. They were identified in the pebbles of Barremian-Aptian limestones from the "Upohlav" Conglomerate (Mišík & Sýkora 1981) at the following localities (Fig. 2): Považský Chlmec - Vranie, Považský Chlmec - lom, Kotrčina Lúčka (Pl. V: Fig. 1 - all three localities belong to the Coniacian conglomerates of the Kysuca Succession); Nosice-I - Albian conglomerates, Krivábase - conglomerates of Cenomanian-Turonian, Vrtižer-Chrasť - Senonian conglomerates (all three occurrences in the Klape Succession); clasts of carbonate sandstone and microconglomerates of the Middle Cretaceous: Vrtižer-roadcut; conglomerates of Cenomanian-Turonian: Vrtižer-Chrasť and Teplička n/V. - Senonian conglomerates (all cases from the Klape Succession). Albian sandstones from the Krížna Nappe - Horná Poruba, Strážovské Vrchy Mts. (Jablonský 1978, Pl. II: Fig. 1); Albian sandstones of Drietoma Succession - Moravské Lieskové, Albian sandstones of Klape Succession - quarry Uhry, Senonian sandstones of Jarmuta Fm., Pieniny Klippen Belt - Jelšava, Orava (these three localities were ascertained by J. Jablonský); pebble of Upper Campanian - Lower Maastrichtian limestone in the Paleocene Proč Conglomerate of the Pieniny Klippen Belt - Beňatina-II (Mišík et al. 1991, p. 45), pebble of Aptian limestone of the Senonian Valchov Conglomerate of the Brezová Group - Bzince - Rubaninské (Pl. IV: Figs. 2, 3; Mišík 1991, p. 23); a clast in the carbonate Middle Cretaceous microbreccia in the same lithostratigraphic member - Hrušové (Pl. V: Figs. 5, 6; l.c. p. 25-26). Senonian sandstones of Glinzendorf Syncline (the basement of the Slovak part of Vienna Basin), borehole Gajary Ga-125, core No. 11 (Mišík 1994b, Pl. II: Figs. 6, 7). Lower Miocene microbreccias of Vienna Basin, borehole Senica-2, core No. 2.

Plate V: Redeposited authigenic quartz. **Fig. 1** - Redeposited authigenic quartz with zonally arranged inclusions, mostly illite flakes; Barremian-Aptian limestone, a pebble from the Lower Senonian "Upohlav" Conglomerate, Kysuca Succession, Pieniny Klippen Belt, Kotrčina Lúčka near Žilina; thin section No. 9592, ×60. **Fig. 2** - The same in the Aptian limestone, pebble from the Campanian Valchov Conglomerate, Bzince-Rubaninské, Čachtické Karpaty Mts., thin section No. 14560, ×95. **Fig. 3** - The same, thin section No. 18147, ×80. **Fig. 4** - Authigenic quartz with zonally arranged inclusions in an anhydritic rock with accessory carbonate grains and claystone fragments. This photography is reproduce for the comparison with the analogic but redeposited quartz grains at the Figs. 1, 2, 3, 5, 6. Lower Triassic, Biele Vody near Mlynky, northern part of the Spišsko-Gemerské Rudohorie Mts., borehole SB-12, 25 m, ×160. **Fig. 5** - Redeposited authigenic quartz with zonally arranged flaky inclusions; pebble of a Middle Cretaceous (?) fine-grained carbonate breccia in the Campanian Valchov Conglomerate, Hrušové, Čachtické Karpaty Mts., thin section No. 12795, ×95, polarized light. **Fig. 6** - Redeposited authigenic quartz with zonally arranged inclusions formed by two optical individuals. Other pebble of the same rock as previous, thin section No. 18196, ×20, polarized light. **Fig. 7** - Redeposited authigenic quartz with inclusions; in the lower part a tiny anhydrite (?) crystal. Fine-grained dolomite breccia (Hauptdolomite), Upper Triassic of the Lunz Nappe, basement of the Vienna Basin, borehole Kuklov-3, thin section No. 2953, ×76.

These grains of authigenic quartz are certainly redeposited. They have nothing in common with the host carbonate rock, and did not contain any calcitic inclusions. Their oriented flaky, probably illitic inclusions were rhytmically added on the crystal planes during the crystal growth. The eventual cutting of allochems in the host rock was realised by pressure solution. Most euhedral crystals are partly worn and their zonality is asymmetrical to the grain outline. Grains composed of two optic individuals were also found (Pl. V: Fig. 6).

According to the preliminary oral communication of V. Hurai the inclusions with a fluid and gaseous phase from the locality Hrušové point to a crystallization temperature above 150 °C, probably to anchimetamorphosed rocks. The inclusions formed by CO_2 with a high density of water solution from the locality Kotrčina Lúčka are indicative for the greenschist facies. Other grains did not contain liquid-gaseous inclusions.

The source rock for the mentioned type of quartz remains unknown. We suppose some anchimetamorphosed salt-bearing marls, or rauwackes accompanying Permian or Lower Triassic evaporite bodies. Authigenic euhedral quartz crystals with zonal arrangement of inclusions can be compared with those found within an anhydritic rock at the locality Biele Vody (Pl. V: Fig. 4; Mišík 1962). The flakes of clay minerals enclosed within the quartz grains probably originated from a very diluted suspension derived from claystone fragments.

Authigenic quartz grains loosened from their mother rock which cropped out in an exotic source area denominated the Pieniny "Exotic" Ridge entered the exotic sedimentary zone during the Barremian-Aptian (Fig. 2). In the Albian they penetrated into the Klape and Krížna sedimentary zones, which indicates a common source of the clastic material for both. The transport into the Peri-Klippen and Klippen area lasted until the Paleocene. From the mentioned zones a further redeposition took place into the Senonian basin of the Gosau type and into the Lower Miocene sediments of the Vienna Basin.

Authigenic quartz derived from evaporites and redeposited after their dissolution is rarely quoted in the literature (Pittman & Folk 1971; Schreiber 1974). We found such grains with inclusions of tiny rectangular probably anhydrite crystals in a fine-grained carbonate breccia of Upper Triassic (Lunz Nappe), in the basement of the Slovak part of Vienna Basin - borehole Kuklov-3 (Pl. V: Fig. 7).

Summary

During the late diagenetic (pre-metamorphic) thermal exposition of carbonate rocks euhedral authigenic quartz crystallized. Under metamorphic conditions xenomorphic quartz grains originated (their special case is the selective replacement of ooid cortex); clastic quartz was their main source. The youngest authigenic euhedral quartz grains in the Western Carpathians were found in Eocene limestone pebbles from the Šambron Conglomerate.

The frequency of the authigenic quartz in carbonate rocks (Tab. 1) combined with some complementary data enable us to distinguish three categories of tectonic units in the Western Carpathians: **1** - unaffected complexes (Pieninicum, Silicicum), **2** - strong diagenetic (pre-metamorphic) effects (e.g. Krížna Nappe), **3** - anchimetamorphic (e.g. Donovaly Succession of Tatricum) to epimetamorphic stage (e.g. Borinka Succession).

The dating of authigenic quartz can be deduced from its relation to compaction, lithification, dolomitization, microstylolites, veinlets and tectonic pressure.

Redeposited authigenic quartz with zonally arranged inclusions of micaceous minerals originating from an unknown rock and exotic source (Fig. 2) is a peculiar typomorphic terrigenous component in the Cretaceous and Tertiary sediments in the vicinity of the Pieniny Klippen Belt.

References

Borza K. & Michalík J., 1987: On stratigraphy and lithology of Czorsztyn limestone Formation in the Central Western Carpathians (Jurassic, Malm). *Geol. Zbor. Geol. Carpath.*, 38, 3, 259-284.

Fabricius J., 1984: Formation temperature and chemistry of brine inclusions in euhedral quartz crystals from Permian salt in Danish Trough. *Bull. mineral.*, 107, 203-216.

Ferrill D.A., 1991: Calcite twin widths and intensities as metamorphic indicators in natural low-temperature deformation of limestones. *J. Struct. Geol.*, 13, 6, 667-675.

Grim W.D., 1962: Ausfällung von Kieselsäure in salinar beeinflussten Sedimenten. *Z. Geol. Gesell. (Berlin)*, 114, 3, 59-619.

Hurai V., Franců J., Bajová L. & Gavačová H., 1989: Hydrocarbon inclusions in "Marmarosh diamonds" from flysch sediments of eastern Slovakia. In: E. Roedder (Ed.): *Fluids in geological processes. Abstracts. Comenius University, Geol. Inst.*, Bratislava, 173-174.

Jablonský J., 1978: Contribution to knowledge of the Albian of the Zliechov Group in the Strážovské vrchy Mts. In: J. Vozár (Ed.): *Paleogeographic evolution of the West Carpathians. GÚDŠ*, Bratislava, 175-187 (in Slovak, English summary).

Konta J., 1954: Contribution to the genesis of smoky quartz from Cinvald. *Rozpr. Čs. Akad. Věd, R. mat. prir. Věd*, 64, 4, 1-10 (in Czech).

Marschalko R., Mišík M. & Kamenický L., 1976: Petrographie der Flysch-Konglomerate und Rekonstruktion ihrer Ursprungszonen (Paläogen der Klippenzone und den angrenzenden tektonische Einheiten der Ostslowakei). *Západ. Karpaty, Sér. Geol.*, 1, 7-124.

Matkovskiy O.I., 1961: About so-called Maramuresh diamonds. *Mat. kom. min. geoch., Mežd. geol. Kongress Karp.-Balk. Associacii, Izd. Ľvovskogo Univ.*, Ľvov, 149-158 (in Russian).

McBride E.F. & Folk R.L., 1977: The Caballos Novaculite revisited. Part II. Chert and shale mebers and synthesis. *J. Sed. Petrology*, 47, 1261-1286.

Mello J., 1975: Triassische Biohermkalke im östlichen Teil des Slowakischen Karstes. *Geol. Zbor. Geol. Carpath.*, 26, 1, 21-46.

Mišík M., 1962: Contribution to the petrography of the Werfenian gypsum-anhydrite rocks of Gemerikum. *Geol. Sbor. Slov. Akad. Vied*, 18, 1, 149-160 (in Slovak, French summary).

Mišík M., 1963: Authigenic quartz and authigenic feldspars in Mesozoic limestones of West Carpathians. *Geol. Sbor. Slov. Akad. Vied*, 14, 2, 295-300.

Mišík M., 1971: Observations concerning calcite veinlets in carbonate rocks. *J. Sed. Petrology*, 42, 2, 450-460.

Mišík M., 1972: Lithologische und fazielle Analyse der Mittleren Trias der Kerngebirge der Westkarpaten. *Acta geol. geogr. Univ. Comen., Geol.*, 22, 5-154.

Mišík M., 1991: Pebble composition and source areas of Senonian Valchov conglomerates (Brezovské and Čachtické Karpaty Mts.). *Acta geol. geogr. Univ. Comen., Geol.*, 47/II, 5-35.

Mišík M., 1994a: Authigenic feldspars in carbonate rocks of the Western Carpathians. *Geol. Carpathica*, 45, 2, 103-111.

Mišík M., 1994b: Senonian continental sediments with marine intercalation (Gosau complex) in the basement of the Slovakian part of Vienna basin (borehole Gajary-125). *Miner. slovaca*, 26, 297-310.

Mišík M., 1995: Selective silicification of calcitic fossils and bioclasts in the West Carpathian limestones. *Geol. Carpathica*, 46, 3, 151-159.

Mišík M., Jablonský J., Mock R. & Sýkora M., 1981: Konglomerate mit exotischem Material in dem Alb der Zentralen Westkarpaten - paläogeographische und tektonische Interpretation. *Acta geol. geogr. Univ. Comen., Geol.*, 37, 5-55.

Mišík M. & Sýkora M., 1981: Pieniny Exotic Ridge interpreted from the pebbles of carbonate rocks in the Cretaceous conglomerates of the Pieniny Klippen Belt and Manín unit. *Západ. Karpaty, Sér. Geol.*, 7, 7-111 (in Slovak, German summary).

Mišík M., Sýkora M. & Jablonský J., 1991: Strihovce conglomerates and South-Magura Exotic ridge (West Carpathians). *Západ. Karpaty, Sér. Geol.*, 14, 7-72 (in Slovak, English summary).

Molenaar N. & de Jong A.F.M., 1987: Authigenic quartz and albite in Devonian limestones: origin and significance. *Sedimentology*, 34, 4, 623-640.

Noble J.P.A. & Van Stempvoort D.R., 1989: Early burial quartz authigenesis in Silurian platform carbonates, New Brunswick, Canada. *J. Sed. Petrology*, 59, 1, 65-76.

Pittman J.S. & Folk R.L., 1971: Length-slow chalcedony after sulphate evaporite minerals in sedimentary rocks. *Nature*, 230, 64-65.

Plašienka D., Korikovsky S.P. & Hacura A., 1993: Anchizonal alpine metamorphism of Tatric cover sediments in the Malé Karpaty Mts. (Western Carpathians). *Geol. Carpathica*, 44, 6, 365-371.

Ramsay J.G., 1980: The crack and seal mechanism of rock deformation. *Nature*, 284, 135-139.

Řehánek J., 1977: Limestone silicification of the autochthonous Mesozoic SE slopes of the Bohemian Massif. *Zem. Plyn Nafta*, 22, 2, 159-162 (in Czech).

Schreiber B.Ch., 1974: Vanished evaporites: revisited. *Sedimentology*, 21, 2, 239-331.

Turan J. & Vavro L., 1970: Occurrence of the authigenic feldspars and quartz in the Borinka limestones in Malé Karpaty Mts. *Acta geol. geogr. Univ. Comen., Geol.*, 19, 165-175 (in Slovak, German summary).