

ALEKSANDRA KOSTECKA¹

CALCITE PARAMORPHS IN THE ARAGONITE CONCRETIONS

(Pl. XXXV—XXXVIII and 1 Fig.)

Paramorfozy kalcytu w aragonitowych konkrecjach

(Tabl. XXXV—XXXVIII i 1 fig.)

The concretions described in this paper were found in the quarry at Wolica (Holy Cross Mts.) within the *Lima striata* beds (H. Senkowi-czowa, 1957) (Pl. XXXV, Fig. 1, 2, 3, Pl. XXXVIII, Fig. 1, 2). The concretions occur either as single, rod-shaped forms (Pl. XXXV, Fig. 1, Pl. XXXVIII, Fig. 1, 2) or as aggregates of numerous spheroidal individuals (Pl. XXXV, Fig. 2, 3). The rod-shaped concretions are 2—12 cm long while their diameters range from 12 mm to 35 mm. The long axis is either straight, or twisted, resulting in a more or less pronounced S-shape of the concretion.

The diameters of the spheroidal individuals in aggregates are varying in the same range. The size of the aggregates is variable, depending upon the number of individuals occurring together.

The both forms of concretions are present in marly micritic limestones and in pure fine-grained calcarenites. The concretions can be easily separated from the weathered rock, as they are more resistant to alteration. Consequently they are most frequently found in weathered rubble, and rarely in fresh rock.

The external surface of all concretions is rough, covered by numerous small crystals (Pl. XXXV, Fig. 1, 2, 3).

In cross-section the individual concretions display a radial structure (Pl. XXXVI, Fig. 1, Pl. XXXVII, Fig. 1, 2). Numerous sections made in perpendicular and oblique planes proved that the spheroidal individuals consist of a core surrounded by radially arranged elongated crystals (Pl. XXXVI, Fig. 1, Pl. XXXVII, Fig. 1, 2) producing the druse-like appearance of the external surface. Such individuals should be regarded as radial concretions.

The rod-shaped forms have a more complicated internal structure, as there are several cores aligned along the axis, and each core is surrounded by radially arranged crystals (Pl. XXXVII, Fig. 1).

The radial crystals stemming from two neighbouring cores are inter-growing, thus connecting several individual sphaeroidal concretions into a rod-shaped composite concretion, while the individual character of the components is obliterated.

The aggregates of sphaeroidal concretions are formed in a similar way,

¹ Instytut Geologii Regionalnej i Złóż Węgla AGH, Kraków, al. Mickiewicza 30.

but the positions of the cores of the individuals are not aligned, resulting in the formation of composite concretions with widely varying shapes.

The internal structure of individual concretions do not correspond exactly to their external appearance, as indicated by following observations:

1. The radial „crystals” up to 8 mm long and up to 3 mm in diameter consist of a mosaic of druse calcite (Pl. XXXVIII, Fig. 3, 4). Therefore neither the shape of these „crystals” nor their external appearance are corresponding to the internal structure. Thus the original substance of the „crystals” was clearly replaced by calcite. In order to stress the purely morphologic character of the „radial crystals” this term is put here between quotation marks.

2. The core as an element distinguishable from the remaining part of the concretion is practically non-existent. The central zone is composed of very fine calcite crystals (diameters ranging from 5 to 20 microns), forming radial aggregates of very thin „filaments” (Pl. XXXVI, Fig. 3). Locally the „filament” structure is obliterated, and replaced by disordered structure.

3. Chalcedony is present in the central part of most of the concretions, in the form of irregular aggregates with subrounded surfaces (Pl. XXXVI, Fig. 3). It is secondary in relation to calcite, as indicated by presence of fragments of the calcite „filaments”, continuing beyond the space occupied by the chalcedony.

4. Not taking into account the formation of the pseudomorphic calcite, the sequence of events in the formation of the primary structure of the concretion was following: in the central zone radial tufts of thin calcite „filaments” are formed (Pl. XXXVI, Fig. 3). Farther away from the centre the „crystals” become gradually longer and thicker, the largest reaching the surface of the concretion. Each „crystal”, with the exception of the poorly individualized „filaments” is covered by a thin coat of calcareous or marly-calcareous material, separating the neighbouring „crystals” (Pl. XXXVIII, Fig. 3, 4). The contours of these coats are distinct and clear-cut. Owing to the presence of the coats, the „crystals” are well visible both macro- and microscopically, in spite of the pseudomorphic alteration of their structure. The presence of the coats is related with the formation of the „crystals” in a loose calcareous or marly-calcareous sediment, and expulsion of the sediment during the growth of the „crystals”.

5. The calcareous or marly coat of the „crystals” corresponds exactly to the rock enclosing the concretion. The most frequent type of sediment enclosing the concretions is a slightly marly biomicrite, containing numerous sponge spicules, small pellets, foraminifers and single echinoderm plates. Some staining by iron oxides is usually present in the weathered rock.

6. Chalcedony is present not only in the central part of the concretion but also replaces calcite within the „crystals” (Pl. XXXVI, Fig. 2). The appearance of the „crystals” in the outer zone depends upon the degree of replacement of the calcite by silica. In case of complete replacement the faces of the „crystals” are smooth (Pl. XXXVII, Fig. 3), while incomplete replacement results in strongly grooved faces of the „crystals” (Pl. XXXVII, Fig. 4). The grooving is related to the specific reniform shape of chalcedony aggregates within the „crystals” (Pl. XXXVIII, Fig. 3, 4) and solution of calcite during weathering.

7. Sponge spicules are the source of silica. A majority of spicules in

the rock was subject to desilicification and calcitization, but some well preserved specimens with a visible central canal were observed.

8. The chalcedony displays a specific feather-like radial inner structure, and locally forms crystals up to 400 microns in diameter, with optical properties corresponding to quartz.

The recognition of the original substance of the radial „crystals” presents the principal problem in this study. The following observations are relevant in this respect:

1. The „crystals” have the form of hexagonal prisms with pinacoidal terminations (Fig. 1; Pl. XXVII, Fig. 3). The two faces of the pinacoid (faces $k-k$ in Fig. 1) are connected by a narrow face (c in Fig. 1 A, Pl. XXXVII, Fig. 3).

2. In sections normal to the „crystal” elongation, the outline of the „crystal” is hexagonal, with two faces ($b-b$ in Fig. 1 A, Pl. XXXVII, Fig. 3) longer and four faces (m in Fig. 1 A) shorter. The „crystals” have a pseudo-hexagonal symmetry.

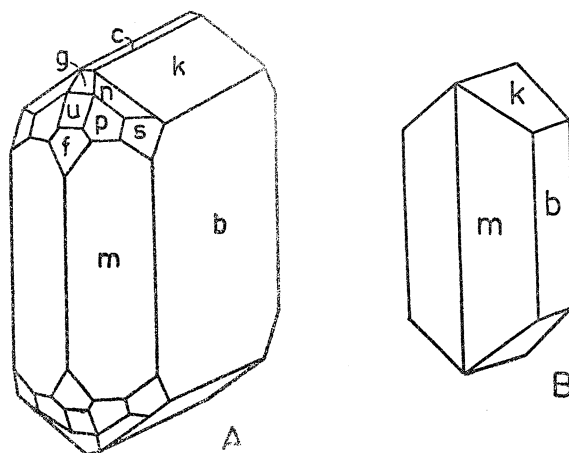


Fig. 1. Kryształy aragonitu (wg J. D. Dana i inn. 1951 — A, i G. Tschermaka, F. Beckego 1931 — B). Objaśnienie w tekście

Fig. 1. Aragonite crystals (after J. D. Dana et al. 1951 — A and G. Tschermak, F. Becke 1931 — B). Explanation in text

3. Normals to the face m (Fig. 1 A) are forming an angle of 64° , while the angle formed by normals to faces b and m is 58° . The axis A forms an angle of 32° with the normal to the face m ($\varrho_1 = A$), while the axis B forms an angle of 58° with the normal to m ($\varrho_2 = B$).

These angles and morphological features of the „crystals” permit to state that the original substance of the „crystals” was aragonite. Fig. 1 A and 1 B present two types of aragonite crystals (J. D. Dana et al., 1951, G. Tschermak, F. Becke 1931, A. Bolewski, 1965) which correspond to „crystals” forming the described concretions. The most frequent type of crystals presented in Fig. 1 A has well developed faces c , b , k and m , and poorly developed faces f , g , n , p , s , u (Fig. 1 A, Pl. XXXVII, Fig. 3), often coalescing. The incomplete development of these faces is probably caused by small dimensions and deformations by paramorphose and partial silicification. Especially the latter process producing the grooving of crystal faces played most probably a great role.

The second morphological type (Fig. 1 B) is sporadically encountered, especially at places where the crystals are densely arranged and show a variable orientation of horizontal crystallographic axes.

Some crystallographic data characteristic for aragonite (J. D. Dana et al., 1951, G. Tschermak, F. Becke, 1931) and results of measurements on the studied crystals are shown in Table 1.

Table 1

Some crystallographic features of aragonite								
Published data					Results of measurements			
	φ	$\varrho = C$	$\varrho_1 = A$	$\varrho_2 = B$	φ	$\varrho = C$	$\varrho_1 = A$	$\varrho_2 = B$
c{001}	0°00'	90°00'	90°00'	0°	90°	90°
b{010}	0°00'	90°00'	90°00'	0°00'	0°	90°	90°	0°
m{110}	58°06'	90°00'	31°54'	58°06'	58°	90°	32°	58°
k{011}	0°00'	35°46 ¹ / ₂ '	90°00'	54°13 ¹ / ₂ '	0°	36°	90°	—

According to G. Tschermak, F. Becke (1931) the angle formed by normals to $m - m$ is 63°48', while the measured angle was 64°. It follows, that differences between published and measured angles are small, in the order of minutes. They were caused by difficulties in measurement.

X-ray analyses were also carried out, with the use of the Debye-Scherrer — Hull method¹ and by the diffraction method with CuK α radiation and tape speed 1°/min.²

The first of the above methods was used to analyse a large „crystal” from the outer part of the concretions. The presence of quartz and calcite was confirmed. The second method was used for analyses of the inner part of the concretion where very fine-crystalline CaCO₃ occurs. Efforts were made to remove silica from the sample, as its presence hampers the identification of other minerals.

The results of the analysis were compared with data for calcite, aragonite and quartz published by W. Mikheev (1957). The presence of small quantities of aragonite is possible, as indicated by the reflexes $d_{hkl} = 1,871 \text{ \AA}$ and $1,737 \text{ \AA}$, which correspond to strong peaks of aragonite. The lack of the strongest reflex $d_{hkl} = 1,917 \text{ \AA}$ is probably caused by superposition of the aragonite, calcite and quartz peaks.

The results of the investigations suggest the following sequence of events leading to the formation of concretions and causing the transformation of their internal structure:

1. In the first stage, calcium carbonate crystallized as aragonite in loose calcareous or marly-calcareous sediment. Aragonite concretions were formed in this stage. A relation of the concretion formation and the activity of mud-eating and burrowing organism cannot be excluded, and the possibility of such a relation is suggested by the shapes of some of the concretions. An example is provided by the concretion presented in Pl. XXXVIII, Fig. 1, 2, which traverses a bed of fine-grained calcarenite. The extremities of the concretion are visible both on the basal (Pl. XXXVIII, Fig. 2) and on the top surface (Pl. XXXVIII, Fig. 1) of the bed, while within the bed the concretion is S-shaped. It is possible that the crystallization occurred in

¹ Analysis carried out by Assoc. Prof. dr J. Kubisz in the Institute of Mineralogy and Mineral Raw Materials, Academy of Mining and Metallurgy.

² Analysis carried out by Dr. M. Kryszowska-Iwaszkiewicz in the Department of Mineralogy and Petrography, Jagiellonian University.

burrowings produced by the activity of the organisms. It is also possible to assume that the presence of organisms created a micro-environment favouring the crystallization of aragonite rather than of calcite.

The formation of aragonite is correlated with high magnesium concentration in the sedimentary environment (Murray, 1954, Bischoff, 1968, Taft, 1967, Yushkin, 1970). Sea water has sufficient magnesium to account for the precipitation and persistence of aragonite (Bischoff, op. cit.). Also Sr^{++} and Pb^{++} ions catalyze the formation of aragonite, but it is questioned, whether these ions are sufficiently concentrated in natural environments (Murray, 1954, Bischoff, 1968).

2. The second stage was characterized by the process of pseudomorphose (paramorphose) of calcite after aragonite. The explanation of this process is difficult, as the problems of paramorphic alteration, inversion and recrystallization are not yet adequately known.

The recent unconsolidated carbonate sediments in shallow-water tropical and sub-tropical environments consist of metastable minerals: aragonite and high-Mg calcite (Stehli and Hower, 1961), while the carbonate rocks consist almost exclusively of stable varieties: low-Mg calcite and dolomite. If these rocks were originally composed of metastable minerals, then their present composition is resulting from processes of recrystallization and inversion; dolomitization is not taken into consideration here (Friedman, 1964, Sanders and Friedman, 1967, Taft, 1967). These processes consist either in solution of the metastable minerals and reprecipitation of the stable ones, or in solid-state recrystallization (Friedman, 1964, Taft, 1967). According to Taft (op. cit.) solution and reprecipitation obliterates the original structure, while the solid-state recrystallization does not.

In the concretions under discussion the process of paramorphose consisted probably in solution of aragonite and reprecipitation of calcite, as suggested by the following observations:

- a) the calcite filling the large „crystals” has the character of a druse mosaic;
- b) corrosion of „crystals” and obliteration of their boundaries is visible locally, but only in small „crystals”;
- c) the calcareous material expelled during the growth of the „crystals” was partly dissolved, leaving only traces consisting of most resistant material: sponge spicules, single foraminiferal tests and small fragments of echinoderms. The solution of the calcareous material occurred chiefly in the central part of the concretions consisting of small „crystals”. Thus the small neighbouring „crystals”, which were initially coated by calcareous material coalesced into larger ones, and their primary outlines are marked only by traces of the incompletely dissolved calcareous material.

3. The next process consisted in replacement of calcium carbonate by silica, leading to the solution of a major part of the carbonate material of the inner part of the concretions and replacement by chalcedony. Calcite was also replaced by silica within the „crystals”. In case of complete replacement the faces of the „crystals” become smooth, while incomplete replacement led to the formation of grooved „crystal” faces.

4. The last process consists in corrosion of chalcedony and replacement of silica by coarse crystalline calcite. This process developed on a small scale, chiefly in the centre of the concretions. Calcite fills small fissures

within the chalcedony aggregates, and gradual replacement of silica is noted along these fissures.

The occurrence of aragonite crystals in Middle Triassic rocks is widespread. Already at the end of 19th century aragonite crystals found in ore-bearing dolomites in the region of Tarnowskie Góry were described as tarnovicite by A. Des Cloiseaux and M. Websky (vide A. Bolewski, 1965, H. Traube, 1888). This name was given to a Pb-rich variety of aragonite, presumably differing in origin from the concretions described here. Forms identical with these described here were found by Dr E. Morycowa in the region of Strzelce Opolskie, who kindly supplied them for comparison.

The author expresses her thanks to Prof. dr A. Gawel and Prof. dr T. Wieser for discussions, and to Assoc. Prof. dr J. Kubisz and Dr. M. Kryowska-Iwaszkiewicz for X-ray analyses.

*Academy of Mining and Metallurgy
Institute of Regional Geology and Coal Deposits
Cracow*

WYKAZ LITERATURY

REFERENCES

- Bischoff J. L. (1968), Catalysis, inhibition, and the calcite-aragonite problem. II. The vaterite-aragonite transformation. *Amer. J. Sci.*, 266, pp. 80—90.
- Bolewski A. (1965), *Mineralogia szczegółowa*, Warszawa.
- Dana J. D., Dana E. S., Ch. Palache, H. Berman, C. Frondel (1951), The system of mineralogy, vol. II., Moskwa, 1953 (Russ. transl.).
- Friedman G. M. (1964), Early diagenesis and lithification in carbonate sediments. *J. Sedim. Petrol.*, 34, pp. 777—813.
- Murray J. W. (1954), The deposition of calcite and aragonite in caves. *J. Geol.*, 62, pp. 481—492.
- Sanders J. E., G. M. Friedman, (1967), Origin and occurrence of limestones. In: G. V. Chilingar, H. J. Bissel and R. W. Fairbridge (Editors): Carbonate rocks, 9 A, *Elsevier*, Amsterdam, pp. 169—265.
- Senkowiczowa H. (1957), The Muschelkalk on the southern slope of the Święty Krzyż Mts. between Czarna Nida and Chmielnik. *Biul. Inst. Geol.*, 122, (in Polish), pp. 5—67.
- Stehli F. G., J. Hower (1961), Mineralogy and early diagenesis of carbonate sediments. *J. Sedim. Petrol.*, 31, pp. 358—371.
- Taft W. H. (1967), Physical chemistry of formation of carbonates. In: G. V. Chilingar, H. J. Bissel and R. W. Fairbridge (Editors): Carbonate rocks, 9 B, *Elsevier*, Amsterdam, pp. 151—167.
- Traube H. (1888), *Die Minerale Schlesiens*. Breslau, *J. U. Kern's Verlag*.
- Tschermak G., F. Becke, *Podręcznik mineralogii*, Warszawa, 1931 (Polish trans).
- Mikheev V. J. — Михеев В. И. (1957), Рентгенометрический определитель минералов, Москва.
- Yushkin N. P. — Юшкин Н. П. (1970), Онтогенез и филогения карбонатов из некоторых месторождений серы. Онтогенические методы изучения минералов. Наука, Москва.

STRESZCZENIE

W warstwach z *Lima striata* (dolny wapień muszlowy) w Wolicy (Góry Świętokrzyskie) zostały znalezione konkrecje węglanowe (tabl. XXXV, fig. 1, 2, 3, tabl. XXXVIII, fig. 1, 2). Każda konkrecja składa się ze strefy jądrowej, zbudowanej z cienkich, „włóknistych” kryształów (tabl. XXXVI, fig. 3); w miarę oddalania się od centrum pojawiają się coraz dłuższe i grubsze kryształy, z których na koniec wyodrębniają się największe, osiagające strefę powierzchniową. Wszystkie kryształy ułożone są promieniście (tabl. XXXVI, fig. 1, tabl. XXXVII, fig. 1, 2). Wykazują one pseudoheksagonalną symetrię (fig. 1; tabl. XXXVII, fig. 3), a ich cechy krystalograficzne (tabela 1) odpowiadają kryształom aragonitu. Aragonit, jako minerał metastabilny, uległ rozpuszczeniu, po czym substancja węglanowa wykryształizowała ponownie w postaci kalcytu. W związku z tym promieniście narastające kryształy są obecnie zjawiskiem wyłącznie morfologicznym, a ich wnętrze wypełnia druzowo narastający, paramorficzny kalcyt (tabl. XXXVIII, fig. 3, 4). Analiza rentgenowska wykazuje, że obecność aragonitu w bardzo drobnych ilościach jest możliwa.

W obrębie konkrecji stwierdzono także obecność chalcedonu, który miejscami zastępuje substancję węglanową (tabl. XXXVI, fig. 2, 3, tabl. XXXVIII, fig. 3, 4). Źródłem krzemionki były licznie występujące w otaczającej skale spikule gąbek. Aragonit krystalizował w luźnym osadzie wapiennym, wykorzystując, być może, kanały powstałe w osadzie w wyniku działalności organizmów mułozernych (tabl. XXXVIII, fig. 1, 2).

Akademia Górniczo-Hutnicza
Instytut Geologii Regionalnej
i Złóż Węgla

OBJAŚNIENIA TABLIC EXPLANATION OF PLATES

Tablica — Plate XXXV

- Fig. 1. Wałeczkowata konkrecja złożona
Fig. 1. Composite rod-shaped concretion
Fig. 2. Nieregularna konkrecja złożona
Fig. 2. Irregular, composite concretion
Fig. 3. Ta sama konkrecja, widoczna strona przeciwna
Fig. 3. The same concretion, visible the opposite side

Tablica — Plate XXXVI

- Fig. 1. Przekrój przez pojedynczą konkrecję sferoidalną. Widoczna budowa promienista. Część centralna wypełniona chalcedonem (A). Zgład
Fig. 1. Section through the single sphaeroidal concretion. Note the radial development of „crystals”. The central part is built of chalcedony (A). Polished section
Fig. 2. „Kryształ” wypełniony chalcedonem (A). Kalcyt występuje jedynie w jego peryferycznej części. Płytką cienką, 1 nikol
Fig. 2. „Crystal” built of chalcedony (A). Calcite is present only in the peripheral part of this „crystal”. Thin section, 1 nicol

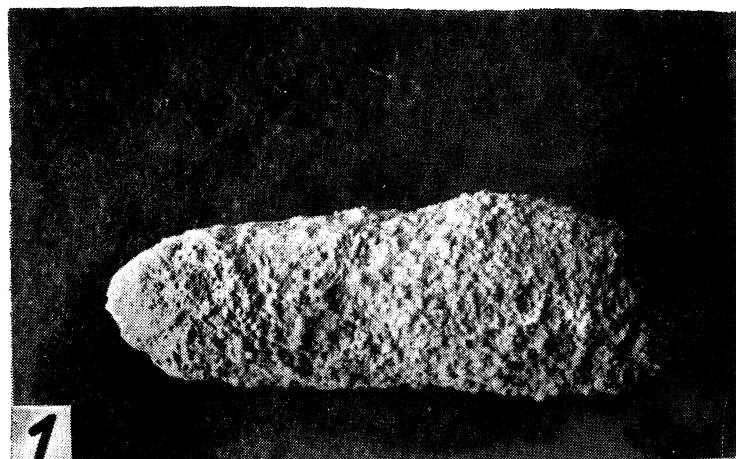
- Fig. 3. „Kryształy włókniste” budujące jądrową strefę konkrecji. W lewym dolnym narożu chalcedon (A). Płytką cienką, 1 nikol
- Fig. 3. „Filamentary crystals” building the internal zone of the concretion. In the left lower corner — chalcedony (A). Thin section, 1 nicol

Tablica — Plate XXXVII

- Fig. 1. Przekrój przez konkrecję złożoną. Widoczna budowa promienista oraz wzajemne przerastanie „kryształów” w strefie zewnętrznej. Część centralna silnie skrzemionkowana. Zgląd
- Fig. 1. Section through the composite concretion. Note the radial arrangement of „crystals” and their mutual overgrowing in the external zone. The central part of the concretion is silicified. Polished section
- Fig. 2. Fragment przekroju przez pojedynczą sferoidalną konkrecję. Widoczny stopniowy rozwój „kryształów” od drobnych w części centralnej do dużych w części zewnętrznej. Biała substancja oddzielająca „kryształy” jest materiałem wapiennym (B). W części centralnej kilka skupień chalcedonowych (A). Płytką cienką, odbitka negatywowa
- Fig. 2. Fragment of section through the single sphaeroidal concretion. Note the grading development of „crystals” from the central part to the external zone. The white substance separating the „crystals” one from another is calcareous material (B). Some concentrations of chalcedony are visible in the central part of the concretion (A). Thin section, negative print
- Fig. 3. Fragment zewnętrznej powierzchni konkrecji z widocznymi „kryształami” o przekroju sześciobocznym. Na kilku z nich widoczna ściana $c\{001\}$
- Fig. 3. Fragment of the external surface of the concretion. Note the hexagonal shape of „crystals”. Some of them show the face $c\{001\}$
- Fig. 4. Powierzchnia konkrecji z poślózionymi „kryształami” w wyniku częściowego zastąpienia kalcytu chalcedonem
- Fig. 4. The concretion surface with grooving „crystals” produced by incomplete replacement of calcite by silica

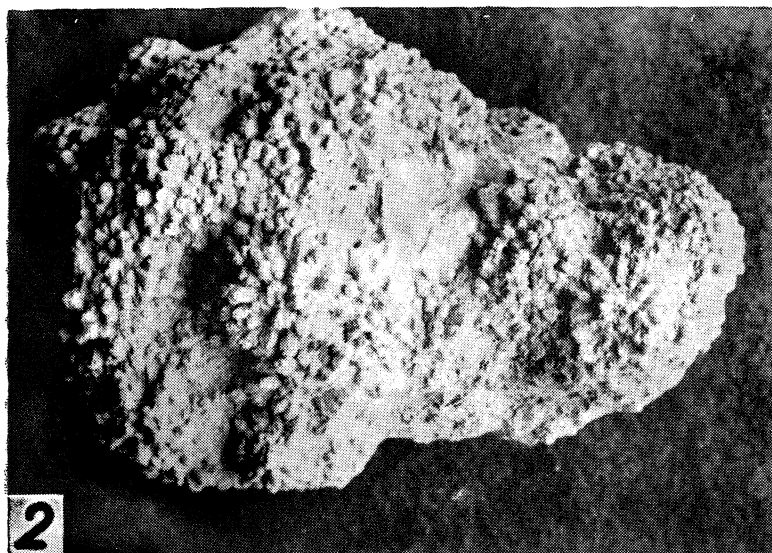
Tablica — Plate XXXVIII

- Fig. 1. Stropowa powierzchnia ławicy z konkrecją w kształcie litery S
- Fig. 1. Top surface of a bed with S-shaped concretion
- Fig. 2. Spagowa powierzchnia tejże ławicy z tą samą konkrecją
- Fig. 2. The same concretion visible on the bottom surface
- Fig. 3. Wewnętrzna budowa „kryształów”. Widoczna paramorfoza kalcytu po aragonicie. A — skupienia chalcedonu. Wokół „kryształów” substancja wapienna. Płytką cienką, 1 nikol
- Fig. 3. Inner structure of „crystals”. Calcite paramorphic replacement after aragonite is visible. The black substance around the „crystals” is calcareous material. A — chalcedony. Thin section, 1 nicol
- Fig. 4. Wewnętrzna budowa „kryształów”. Przekrój przez doskonale wykształcone „kryształy”, otoczone substancją wapienną. A — skupienia chalcedonu. Płytką cienką, 1 nikol
- Fig. 4. Inner structure of „crystals”. Section through the well developed „crystals” surrounded by calcareous material. A — aggregates of chalcedony. Thin section, 1 nicol



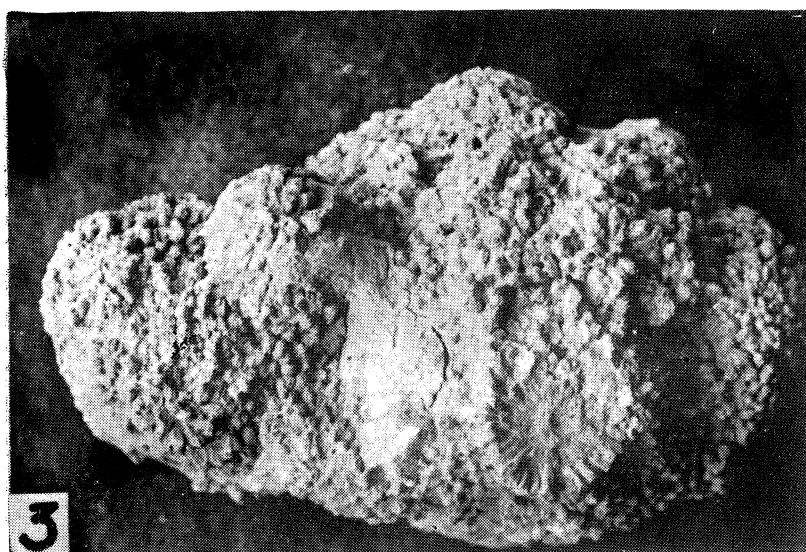
1

1cm



2

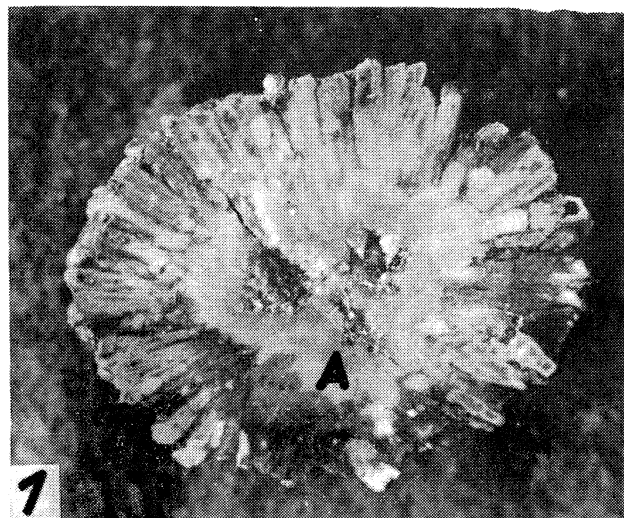
1cm



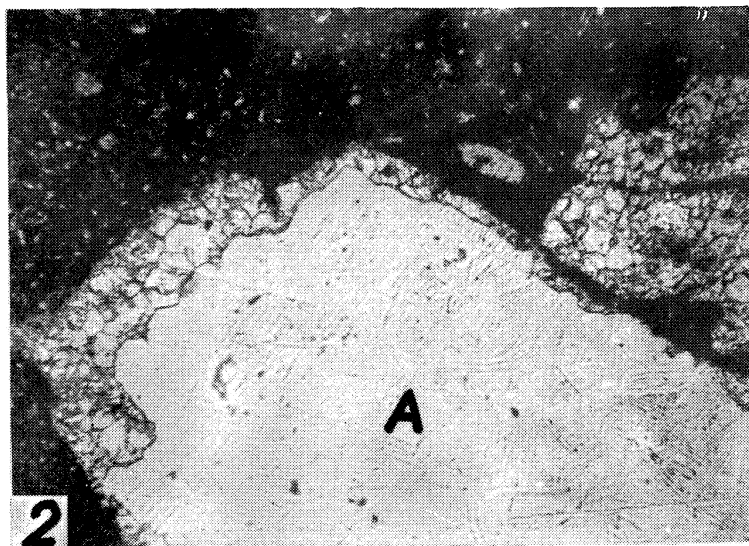
3

1cm

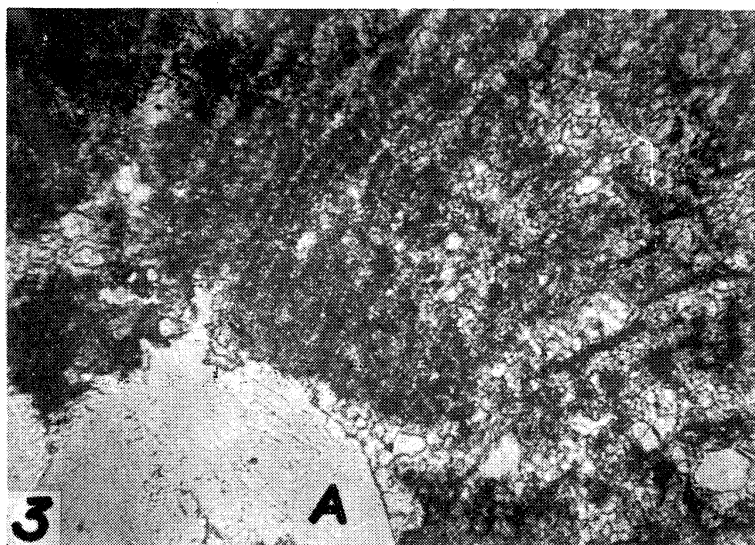
A. Kostecka



7mm

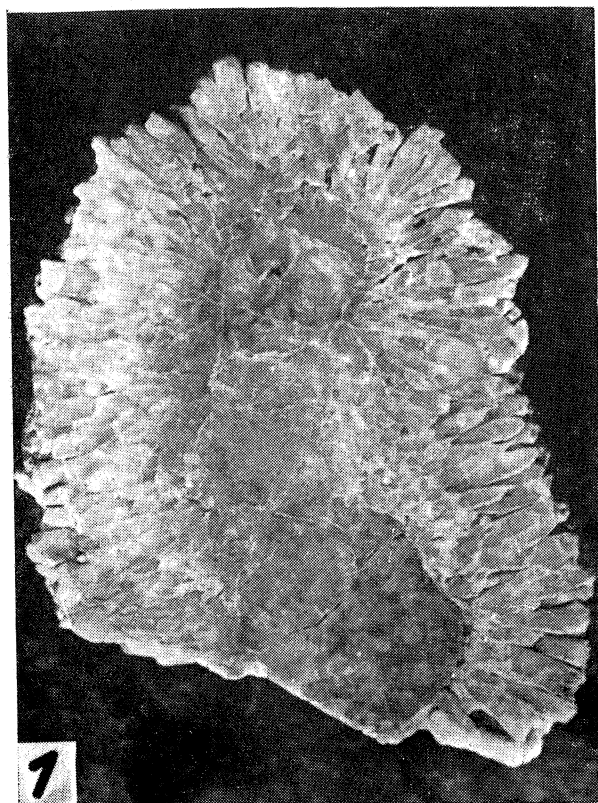


0,2mm

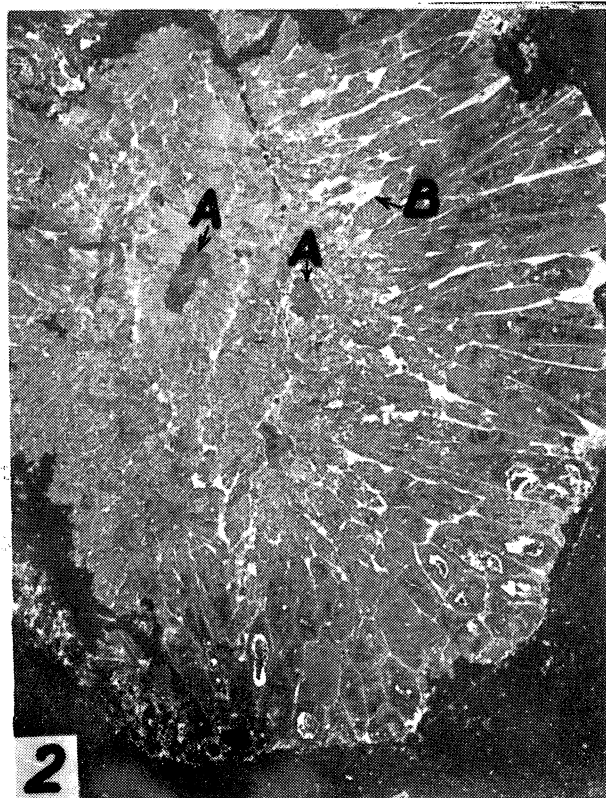


0,2mm

A. Kostecka



5mm



6mm

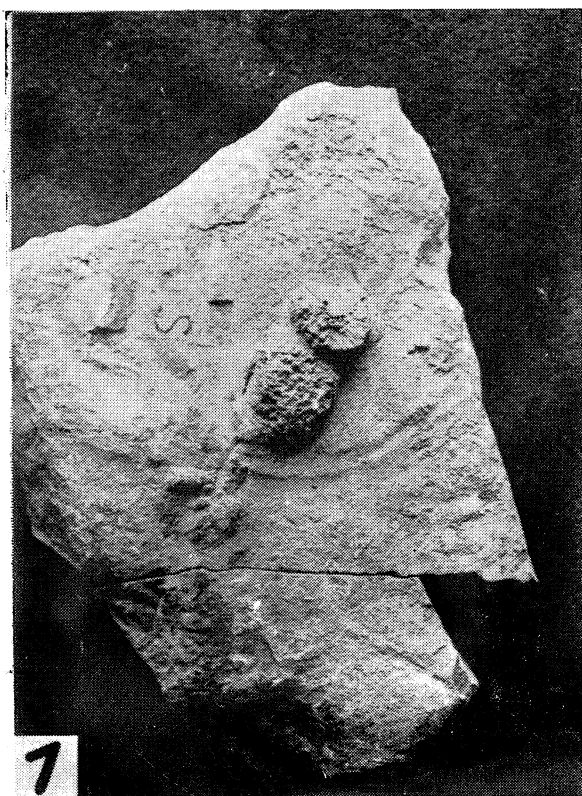


1mm

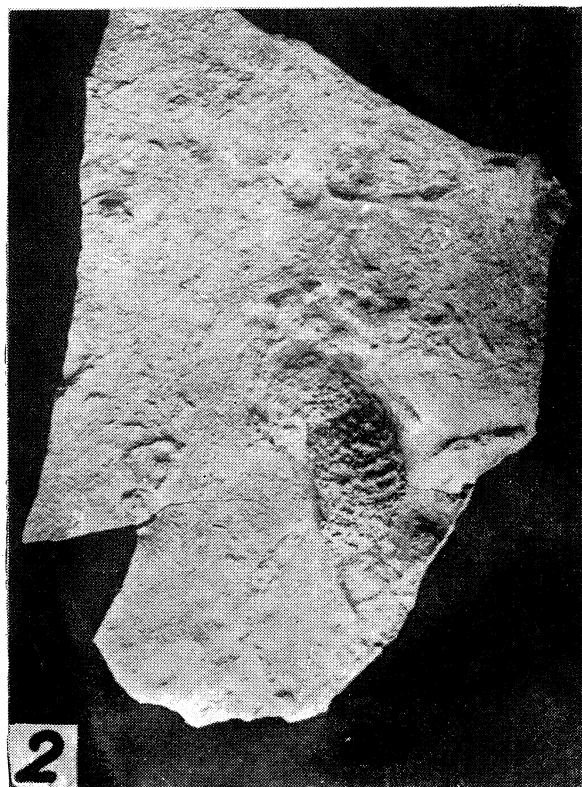


1mm

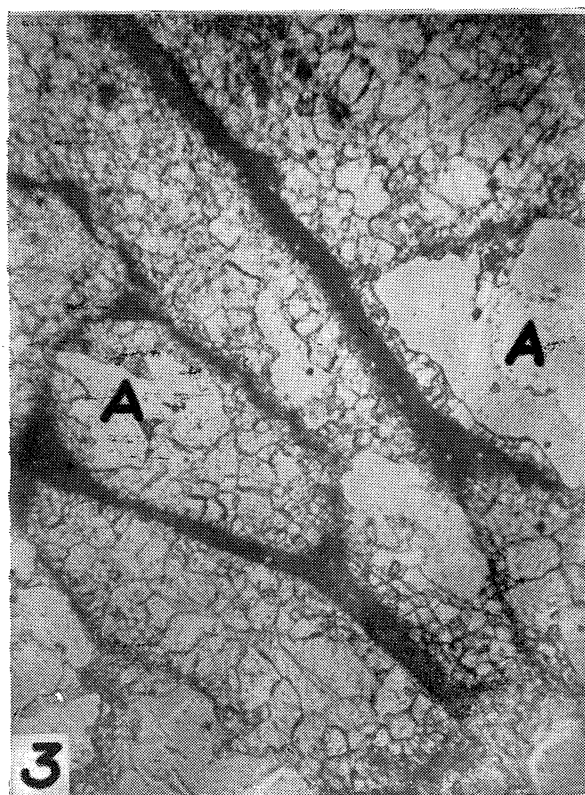
A. Kostecka



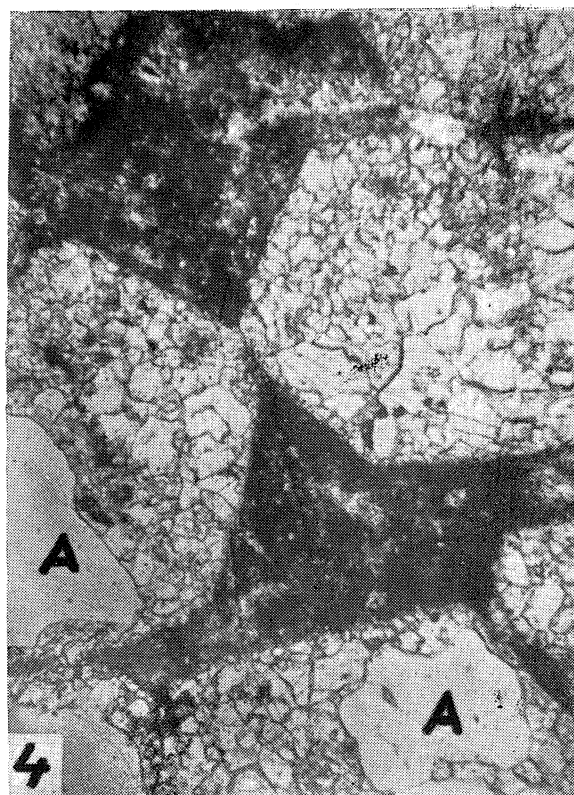
50mm



45mm



0.2mm



0.2mm

A. Kostecka