Annales Societatis Geologorum Poloniae (1987), vol. 57: 37-58
PL ISSN 0208-9068

MINERAL WATER DEPOSITS IN VICINITY OF TYLICZ (BESKID NISKI RANGE, POLISH FLYSCH CARPATHIANS)

Aleksandra Kostecka[1]
& Stanisław Węcławik[2]

[1] *Institute of Geology and Mineral Resources,*
Academy of Mining and Metallurgy, al. Mickiewicza 30,
30-059 Kraków, Poland
[2] *ul. Smoleńska 50/51, 30-112 Kraków, Poland*

Kostecka, A. & Węcławik, S., 1979. Mineral water deposits in vicinity of Tylicz (Beskid Niski Range, Polish Flysch Carpathians). *Ann. Soc. Geol. Polon.*, 57: 37-58.

Abstract: Numerous fragments of mineral water deposits were found in a locality at Tylicz, near Krynica. These are cemented deposits developed as concretions and crusts accompanied by phreatic druzy calcite and vadose calcite sinter. The concretions and the crusts consist of silt and very fine quartz sand cemented with low-magnesium calcite. The clastic material is derived from the flysch rocks. The carbonate cement of these rocks was removed by aggresive water rich in carbon dioxide and the grains were deposited in fissures and caverns. Fine, funnel-shaped concavities occur on surfaces of the concretions and crusts. They are supposed to be due to the escape of liquefied silt or water under the pressure of carbon dioxide. Due to the rapid escape of carbon dioxide and precipitation of calcite the sediment accumulated in fissures and caverns turned into solid rock containing in places lenses of loose material. Circulating water washed it away leaving flattened voids, which were later lined with phreatic druzy calcite. The growth of druzy calcite on the bottom surface of some voids was stopped due to accumulation of fine, clastic internal sediment. In vadose conditions, the layers of druzy calcite were locally covered by calcite sinter.

Key words: Internal sediments, sandy concretions, sandy crusts, druzy calcite, calcite sinter, mineral water, phreatic-vadose deposits, Tertiary flysch, Carpathians.

Manuscript received May 1986, accepted July 1986

INTRODUCTION

Tylicz, a small village located 5 km to SE from Krynica (Fig. 1), is well known owing to its mineral waters containing free carbon dioxide (bicarbonate waters), which were first referred to in the literature at the beginning of the nineteenth century (see Świdziński & Węcławik, 1971).

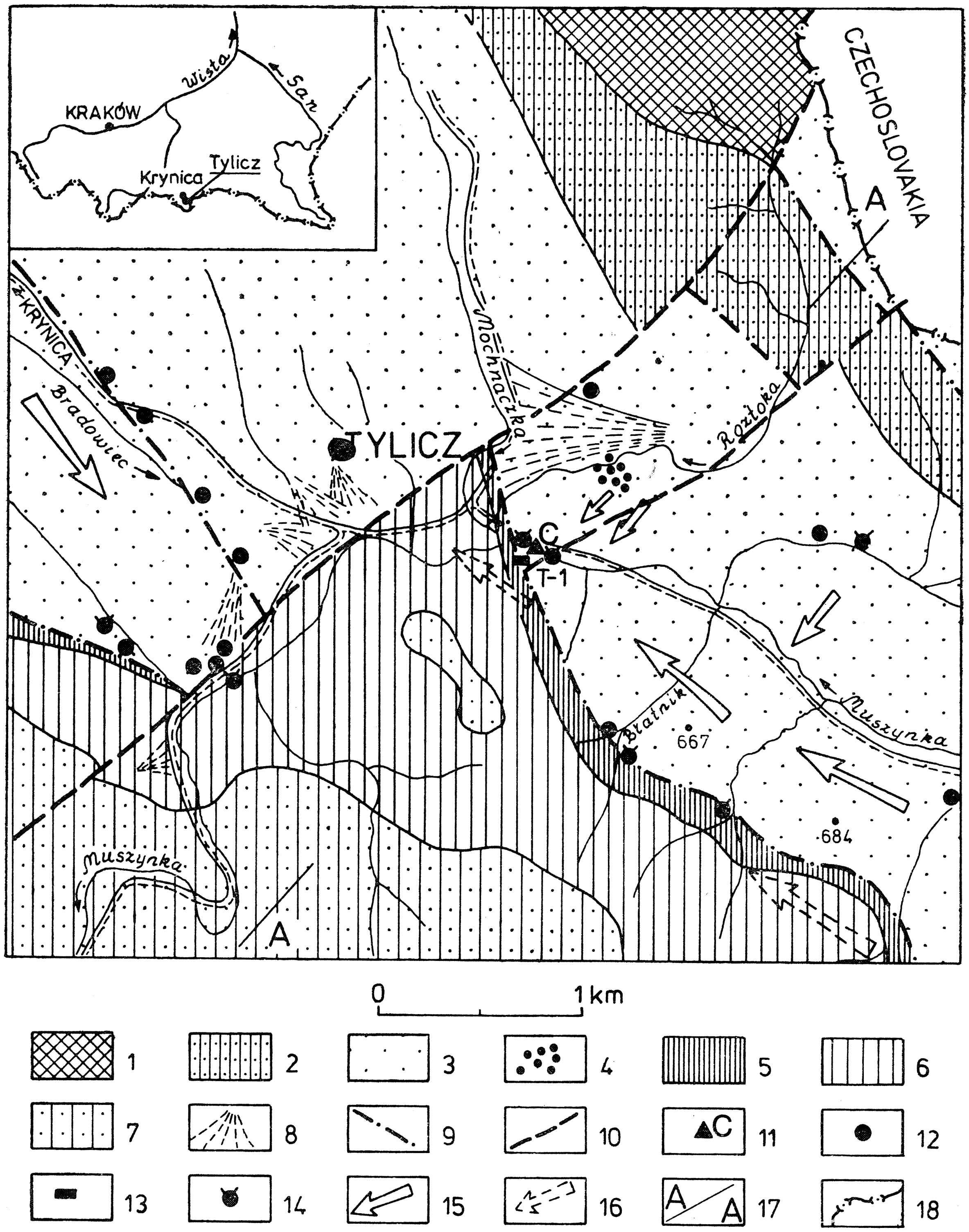

Fig. 1. Map showing situation of trench with mineral water deposits against geological structure of Tylicz area. *1* — variegated shales containing *Glomospira*; *2* — Beloveza Beds; *3* — Łącko Beds; *4* — poorly cemented sandstones of Łącko Beds; *5* — red shales containing *Cyclammina amplectens*; *6* — Hieroglyphic Beds; *7* — Magura Beds; *8* — alluvial fans; *9* — longitudinal dislocations; *10* — transversal dislocations; *11* — trench with mineral water deposits; *12* — mineral water springs; *13* — main mineral water spring (bicarbonate water); *14* — exhalation of free CO_2; *15* — directions of subsurface water downflow in Łącko Beds overlain by Quaternary deposits; *16* — directions of subsurface water downflow in Łącko Beds overlain by red shales and younger sediments; *17* — cross-section line; *18* — state boundary

There are approximately twenty springs (Chrząstowski *et al.*, 1975) at Tylicz, the main one is located on the left side of the Muszynka River (Fig. 2).

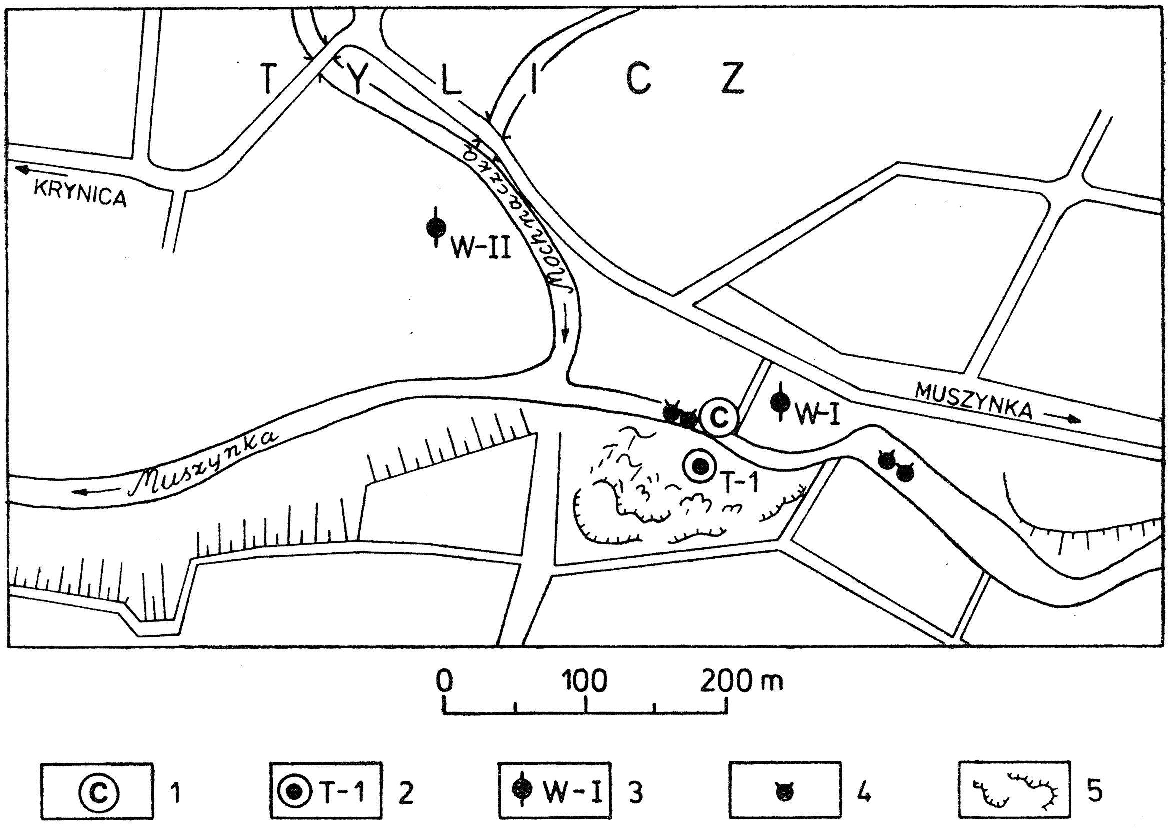

Fig. 2. Map of Tylicz showing position of trench with mineral water deposits. *1* — trench; *2* — main mineral water spring of Tylicz; *3* — wells; *4* — exhalation of free CO_2; *5* — slumps

In 1961, on the right riverside of Muszynka, opposite the main spring, a trench 2.5 m deep was dug. The authors were informed that the topmost 0.6 m of the deposits were Quaternary clayey gravels underlain by sandstones and shales of the flysch. During the digging, the trench filled with water; the water-level was approximately one m above that in the Muszynka River. The water in the trench was saturated with carbon dioxide, which resulted in water effervescence. The chemical content of the trench water is not known. The results of analyses of water from the main spring (T-1) and from drillings (W-I and W-II) are shown in Table 1. In 1963 the trench was filled up with earth.

Concretions (Pl. I: 1), often covered with clay, and crusts (Pl. II) overgrown with druzy calcite and coloform sinter of smooth surface (Pl. I: 2) formed in rock fissures or on single rock fragments were found in the trench beside fragments of flysch rocks. The present paper deals with the description, geological position, and origin of the deposits mentioned. Such deposits have not been known from the Carpathian flysch before.

GEOLOGY AND MINERAL WATERS OF TYLICZ

Tylicz area consists of flysch of the Magura Nappe. The oldest deposits are Paleocene—lower Eocene variegated shales, containing abundant foraminifers, mainly *Glomospira*, accompanied by subordinate, thin bedded, fine sandstones. The variegated shales are overlain (Fig. 3) by lower Eocene Beloveza Beds consisting of alternating thin beds of bluish-greenish clay and sandstone. In the higher part of the Beloveza Beds, the intercalations of fine sandstones are up to 0.5 m thick.

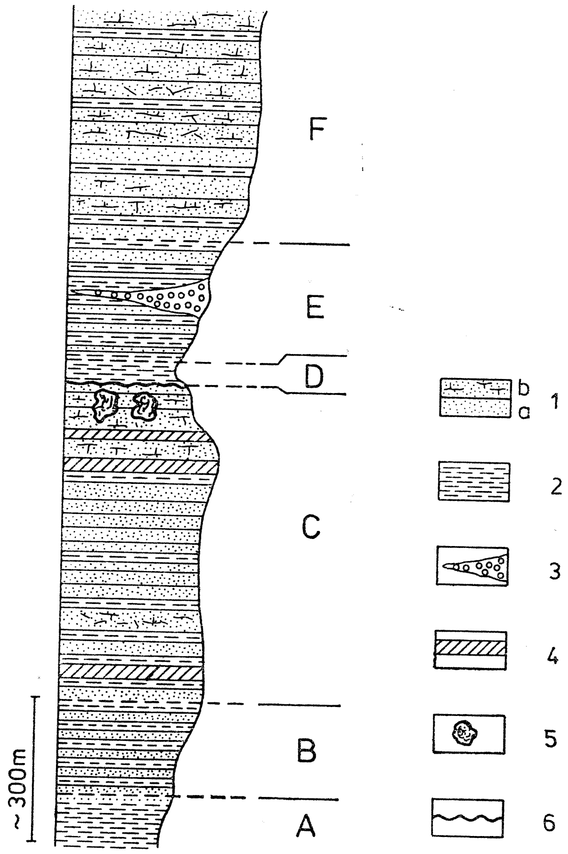

Fig. 3. Schematic lithostratigraphic section of Tylicz area. *A* — variegated shales containing *Glomospira* (Paleocene—lower Eocene); *B* — Beloveza Beds (lower Eocene); *C* — Łącko Beds (undifferentiated, lower Eocene); *D* — red shales containing *Cyclammina amplectens* (middle Eocene); *E* — Hieroglyphic Beds (middle-upper Eocene); *F* — Magura Beds (upper Eocene); *1* — sandstones (*a* — solid, *b* — fissured); *2* — shales; *3* — conglomerates; *4* — marls; *5* — mineral water deposits; *6* — unconformity

To the NW of Tylicz, in the upper part of the Beloveza Beds, there occur intercalations of marls. Marls of similar type, some of them silicified (Łącko marls), are the characteristic element of the lower Eocene Łącko Beds (Węcławik, 1969) which overlie the Beloveza Beds. The Łącko Beds consist mostly of medium- and thick-bedded, green, fine sandstones containing, beside marls, scarce intercalations of shales and friable sandstones. The latter contain sharp-edged fragments of shales.

The Łącko Beds and the overlying red shales containing *Cyclammina amplectens* (Grzybowski), included in middle Eocene, are covered by Hieroglyphic Beds represented by fine-rhythmic flysch containing conglomerates composed of exotic material (middle and upper Eocene). The Hieroglyphic Beds are overlain by sandstones (upper Eocene) of Magura Beds type.

The Paleocene—upper Eocene flysch deposits of the Tylicz area are folded and displaced along transverse dislocations. One of these, of the SW-NE direction, divides this area into two blocks. Within the folded western block, in the core of the NW-SE anticline, the red shales containing *Cyclammina*, and the younger deposits are thrust over variegated shales with *Glomospira*, and folded Beloveza Beds, and Łącko Beds (Fig. 1). In the eastern block, the variegated shales are not exposed on the surface. Along a longitudinal dislocation, the more strongly folded Beloveza Beds contact from the north and locally from the south the less intensely folded Łącko Beds (Figs 1, 4). Within the middle part of the eastern block, the red shales and the overlying deposits are flatwise overthrust by folded and faulted Łącko Beds (Figs 1, 4).

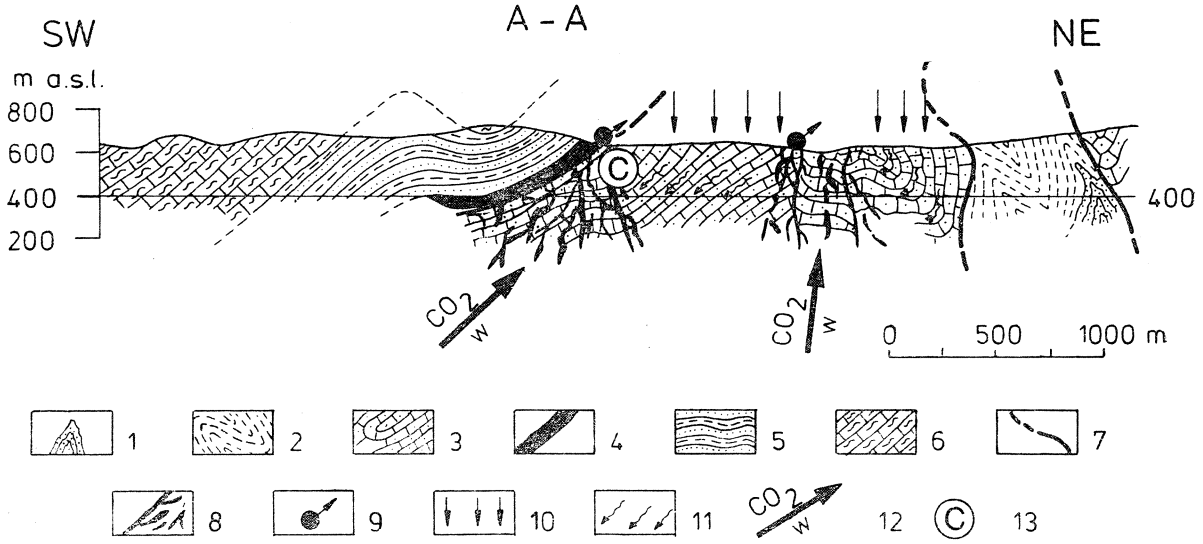

Fig. 4. Geological cross-section of Tylicz area showing situation of mineral water deposits. *1* — variegated shales containing *Glomospira*; *2* — Beloveza Beds; *3* — Łącko Beds; *4* — red shales containing *Cyclammina amplectens*; *5* — Hieroglyphic Beds; *6* — Magura Beds; *7* — dislocations; *8* — dislocations and fissures; *9* — mineral water springs; *10* — area of meteoric water inflow; *11* — directions of subsurface water circulation in Łącko Beds; *12* — supply of free CO_2 and possibly of deeper circulation water; *13* — situation of mineral water deposits

The mineral waters of Tylicz belong to the central hydrochemical zone of the Magura nappe (Węcławik, 1967). These are cool waters of weak mineralization, containing free carbon dioxide of partial pressure *ca* 1.2 atm (Leśniak & Węcławik, 1984). The host rocks of the Tylicz bicarbonate waters are the Łącko Beds. According to the anion-cation classification, the Tylicz bicarbonate waters represent two main types of water:

1. The bicarbonate water of the HCO_3Ca (occasionally Mg) type. This is known exclusively from springs associated with zones of strong tectonic involvement.

Circulation of this water takes place in the zone close to the surface where the inflow of meteoric water is considerable. The meteoric water infiltrates down the Łącko Beds within the outcrop zone and circulates according to the strike. Water circulates within the Łącko Beds covered either solely by permeable Quaternary sediments or by red shales and younger deposits (Fig. 1). The mixing of meteoric water with free carbon dioxide derived from deep-sited source (Leśniak & Węcławik, 1984) takes place within the Łącko Beds. In the same time, the water becomes enriched in the HCO_3^-, Ca^{2+} and, partly, in Mg^{2+} ions owing to dissolution of the cement of sandstones and marls of the Łącko Beds. The influence of the deeper water containing the Na^+ ions is inconsiderable.

2. The bicarbonate water of the HCO_3CaNa (occasionally Mg) type. This is known from a few springs of the eastern block, and from some boreholes. In this water, the amount of dissolved substances varies. In the springs and shallow wells (up to 50 m deep) situated over the Łącko Beds covered solely with Quaternary sediments, mineralization is up to 3.6 g/dm³ (Chrząstowski *et al.*, 1975). In a deeper well (135 m) where the host rocks are covered by impermeable clay (red shales, Hieroglyphic Beds) the mineralization is nearly twice as high (Tab. 1). This is due

Table 1

Physico-chemical analyses of Tylicz mineral waters (data from Laboratory of Hydrogeological Enterprise in Kraków)

Name of intake		Spring T-1		Well W-1		Well W-2	
Kind of intake and depth		Concrete cylinder 0,5 m		Well 50 m		Well 135 m	
Date of sample collection		1975		1974		1975	
Temperature in °C		9,2		10,1		11,0	
pH		6,0		7,0		7,5	
		mg/dm³	mval %	mg/dm³	mval %	mg/dm³	mval %
Kations:	Na^+	110,0	12,76	276,0	32,80	408,0	21,30
	K^+	14,0	0,96	13,0	0,85	26,0	0,80
	Ca^{2+}	496,13	66,05	307,7	50,56	1174,9	70,52
	Mg^{2+}	84,67	18,57	65,7	14,76	65,7	6,50
	Fe^{2+}	12,8	1,23	10,4	1,03	20,5	0,88
Anions:	Cl^-	5,29	0,40	17,8	1,37	14,2	0,34
	Br^-			not recorded			
	J^-			not recorded			
	SO_4^{2-}	66,0	3,65	17,3	1,37	12,4	0,33
	HCO_3^-	2196,6	95,95	2171,9	97,64	5003,5	99,33
	NO_3^-	not recorded		0,1	0,0	not recorded	
H_2SiO_3		52,0		25,0		37,0	
Sum of solid components		3044,60		2968,4		6762,1	
Free CO_2		2838		2726		2562	
Type of biocarbonate waler		HCO_3-Ca, Fe		$HCO_3-Ca-Na$, Fe		$HCO_3-Ca-Na$, Fe	

to the isolation of the basin from the inflow of meteoric water and, probably, to the smaller width of fissures, which suppresses water exchange. The enrichment in the Ca^{2+}, Mg^{2+} and HCO_3^- ions proceeds in a similar way as in the case of the bicarbonate water of the HCO_3Ca type. The hindered circulation of water makes its contact with the surrounding rocks longer, which results in dissolution of more solid substance including the Na^+ ions which were released in the process of kaolinization of feldspar of the Łącko Beds sandstones. This enriches the water of deeper circulation.

MINERAL WATER DEPOSITS

Both the concretions and crusts were found in the waste along the water-filled trench. Thus, it was essential to determine the base and top of the specimens. There were the following mineral water deposits: cementation concretions (Pl. I: 1), crusts (Pl. II), druzy calcite crusts (Pl. II), coloform calcite sinter (Pl. I: 2).

CEMENTATION CONCRETIONS

Concretions occur as single, more or less sphaerical nodules or clusters of nodules (Pl. I: 1). Within the latter, there occur numerous tunnels and deep furrows. The concretions are similar to those from the cave Studnisko (Wójcik, 1958).

The surface of the concretions is smooth or crustaceous. The concretions which have crustaceous surface are formed by superimposed layers of different extent. Usually, the topmost layer is the smallest one and the older layers of successively larger extent are visible below (Fig. 5). The layers are strongly cemented to one another and do not reveal any traces of detachment.

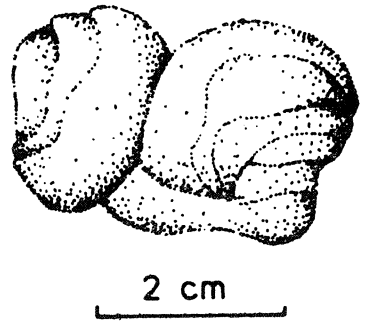

Fig. 5. Sketch drawing of concretion of crustaceous surface

Concavities, scattered all over the concretion surface, are a common feature; some represent casts due to detachment of sandstone and shale fragments cemented with fine clastic material. The casts are of sharp contours and the imprints of the sides and apices of the fragments are well visible. In some of the casts, fragments of shales or sandstones are still in place. Similar fragments occur inside the concretions.

The second type of concavities are the funnel-shaped ones reminding somewhat of mud or sand volcano craters. The diameter of those concavities, at the concretion surface, is about 2 to 3 mm, and the depth is approximately 2 to 4 mm. A low centrifugal barrier is occasionally present at the crater edge (Pl. III: 2). Identical, funnel-shaped concavities and fine domes without craters are also visible on the crust surface (Pl. III: 1).

The funnel-shaped concavities are similar to, but not identical with the pit and mound structures or gas pits (Shrock, 1948) resulting from gas escape or outflow of some liquefied matter (sand volcanoes, Gill & Kuenen, 1958). It seems that the above structures are due to the escape of carbon dioxide. The absence of mounds may be interpreted as resulting from low viscosity of liquified matter or the outflow of water carrying small amount of sediment. In both cases, the source of energy must have been the carbon dioxide pressure. The fine domes on the crust surface (Pl. III: 1) are probably due to concentration of gas bubbles under the thin deposit surface. The carbon dioxide escaped by a system of fine microfissures, now sealed, the traces of which are still visible on the dome surfaces.

The area of occurrence of the funnel-shaped concavities is restricted to the small, compact part of concretion surface. If the presented interpretation is correct these areas represent the top part of the concretions.

The concretions are composed of silt and very fine quartz sand accompanied by muscovite flakes and occasionally by kaolinized feldspar, single grains of shales, quartz sandstone, and inconsiderable amount of clay. The cement is low-magnesium calcite, which is indicated by the negative result of the titan yellow test (Choquette & Trusell, 1978). Small concentrations of pale pink cement whose colour is due to a little higher content of the Mg ions, were seen only occasionally. The degree of cementation is usually high but lenses of loose deposit were also observed.

Each concretion cut across the vertical plane has different internal structure.

The concretion A (Fig. 6) has within its basal part a weakly marked lamination; the laminae are approximately 0.5 mm thick and are locally indistinctly deformed. In most part, they are continuous and some assemblages of laminae display indistinct graded bedding with the laminae rich in clay at the top. In top part of the concretions, the lamination disapppears and is replaced by chaotically arranged streaks. These indicate that the sedimentary matter was diversified and that there occurred some factors deforming the original structure of poorly consolidated sediment. In the lower part of the concretions, there is a deep furrow which does not disrupt the lamination. The furrow is a secondary element in the development of the concretion due, in the author's opinion, to corrosion or erosion of consolidated deposit.

The furrows, some of which develop into tunnels penetrating the concretions, may be due to corroding or eroding action of free circulating water. The mechanism of these processes is not clear but one must note that the concretions originated close to the surface where the mixing of meteoric water with ground water saturated with calcium carbonate was probably intense and might have caused mixing corrosion (see Bögli, 1980).

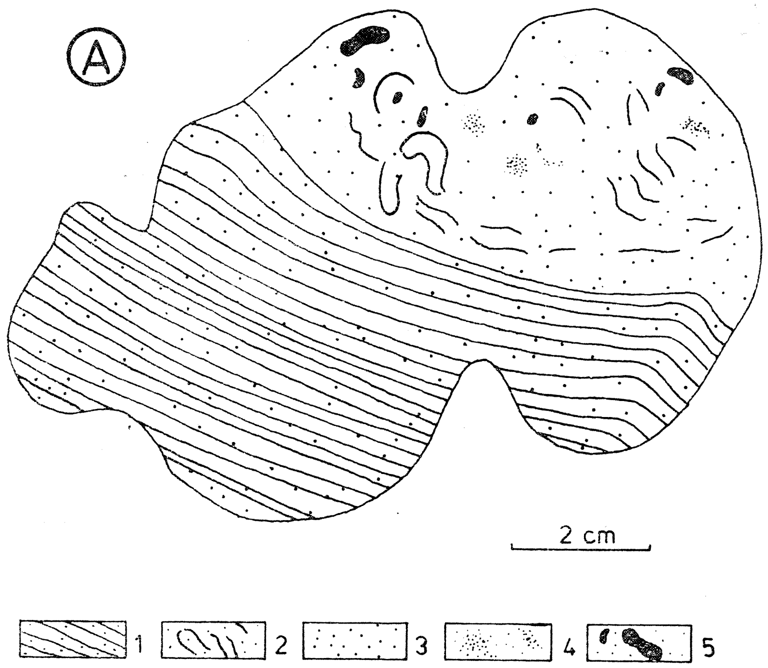

Fig. 6. Concretion *A*, polished section. *1* — laminated clastic deposit; *2* — weakly marked streaks within nonlaminated material; *3* — cemented clastic material; *4* — loose clastic material; *5* — pore spaces

In the upper part of the concretion *A*, there are voids (Fig. 6). Some of these may have originated due to escape of carbon dioxide from the deposit undergoing rapid cementation. This concerns especially those voids which have walls covered by centripetally developing druzy calcite. Some other voids are due to crumbling away of the loose material during cutting and polishing of the samples.

The external shape of the concretion *A* is not related to its internal structure.

The concretion B (Fig. 7) is formed by nodules the surfaces of which are of crust

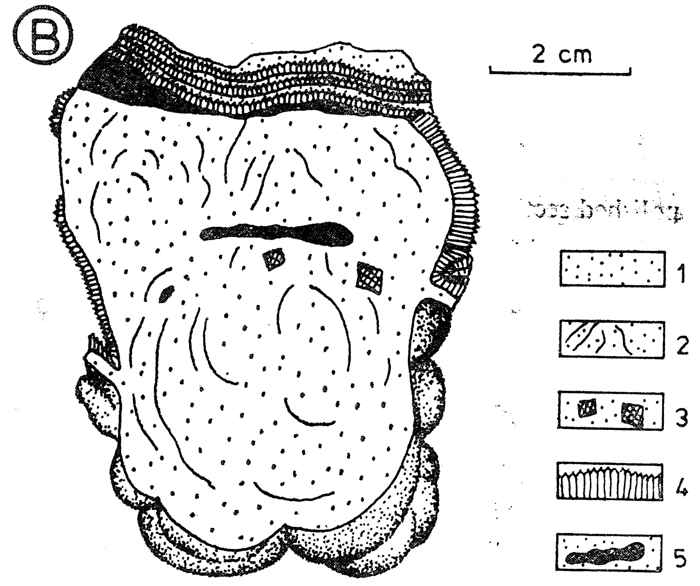

Fig. 7. Concretion *B*, polished section. *1* — cemented clastic material; *2* — weakly marked streaks within nonlaminated material; *3* — rock fragments; *4* — druzy calcite; *5* — pore spaces

character (Fig. 5). Inside the concretion, the lamination is not visible but there are concentric, wavy streaks indicating diversity of the sedimentary matter (Fig. 7). This structure gives the impression of „frozen movement". The shape of the concretion and especially its crust structure reflect to a high degree its internal structure, though it has undoubtedly been modified by corroding or eroding action ot circulating water.

The elongated void in the upper part of the concretion, which originated during cutting and polishing of the section, indicates the local presence of poorly cemented matter. In the vicinity of the void, there occur fine fragments of sandstones. Druzy calcite develops in places along the flanks of the concretion while the top surface is fused with the crust, below which an elongated void filled with loose material has been formed.

The concretion C (Fig. 8) is intermediate between the concretions *A* and *B*. Its surface is mostly smooth but the top surface is covered by funnel-shaped concavities and casts due to detached sandstone and shale fragments. The lamination is not as clear as that in the concretion *A* but better developed than in the concretion *B*. The laminae form fine fold structure. Above the anticline top, the laminae which terminate at funnel-shaped concavities are disrupted. One of such concavities is visible in the section (Fig. 8). The shape of the concretion does not reflect its internal structure.

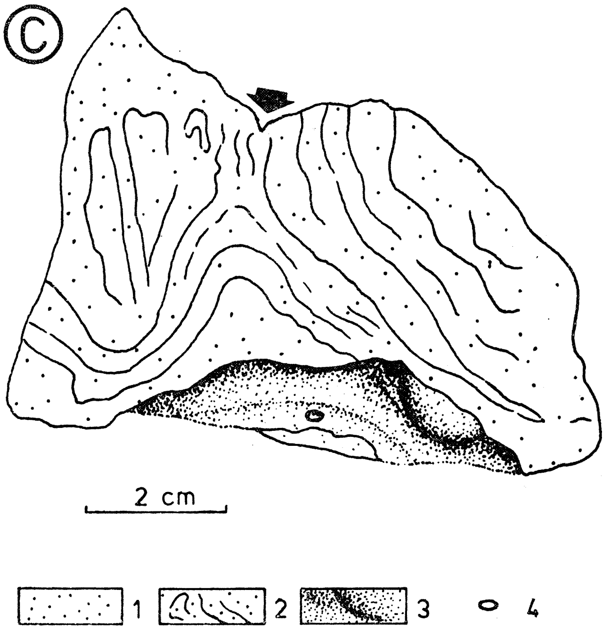

Fig. 8. Concretion *C*, polished section. *1* — cemented clastic material; *2* — marked streaks within nonlaminated material; *3* — empty space within concretion; *4* — funnel-shaped concavity. Arrow indicates funnel-shaped concavity

CRUSTS

The crusts overgrown, as a rule, with druzy calcite consist of silt and fine-grained quartz sand with addition of muscovite flakes and clay minerals. The cement is low-magnesium calcite turning in places into matrix resulting in development of mud-supported texture. The degree of cementation is variable similarly as in the case of the concretions.

The extent of the crust is not known. The superficial measure of the largest specimen found in the waste is 32×20 cm, but this specimen is only a fragment (Pl. III: 1).

The most common are assemblages of superimposed crusts. Their surfaces are not even. Some crusts wedge or are bent (Pl. II). On the top surfaces, beside craters and fine domes, there occur low convexities divided one from the other by narrow, shallow furrows. The bottom surfaces bear fine mammillae or nodules most of which are covered by druzy calcite.

A typical assemblage consisting of four crusts is shown in Fig. 9. The top surface of the first crust (Fig. 9) is more or less smooth and overgrown by a thin calcite layer while its bottom surface is uneven, covered by mammillae. Delicate, laminated deposit in the form of a bar occurs locally within the top part of this crust but structureless material cemented in varying degree dominates. A void whose walls are covered with druzy calcite is also present. The calcite layer on the upper surface of the void is thicker than that on the bottom surface. This is due to the presence of internal loose deposit covering the bottom of the void. Its appearance stopped at some time the development of the calcite crystals.

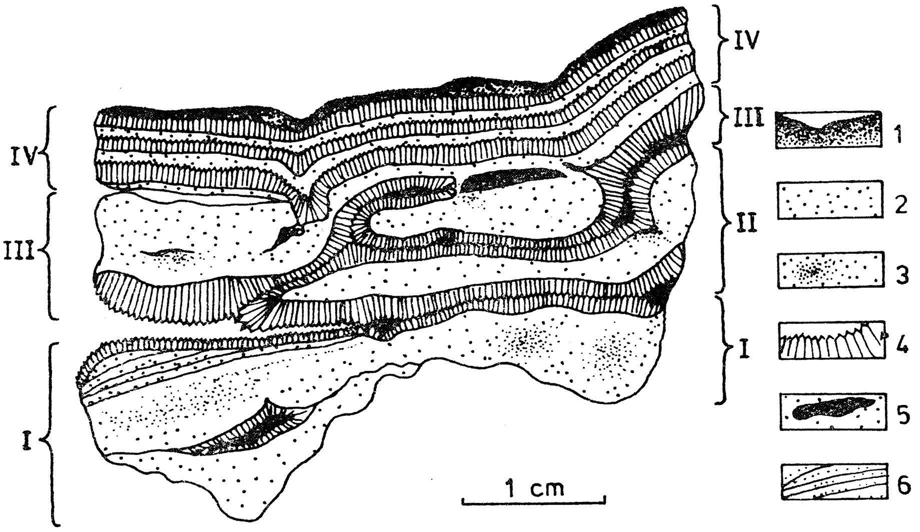

Fig. 9. Assemblage of crusts, polished section. *I, II, III, IV* — crust symbols; *1* — overlying deposit; *2* — cemented clastic material; *3* — loose clastic material; *4* — druzy calcite; *5* — voids within rock; *6* — laminated deposit

The second crust wedges out towards the left side of the drawing while it is bent upwards on the right side (Fig. 9). The crust is formed by structureless material which is strongly cemented or loose in some places. The entire crust surface is covered by druzy calcite. This layer is thicker either on the top surface or on the bottom one.

The third crust, in spite of being continuous (Fig. 9), appears as if consisting of separate lenses or clusters of deposit divided one from the other by layers of druzy calcite. Within this crust, the material is cemented in various degrees; flat and elongated voids due to crumbling out of the sediment during the preparation of the sample are visible in places.

The fourth crust (Fig. 9) is quite strongly fused with the third crust but it differs in structure from the other crusts and because of this it forms an independent part. It is characterized by the presence of alternating sedimentary layers and druzy calcite, the latter being the dominant component (Fig. 10). Within the sedimentary material, the calcite matrix dominates. It contains quartz grains and muscovite flakes. Clay minerals are rather abundant in the laminae *a*, *i* and *l* (Fig. 10). In the other sedimentary laminae (*c*, *e*, *g*) clay is practically absent. The laminae *b*, *d*, *f*, *h* and *k* (Fig. 10) are composed of druzy calcite

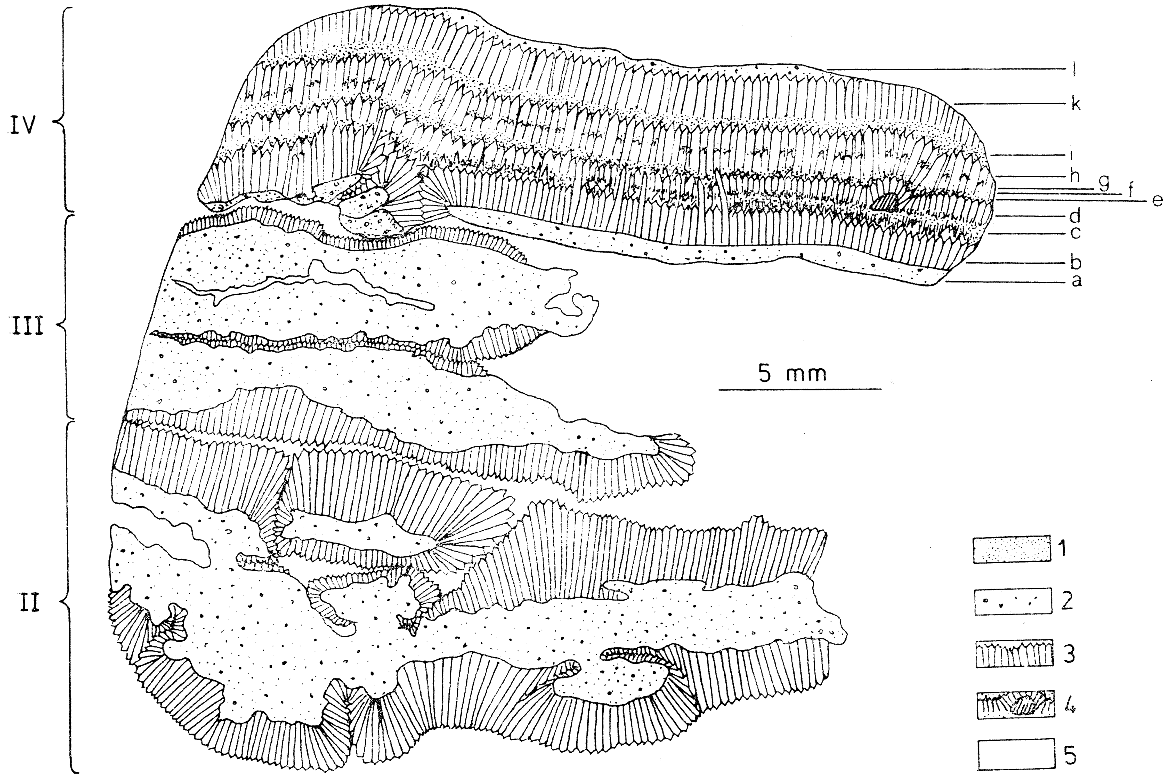

Fig. 10. Assemblage of crusts, thin section. *II*, *III*, *IV* — symbols of crusts; *a—l* — symbols of laminae; *1* — sedimentary laminae within druzy calcite of crust *IV*; *2* — cemented clastic material; *3* — druzy calcite; *4* — fragment of shale overgrown with druzy calcite within sedimentary lamina; *5* — pore spaces

The lamina *a* is in places crumbled (Fig. 10) forming some sort of a collapse. The crumbling was probably due to the lost of support after the underlying loose material had been washed away. The upper surface of the lamina *a* and its fragments were later covered with druzy calcite (lamina *b*, Fig. 10). The development of the calcite crystals was stopped by the appearance of inconsiderable amount of clastic material and precipitation of micrite (lamina *c*, Fig. 10). The deposit, however, did not form a continuous layer and its accumulation occurred at intervals as the lamina *c* consists of a few sublaminae between which there occurs calcite in optical continuity with the underlying lamina *b*. The lamina *c* is covered again by druzy calcite (lamina *d*, Fig. 10), which is in turn covered by thin anls discontinuous sedimentary lamina *e*. This is pierced throughout by some crystad which continue their development in the lamina *f*. The end of the development of the laminae *f* and *h* is caused by the sedimentary lamina *i*, which forms a continuous and relatively thick cover. This lamina is overlain again by well developed layer of druzy calcite *k*, tightly covered by sedimentary lamina *l*.

In the crust IV, it is possible to determine, without doubt, the position of the top of the specimen owing to its characteristic layers of druzy calcite the development of which is being suppressed or stopped by the deposition of sedimentary material.

In some samples, the crust IV is overlain by three superimposed clastic laminae. The two lower ones are of identical features, i. e. are thin (thickness approximately 1 mm), and fragile. The third and topmost layer consists of strongly cemented clastic material and is thicker (approximately 5 mm). On its top surface, there are numerous funnel-shaped concavities and distinct linear ridges indicating the current direction. The funnels are inclined according to this current lineation; at the upcurrent side, a small bar lowering and disappearing upcurrent is developed (Fig. 11). We suggest that this structure originated in the following manner. The free circulating water current forced carbon dioxide present in the unconsolidated sediment to move horizontally just under the deposit surface through a tunnel terminated by an opening (Pl. III: 1; Fig. 11) instead of escaping through a vertical chimney.

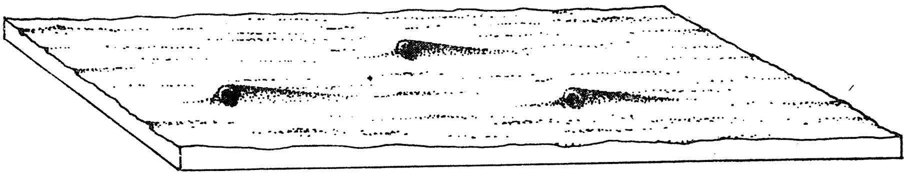

Fig. 11. Sketch drawing of surface displaying current lineation and inclined escape structures. Details in the text

If the druzy calcite overgrowing crust surfaces was removed, it would appear that the sedimentary material of the crusts (Figs 9, 10) forms irregular, separate layers or lenses arranged stepwise and divided by flattened voids. These forms remind at the first glance of speleothems known as shelfstone (Hill, 1976). They are formed due to continuous precipitation of calcium carbonate at the water-air boundary in basins of constant water level (Hill, 1976; Bögli, 1980). The similarity is only superficial as the origin of shelfstone is not related to cementation process in clastic material.

ORIGIN OF CONCRETIONS AND CRUSTS

In cementation process, the important factor is aggresive mineral water contaning carbon dioxide and considerable amount of diluted calcium carbonate. This water: (1) eroded and dissolved rocks along the circulation routes, i. e. along fissures and tectonic cracks; (2) transported unconsolidated clastic material derived from disintegration of rocks, depositing it in elongated voids formed, at least in part, by the same water; (3) was the source of calcium carbonate. The process of key importance for precipitation of calcium carbonate was carbon dioxide degassing (see Hanor, 1978).

The zone in which cementation deposits were formed may be considered as transitory between the vadose and phreatic ones. Calcium carbonate precipitated probably in intergranular pore spaces at the air/water boundary as the result of rapid escape of carbon dioxide. The occurrence of the latter process is evidenced by the presence of craters. This boundary, corresponding to the ground water level (mineral water), migrated undoubtedly several times. The deposit-forming activity of mineral water overlapped with the corrosive one of the meteoric water which penetrated downwards to the subsurface basin and turned gradually into mineral water owing to its saturation with carbon dioxide. The presence of current lineation indicates the occurrence of free water circulation, at least locally. In the process of crust formation this water activity was limited to erosion and transport of loose material.

The very fine clastic material transported by mineral and meteoric waters was trapped in voids. The accompanying coarser material (fragments of sandstones and shales) was derived from fragmented local rocks. It remains an open question whether the whole material had accumulated before it became cemented or whether it was being supplied rhytmically. The latter possibility seems more probable. The process of cementation was controlled by the water-air interface position in sediments. As the boundary surface migrated, cementation developed irregularly leaving some parts of the sediment unconsolidated. This resulted in the formation of strongly cemented layers and lenses alternating with loose material. During the periods of stronger circulation of water, the loose material was locally carried away leaving behind voids. Erosion did not affect druzy calcite which indicates that its crystallization must have been a later process.

The development of the concretions was similar. It seems that circulation of mineral waters was of great importance in the formation of the internal structure as they deformed the sediment when forced upwards by the carbon dioxide pressure. In the same time, the rapid escape of carbon dioxide favoured rapid precipitation of calcium carbonate. Owing, to this, the deformation structures were fixed due to rapid cementation. During the period of meteoric water activity, erosion or mixing corrosion resulted in the formation of deep furrows and tunnels and in smoothing concretion surfaces.

DRUZY CALCITE

This is calcite of densely packed crystals which grow from the nucleation surface forming a brushlike isopachous crust. The thickness of such layer depends on the size of the free space and is up to approximately 6 mm.

Druzy calcite has the features of cement and represents normal, length-fast calcite developed, in most cases, in the form of columnar crystals (see Kendall & Broughton, 1978). Needle-like crystals are also present but they occur exclusively in the layer underlying the vadose calcite (see next section).

The columnal crystals are long (up to 6 mm), relatively wide (10—200 μm), and densely packed. In fine pores having flat bottoms, the crystals are orientated normal to the substrate. In larger voids, especially in those having uneven bottom surfaces, the calcite forms fanlike bundles reminding of sphaerulic cement of Schroeder (1973) or botryoidal cement of Ginsburg & James (1976). The crystals are always developed as trigonal prisms (see Binkley *et al.*, 1980), their tips are of steep-sided pyramide shape (Pl. IV: 2), or, not so often, rhombohedral (Pl. V: 1).

The columnar crystals consist of subcrystals displaying indistinct differences in axis orientation, accompanied by characteristic "brush-extinction" (see Kendall & Broughton, 1978). This kind of extinction is especially distinct in the fanlike systems. The change of the *c*-axis orientation is accompanied by the corresponding curvature of cleavage, which is slightly convex away from the substrate.

The druzy calcite is most commonly clear, but occasionally linear inclusions occur in spaces between subcrystals of the columnar crystals (Pl. VI: 1) or between columnar crystals. If such crystals are cut transversally to the *c* axis the inclusions form an equilateral triangle (Pl. IV: 1), which is distinctly visible against the calcite mosaic.

Within the druzy calcite underlying directly layers of vadose calcite (see next section), there occur in places needle-shaped crystals. This term concerns the discrete subcrystals up to 2 μm wide. The characteristic feature of them are flat crystal terminations (Pl. V: 2).

The staining of the druzy calcite with titan yellow gave negative results indicating the lack of such amount of Mg ions which can be detected by the method mentioned. Samples treated with alizarin red S and potassium-ferricyanide became blue violet which is typical of ferroan calcite. Within the blue-violet zones there occur locally zones of pink, nonferroan calcite. The presence of aragonite was ascertained neither by staining with Feigl solution nor by x-ray analysis.

The presence of the Fe^{2+} ions indicates reducing conditions of calcite crystallization. Such conditions are present mainly within phreatic zone. The normal development of the crystals and polygonal contacts between layers of druzy calcite filling the voids (Fig. 9) also suggest the presence of phreatic conditions. According to Shinn (1975, in Longman, 1980) such polygonal boundaries should be treated as one of the criterions of submarine cement in ancient rocks. However, according to Longman (1980), similar boundaries may occur between isopachous crusts crystallizing in phreatic fresh water conditions.

In any void, druzy calcite may form layers of various thickness; thicker layers occur either on the lower (Fig. 10, void between crust II and III) or on the upper surface (Fig. 9, void between crust I and II). The differentiation in calcite layer thickness is, in our opinion, due to two factors. The first one is the deposition of loose internal sediment on the void bottom covered by upward growing crystals, which stops their growth. But, as the internal sediment did not fill the void entirely, the crystals growing from the top surface could still develop. This is exemplified by the layers of druzy calcite in the void between the crusts I and III (Fig. 9). In the void, on the layer of druzy calcite of the crust I, loose internal sediment was found. The second factor may have been oscillation of water level within pores. When the entire space was filled with liquid the calcite development was regular. In a void only partly filled, crystals started to grow on the bottom surface; when the water level reached the top of the void the crystals developed also there, but being retarded they formed only a thin layer. This is exemplified by calcite layers filling the void between the crusts II and III (Fig. 10).

Druzy calcite is a relatively late element in the development of crusts and concretions. The surfaces overgrown by it must have been formed earlier. It seems therefore that the concretions and crusts underwent cementation prior to calcite development. Erosion partly removed the uncemented material creating voids which were subsequently filled with druzy calcite. Only the crust IV (Figs 9, 10) is younger, having been formed in the same time as the druzy calcite on other surfaces. In the development of this crust, the stages of free development of druzy calcite alternated with those of fast precipitation of carbonate mud accompanied by accumulation of inconsiderable amount of clastic material and clay. It seems that the sequence of laminae in the profile of the crust IV is due to oscillation of the ground water level. In phreatic conditions, druzy calcite developed while during the lowering of the ground water level and rapid escape of carbon dioxide, carbonate mud precipitated which was accompanied by sedimentation from suspension of small amount of clay minerals and quartz silt. The development of the crust IV was stopped by accumulation of considerable amount of clastic material.

The crystallization of druzy calcite was occasionally accompanied by deposition of fine internal sediment. The water carrying this sediment did not erode the calcite.

VADOSE CALCITE SINTER

Some rock fragments are covered by coloform calcite sinter having smooth, shining surfaces and slightly rusty colour (Pl. I: 2). In vertical section, the sinter is two layerd (Pl. VII: 1; Pl. VIII: 1). The internal layer adjoining directly the rocky basement consists of calcite of steep sided (Pl. VIII: 1) or flat (Pl. VI: 2) terminations. The external layer has smooth upper surface covered with thin layer of ferrum hydroxide. Within this layer and especially at the contact with the underlying internal layer, there occur abundant inclusions. These cause the calcite to assume a white colour in a hand specimen, similar to the „coconutmeat" layers described by Folk & Assereto (1976). The inclusions impart pseudo-pleochroism to the calcite (see Kendall & Broughton, 1978). The calcite of the outer layer crystallizes in optical continuity with the calcite of the inner layer (Pl. VII: 2; Pl. VIII: 2).

The two-layered structure of the sinter (Pl. VII: 1; Pl. VIII: 1), the presence of pure crystals having normal terminations in the inner layer (Pl. VIII: 1), and abundance of inclusions in the outer layer (Pl. VIII: 1), together with the smooth upper surface of the latter indicate that the conditions of calcite crystallization of both layers were different. This is supported by the results of the staining. It appears that the inner layer consists of ferroan calcite and the outer one contains nonferroan calcite. It is probable that the absence of the Fe^{2+} ions from the outer layer calcite is due to their oxidation and precipitation in the form of ferrum hydroxide on the smooth surface of this layer. Subsequently, only the calcite of the outer layer is sinter deposit originating in oxidation conditions within vadose zone. It grew from a thin water film syntaxially over the underlying druzy calcite which had developed in phreatic conditions.

As was mentioned above, at the boundary between the two layers, there occur crystals of druzy calcite having steep (Pl. VIII: 1) or flat, „square" terminations (Pl. VI: 2). The latter are thought by some authors to indicate the primary presence of aragonite (Folk & Assereto, 1976; Assereto & Folk, 1976; Loucks & Folk, 1976), though this is not an evidence per se (see Kendall & Broughton, 1977; Folk, 1977). The crystals adjoining the boundary surface are triangular in the plane normal to the *c* axis, and on their flat terminations grows „platy", vadose calcite (Pl. V: 2; Pl. V: 3) causing the surface to become smooth (Pl. V: 4). The flat terminations were probably formed when the crystals growing freely under the water level reached the air/water interface (see Binkley *et al.*, 1980).

Beside the flat-topped crystals, there occur, at the boundary of the two layers, steepsided crystals (Pl. VII: 1; Pl. VIII: 1). Their steep terminations project distinctly over the boundary surface penetrating into the vadose layer. In the concavities between the crystal terminations meniscus surfaces are visible (Pl. VIII: 1), similar to those illustrated by Schroeder (1973, fig. 8a-e). It is possible that these crystals were, at first, growing sufficiently deep under water level to develop in a regular way but the exceptional concentration of inclusions within concavities between the crystals resulted in slowing the growth of not so well developed crystallites. Subsequently, the vadose calcite formed smooth surfaces obliterating all fine irregularities of the direct substratum.

KARST OR NO KARST?

The zone of occurrence of the Tylicz mineral waters is strongly involved tectonically. The fissures and cracks are main migration paths of ground water which appears on the surface as mineral water springs. These aggresive waters rich in carbon dioxide dissolved calcium carbonate derived from the Łącko marls and the cement of clastic rocks making the existing cracks wider and transforming them into caverns which became traps for water transported, fine, clastic material. This resulted in the formation of a system of tunnels and voids where ground water and meteoric water could circulate freely. This is evidenced by the lamination of the clastic material of the concretions and crusts, presence of current lineation, traces of erosion and corrosion, removing of loose sediment from between the crusts and wash in of internal sediment. The rapid escape of carbon dioxide near the water surface was the main reason of fast precipitation of calcium carbonate cementing the clastic material. The result of relatively slow cristallization in phreatic conditions is the druzy calcite while crystallization from water film resulted in formation of vadose calcite of speleothem character. Thus, in spite of the fact that the dissolution and precipitation occurred on a relatively small scale, we can call these phenomena karst developed in clastic rocks. The processes of dissolution and leaching undoubtelly occur at present but whether they are accompanied by precipitation of calcium carbonate is an open question.

ACKNOWLEDGEMENTS

The authors express their thanks to dr M. Doktor for making the photographs and to dr L. Chudzikiewicz and M. Bazielich for making the drawings. The SEM micrographs have been made in the Scanning Microscopy Laboratory of PAN. This work has been done within the framework of individual research programme of the Institute of Geology and Mineral Resources AGH and the CPBP programme — 03.05.31.86 (Inst. Geol. i Sur. Min. AGH, Kraków).

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Streszczenie

OSADY WÓD MINERALNYCH W REJONIE TYLICZA (BESKID NISKI, POLSKJE KARPATY FLISZOWE)

Aleksandra Kostecka & Stanisław Węcławik

W Tyliczu koło Krynicy w pobliżu głównego źródła wód mineralnych (szczawa) znaleziono utwory cementacyjne, uważane przez autorów za przejaw działalności wód mineralnych.

Genezę szczaw tylickich wiąże się z wodami pochodzenia atmosferycznego, które szczelinami i fugami międzyławicowymi migrują w głąb podziemnego zbiornika. Tam wody te, nasycone głębinowym dwutlenkiem węgla, stają się chemicznie agresywne, wzbogacając swój skład rozpuszczonymi składnikami skał otaczających. Zbiornikiem wód mineralnych Tylicza są warstwy łąckie, a zwłaszcza ich część związana ze strefami spękań tektonicznych (Fig. 1—4). Wody krążące w przypowierzchniowej strefie spękanego zbiornika podziemnego wzbogacają się w jony Ca^{2+} (i Mg^{2+}) rozpuszczając węglany z margli łąckich i spoiwa piaskowców.

Osady wód mineralnych znaleziono wśród okruchów i fragmentów skał fliszowych na hałdzie wkopu, który w trakcie robót wypełnił się wodą nasyconą dwutlenkiem węgla. Wśród tych utworów wyróżniono: (*1*) konkrecje cementacyjne (Pl. I: 1); (*2*) skorupy cementacyjne (Pl. II); (*3*) kalcyt druzowy narastający na konkrecjach i skorupach cementacyjnych (Pl. II); (*4*) kalcyt naciekowy pokrywający lokalnie warstwy kalcytu druzowego (Pl. I: 2).

Na powierzchniach konkrecji i skorup znaleziono lejkowate zagłębienia (Pl. III: 2), które autorzy uważają za miejsca wypływu upłynnionego materiału lub wody pod ciśnieniem CO_2. Określają one stropową powierzchnię konkrecji i skorup cementacyjnych. Konkrecje są zbudowane z pyłu i bardzo drobnoziarnistego piasku kwarcowego spojonego niskomagnezowym kalcytem. Ich wewnętrzna budowa jest dość zróżnicowana (Fig. 6, 7, 8), a kształt zewnętrzny zmodyfikowany wskutek erozyjnej działalności swobodnie krążących wód atmosferycznych, bądź korozji w strefie mieszania wód gruntowych i atmosferycznych (por. Bögli, 1980).

Skorupy cementacyjne mają skład podobny jak konkrecje. Lokalnie pojawiają się warstewki lub soczewki o rozproszonym szkielecie ziarnowym, w których główną rolę odgrywa muł węglanowy, strącony na granicy woda/powietrze wskutek odgazowania.

Procesy cementacyjne w obrębie materiału osadowego są związane z gwałtowną ucieczką CO_2. W wyniku migracji zwierciadła wód gruntowych (mineralnych), niektóre partie osadu uległy silnej cementacji, inne pozostały w stanie luźnym. W okresie swobodnego przepływu wód osad luźny został częściowo wypłukany i usunięty, a na jego miejscu rozwinęły się płaskie próżnie upodabniając skorupy do tarasów ułożonych jeden na drugim. W próżniach na wszelkich dostępnych powierzchniach rozpoczęła się krystalizacja kalcytu druzowego w warunkach freatycznych. Kalcyt druzowy jest wykształcony w postaci kalcytu kolumnowego (por. Kendall & Broughton, 1978) i tworzy najczęściej wachlarzowate pęki (Pl. VI: 1). Jego zakończenia mają kształt stromościennych piramid trygonalnych (Pl. IV: 2) lub romboedrów (Pl. V: 1). W obrębie pustek warstwy kalcytu druzowego mogą mieć różną grubość. Niekiedy grubsza warstwa pojawia się na stropowej powierzchni próżni, niekiedy na jej powierzchni spągowej. Pierwszy przypadek jest związany z namyciem i depozycją luźnego osadu wewnętrznego na rosnących ku górze kryształach kalcytu, wskutek czego dalszy ich rozwój został zatrzymany, podczas gdy narastające na powierzchni stropowej kryształy mogły nadal kontynuować wzrost (Fig. 9). Drugi przypadek z kolei zachodził wówczas, gdy próżnia nie była wypełniona wodą całkowicie, wskutek czego krystalizacja kalcytu przebiegała pod przykryciem wody tylko na dolnej powierzchni próżni. Po podniesieniu się poziomu wody rozpoczęła się krystalizacja kryształów również na powierzchni górnej (Fig. 10).

Oprócz konkrecji i skorup pokrytych druzowym kalcytem napotkano również groniaste nacieki kalcytowe o gładkich powierzchniach zewnętrznych. Nacieki wykazują dwuwarstwową budowę. Warstwa wewnętrzna rozwinięta bezpośrednio na podłożu skalnym jest wykształcona w postaci druzowego kalcytu (Pl. VII: 1) o stromych (Pl. VIII: 1) bądź płaskich (Pl. V: 2; P. VI: 2; Pl. V: 3) zakończeniach kryształów. Warstwa zewnętrzna zawiera obfite zanieczyszczenia powodujące zjawisko pseudopleochroizmu (Pl. VIII: 1). Jej górna powierzchnia jest gładka, błyszcząca i pokryta cienką warstewką wodorotlenków żelaza. Barwienie obu warstw czerwienią alizarynową i żelazicjankiem potasu pokazało, że warstwę dolną buduje kalcyt żelazisty, górną zaś – kalcyt bezżelazisty. Ten ostatni jest kalcytem krystalizującym w warunkach wadycznych z cienkiego filmu wodnego.

Płaskie zakończenia kryształów kalcytu druzowego na kontakcie z kalcytem wadycznym wytworzyły się wtedy, gdy rosnące w ośrodku wodnym kryształy osiągnęły granicę woda/powietrze (por. Binkley *et al.*, 1980). Od tego momentu rozpoczęła się krystalizacja „płytkowego" (Pl. V: 3; Pl. V: 4) kalcytu wadycznego wygładzającego stopniowo drobne nierówności bezpośredniego podłoża.

EXPLANATIONS OF PLATES

Plate I

1 – Cementation concretion consisting of a few nodules. On left side, deep, transverse furrow, on lower right, similar but longitudinal one

2 – Fragment of sandstone containing coloform calcite sinter

Plate II

Crusts (*S*) divided by flat, elongated voids and overgrown by druzy calcite (*d*). Concretion (*c*) visible in the lower part of illustration

Plate III

1 – Crusts seen from the top, showing tunnels ending in craters (*t*), fine domes without craters (*m*) and current lineation NE-SW

2 – Funnel-shaped concavities of crater character ringed by microbar

Plate IV

1 – Inclusions in intercrystal spaces. Traces of triangular columnal crystals in plane perpendicular to *c*-axis. Thin section, plane polarized light

2 – Druzy calcite, in background steepsided terminations of crystals distinctly visible. SEM micrograph

Plate V

1 – Druzy calcite of rhombohedral crystal terminations. SEM micrograph

2 – Flat ending subcrystals at contact of phreatic and vadose calcite. SEM micrograph

3 – Vadose calcite on flat terminations of subcrystals. SEM micrograph

4 – Surface of vadose calcite above contact with phreatic calcite. SEM micrograph

Plate VI

1 – Columnar calcite (fan-shaped) containing linear inclusions situated in spaces between subcrystals. Thin section, plane polarized light

2 – Flat terminations of druzy calcite crystals at contact with vadose calcite. Thin section, plane polarized light

Plate VII

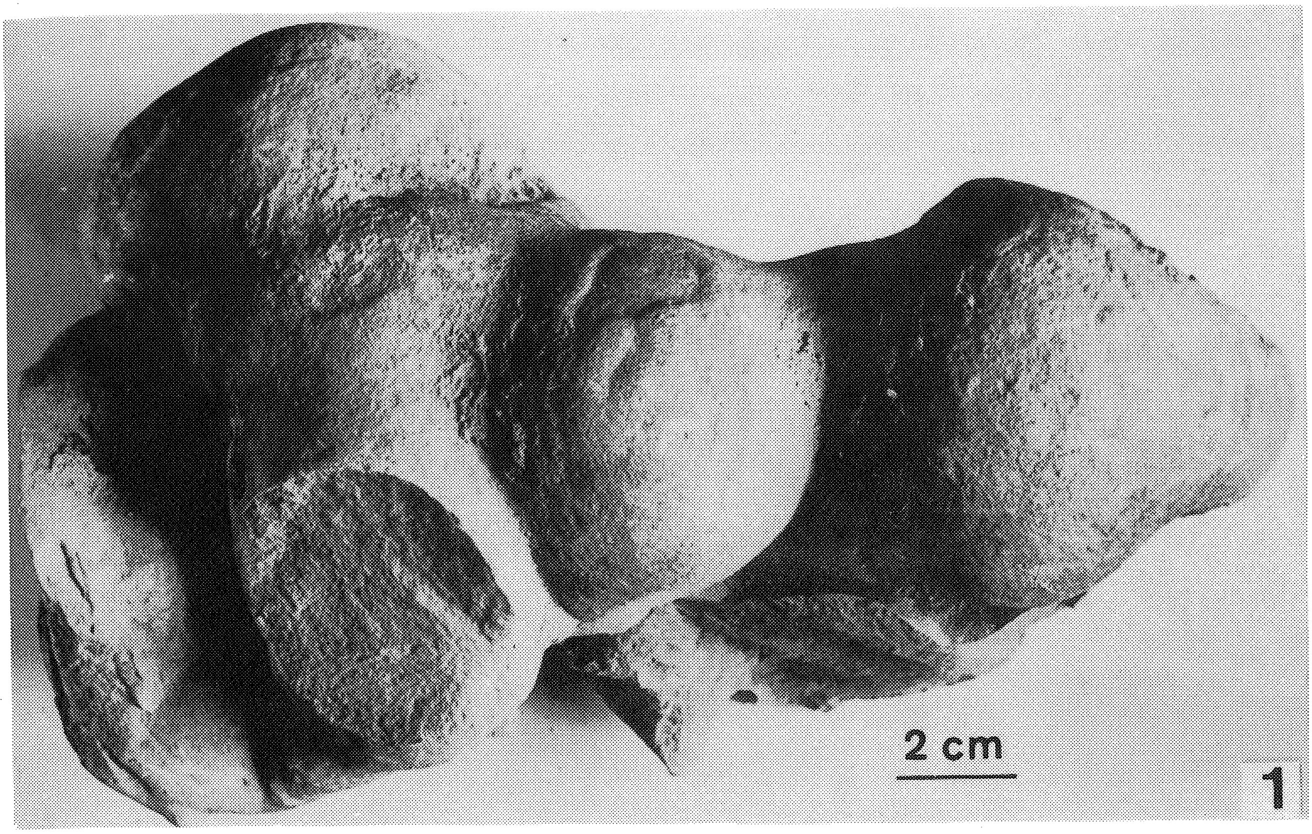
1 — Double layered structure of calcite sinter. Lower layer (*a*) ferroan calcite of steepsided crystals; upper layer (*b*) non-ferroan calcite of smooth top surface. Contact of both layers emphasized by inclusions. Thin section, plane polarized light

2 — As in Pl. VII: 1. Vadose calcite crystallizing syntaxially with phreatic calcite. Crossed nicols

Plate VIII

1 — Steep-sided tips of druzy calcite crystals and meniscus-shaped concavities in between (*m*), at contact with vadose calcite. The contact of both layers emphasized by contamination. Thin section, plane polarized light

2 — As in Pl. VIII: 1. Crossed nicols



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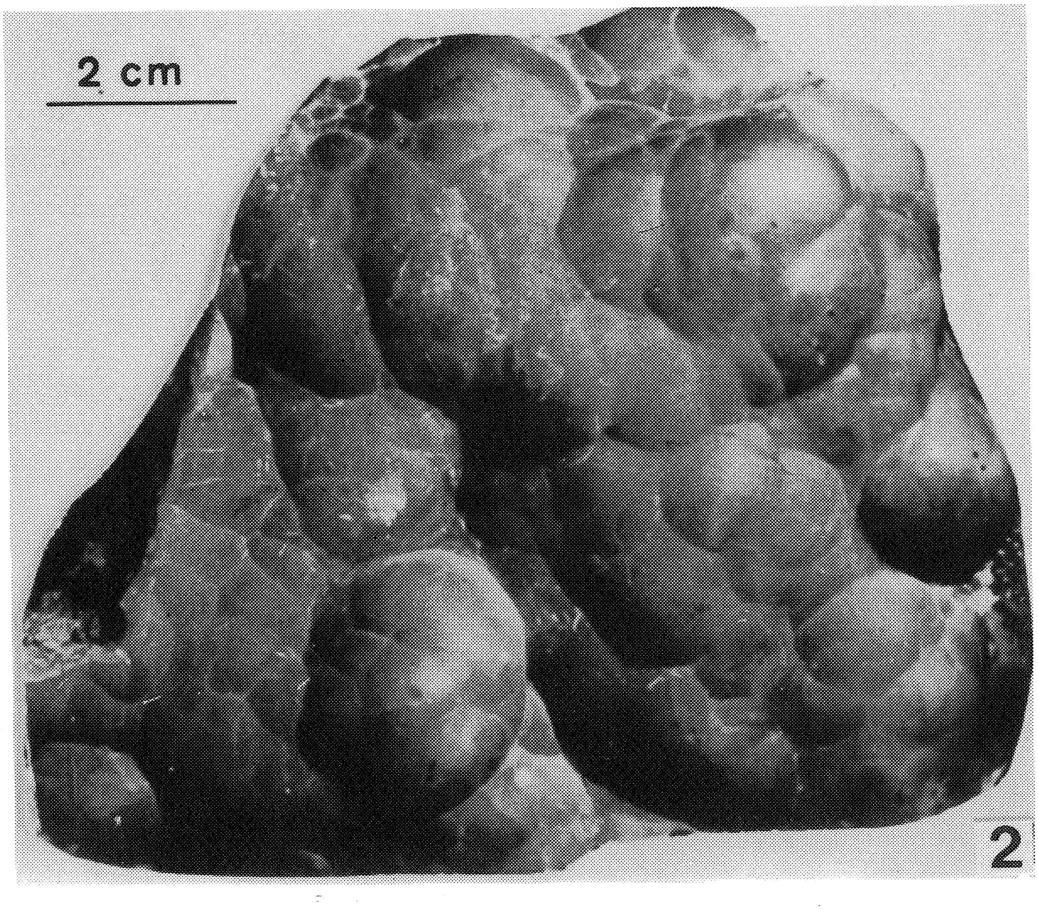

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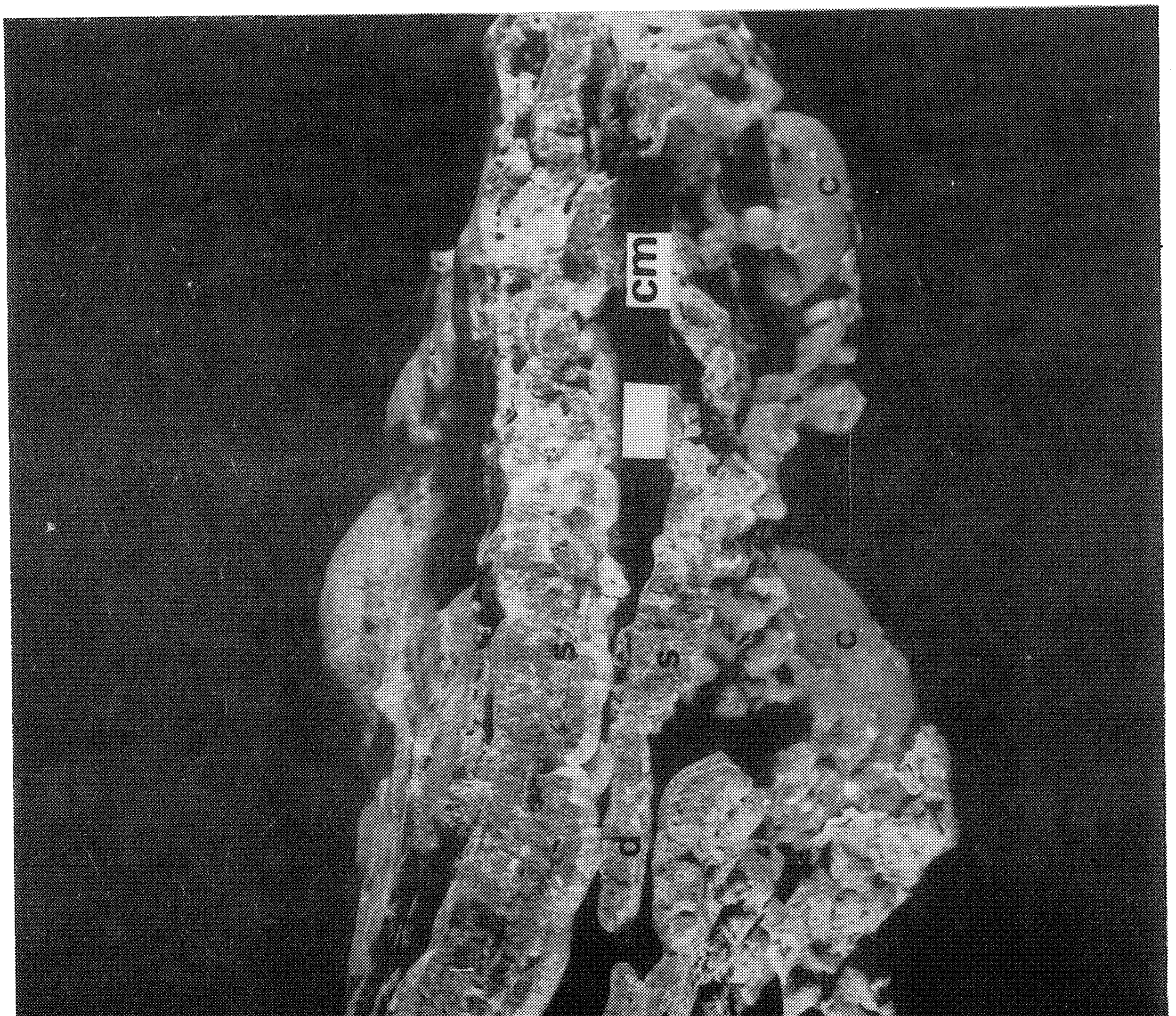
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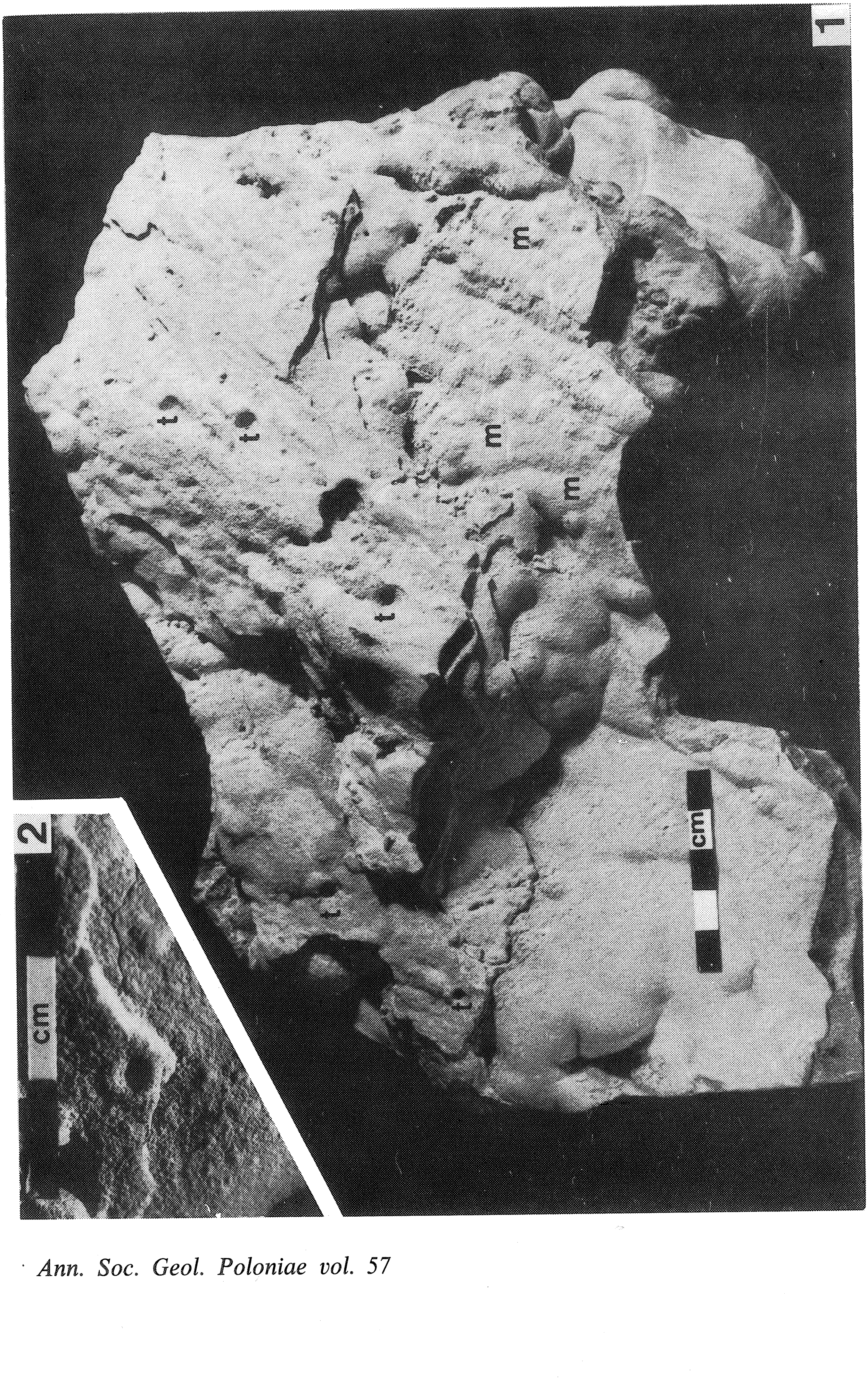
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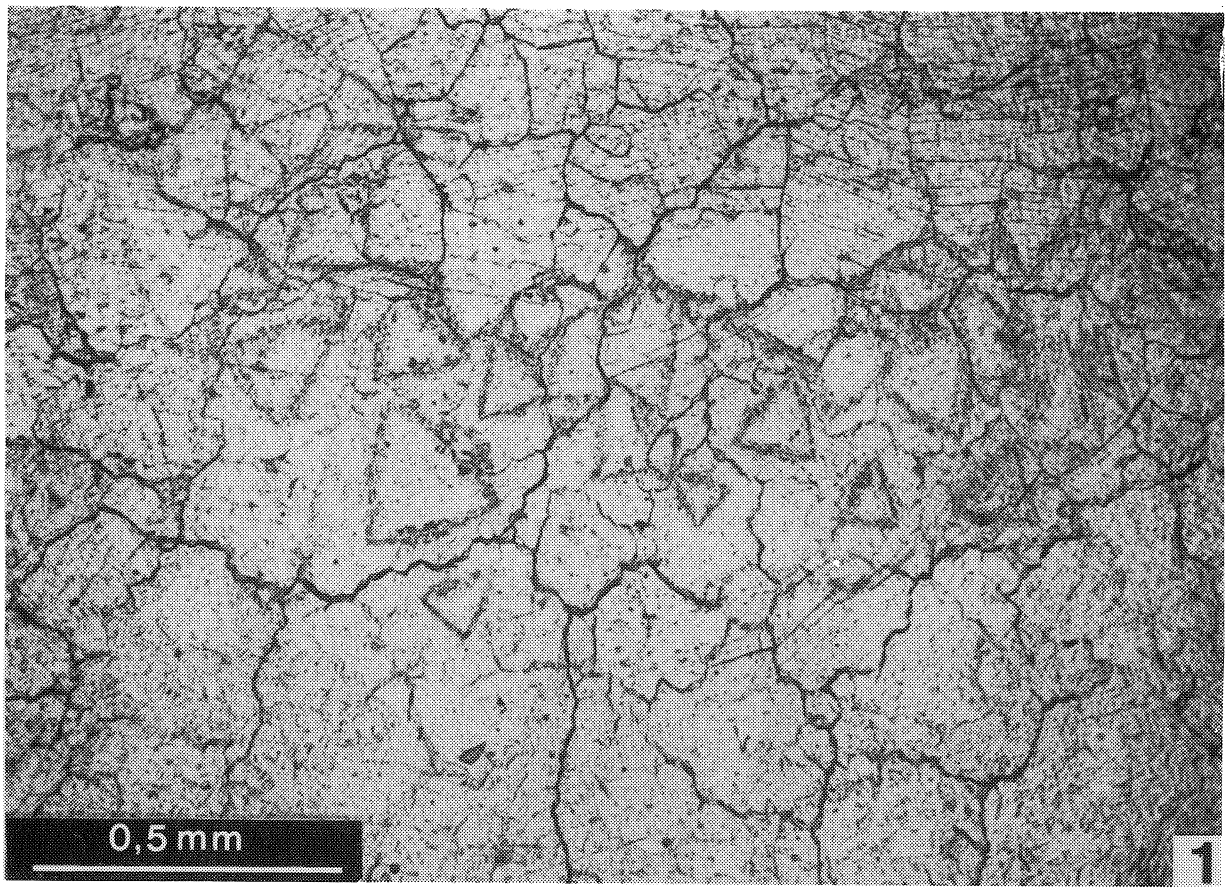

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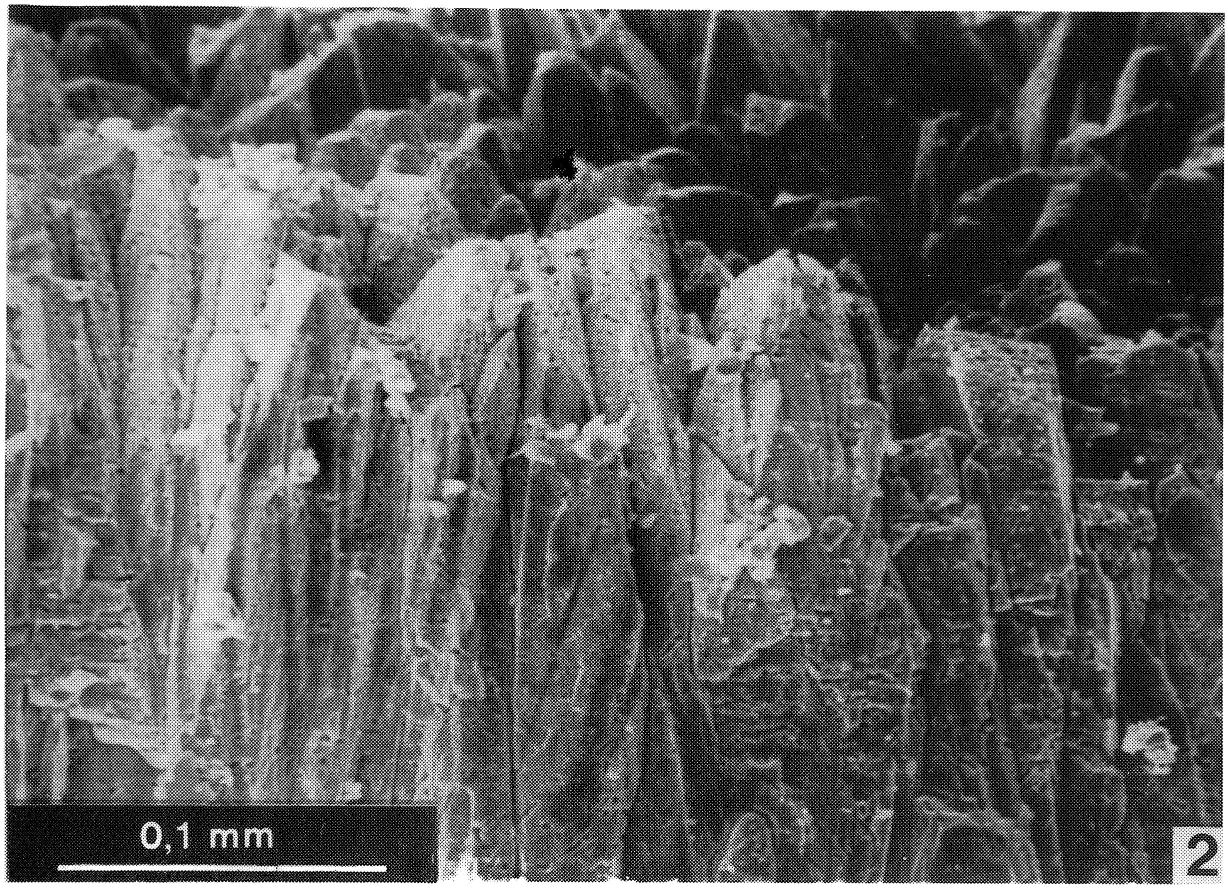

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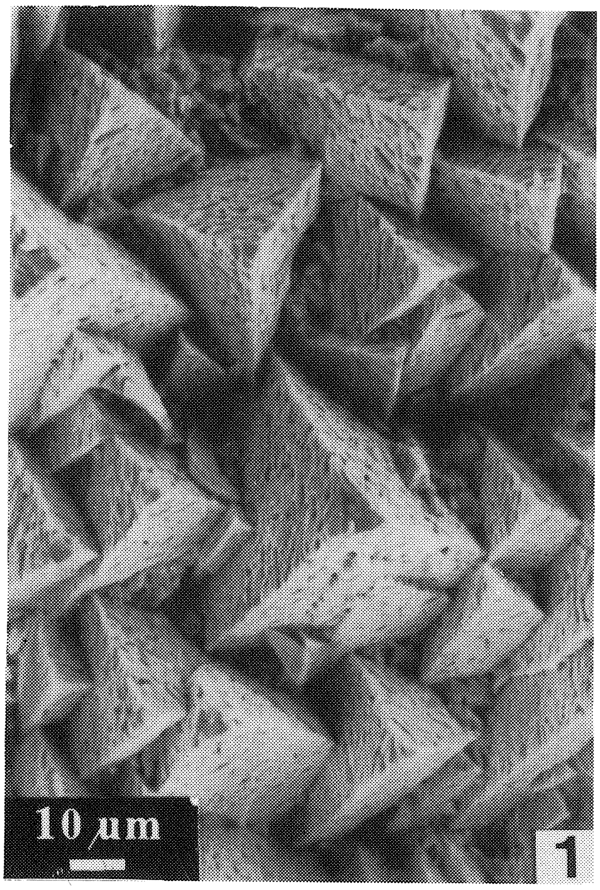
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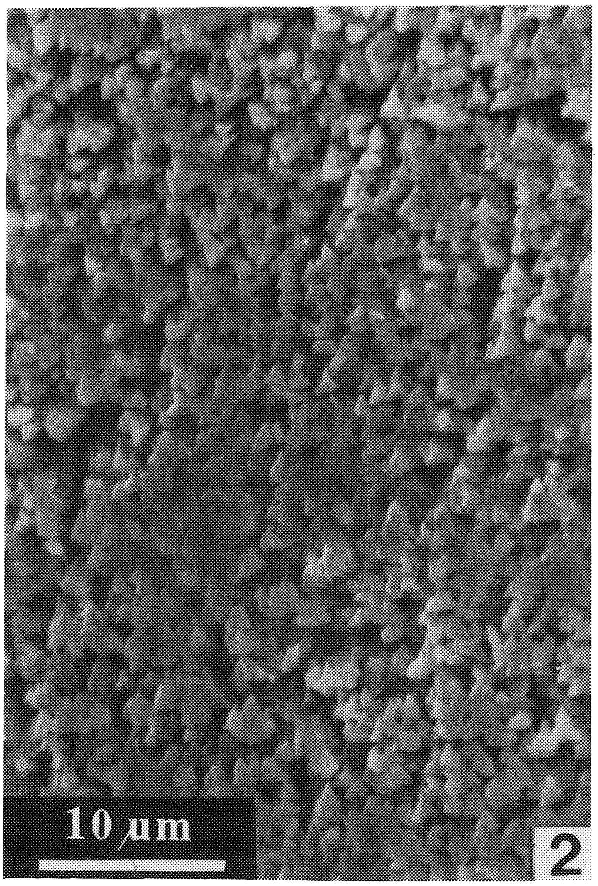
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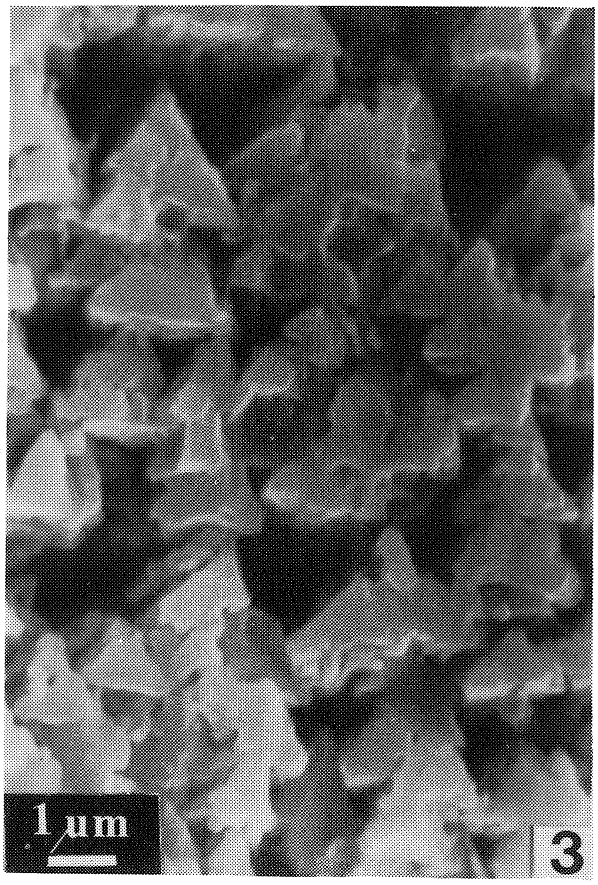
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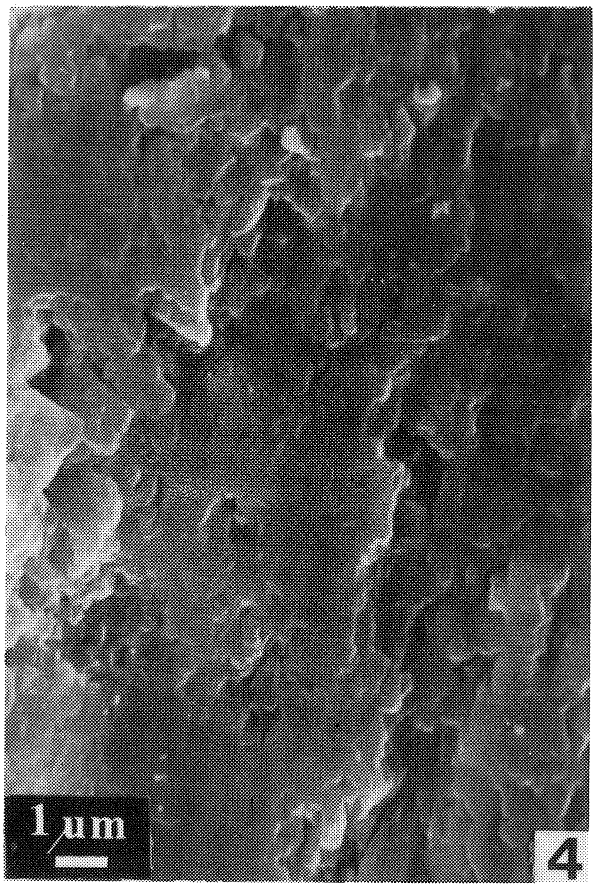
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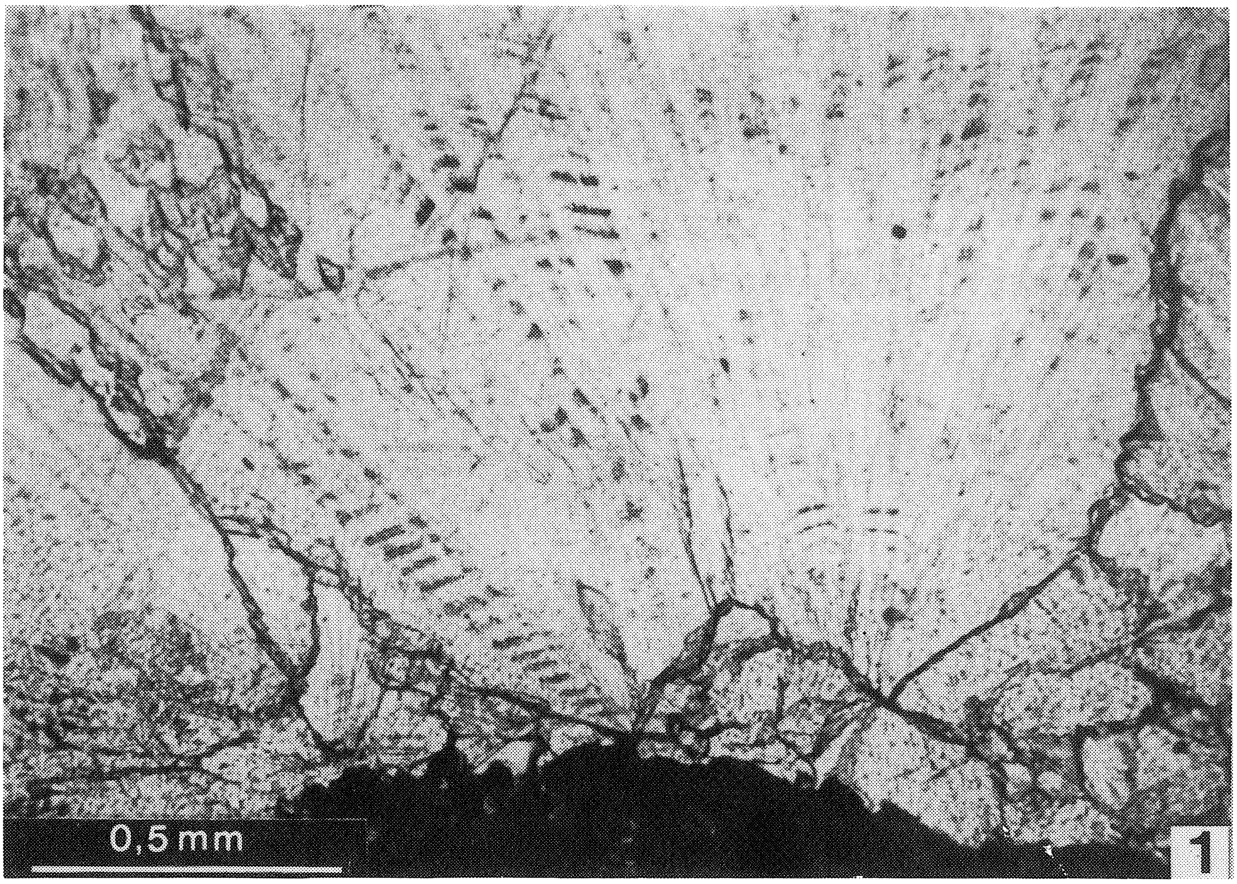
4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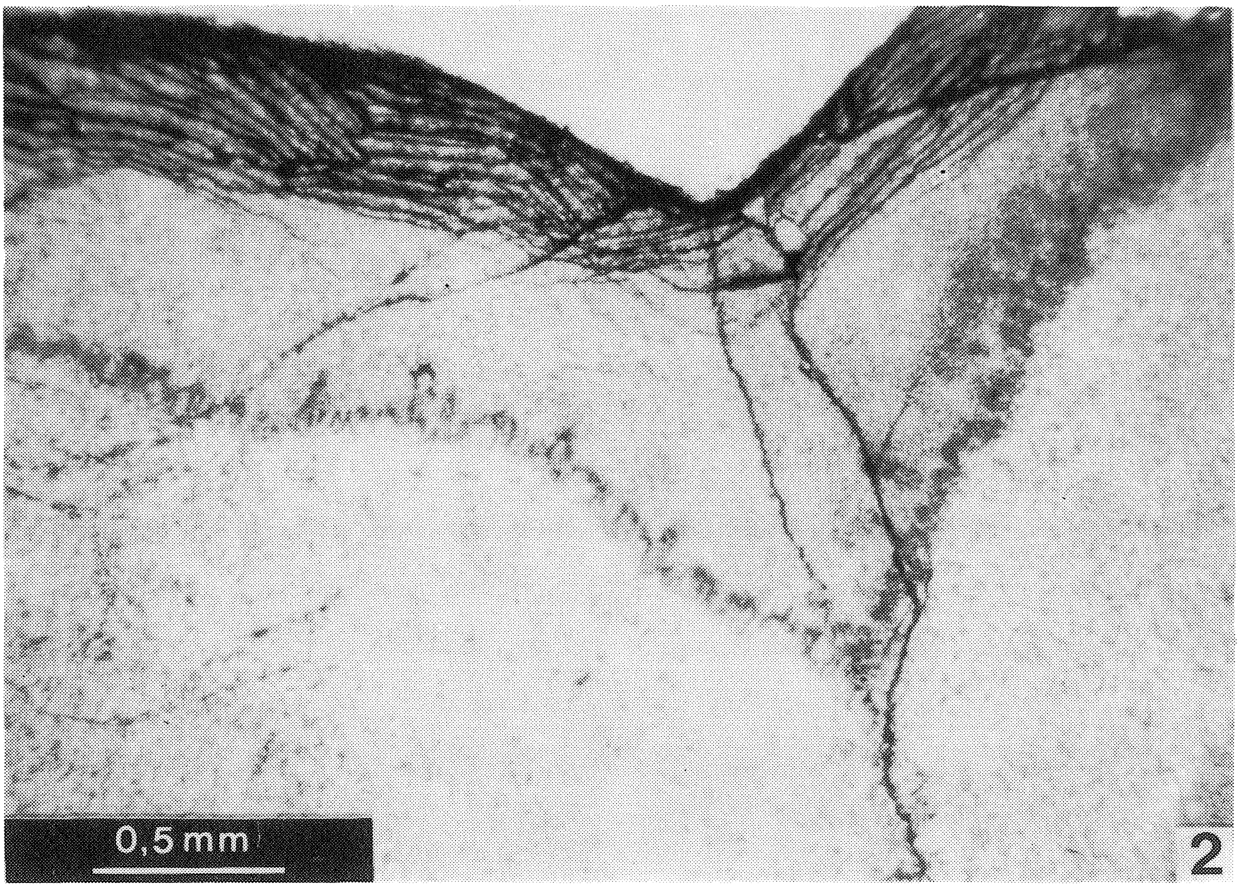
1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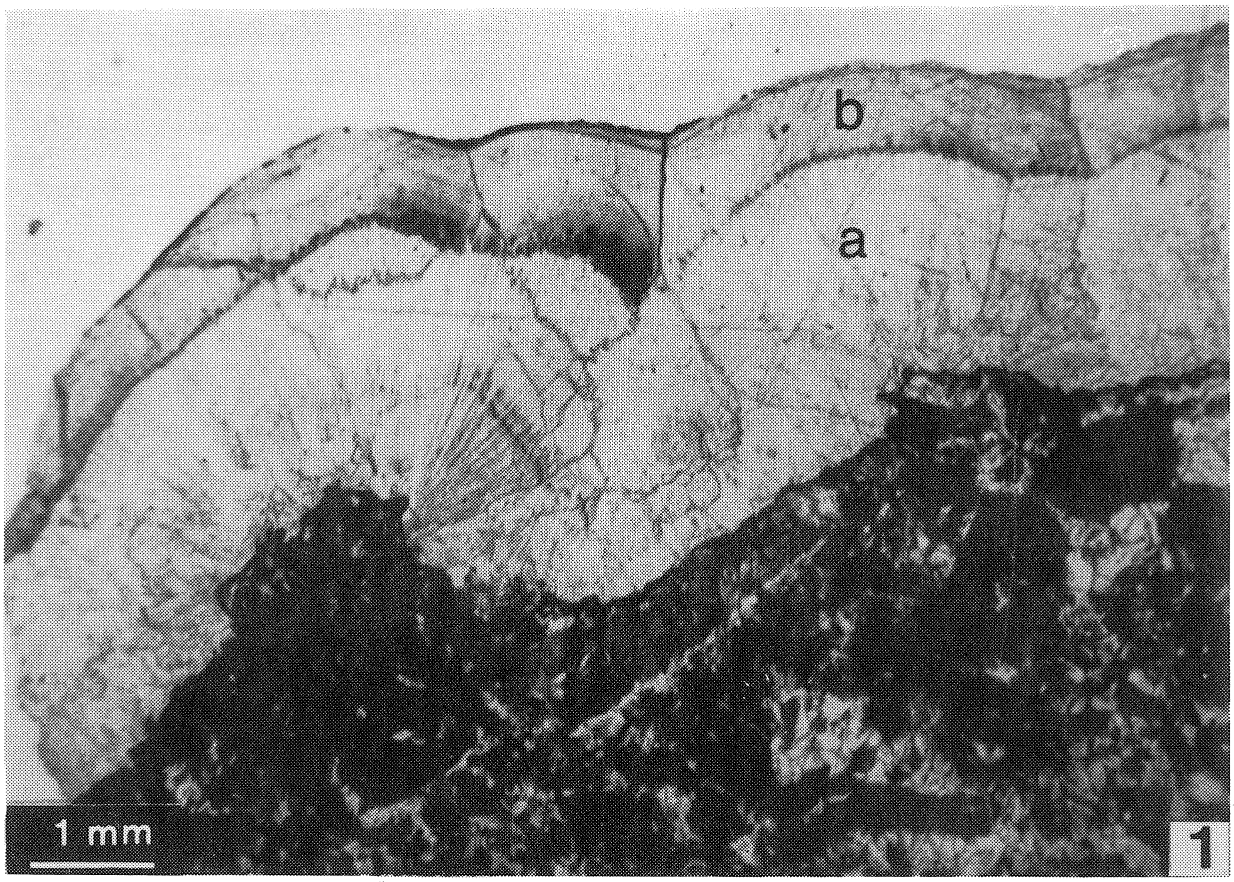
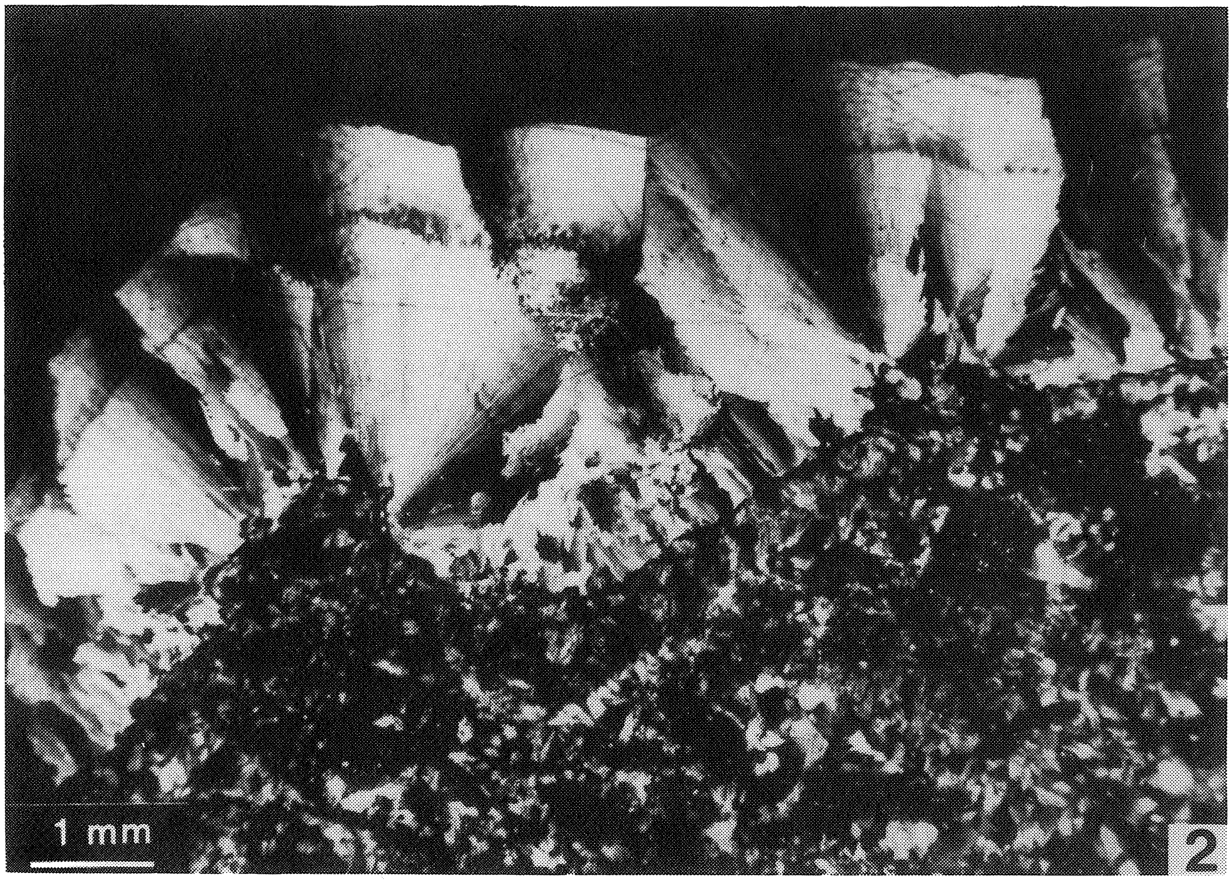
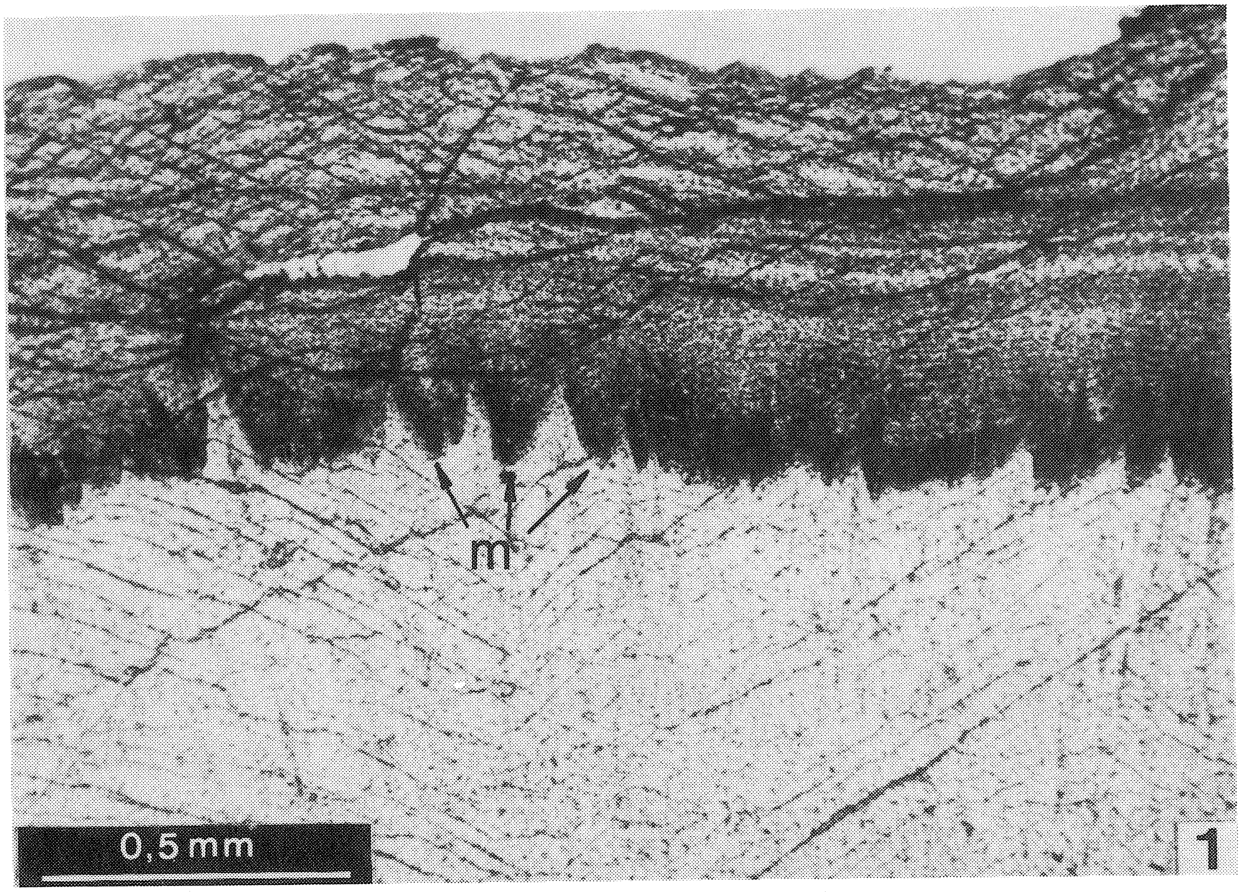

b
a
1 mm
1


1 mm
2


m
0,5 mm
1


0,5 mm
2