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GLAUCONITE FROM THE RED NODULAR LIMESTONES OF JURASSIC AGE (MANÍN GORGE, WESTERN CARPATHIANS)

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Abstract: Glauconite was formed by the diffuse impregnation of biomicrites with *Bositra* and *Globuligerina* microfacies, both in the nodules and matrix of red nodular limestones of Bathonian to Oxfordian age. The granules (aggregates) of glauconite possess dehydratation rims (voids filled by fibrous calcite) and are partly replaced by calcite rhombs. The glauconite belongs to the polytype modification 1 M; the expanding layers are absent and its structure bears an average amount of defects. According to b - parameter it may be placed among the glauconites with a relatively lower content of Fe in the octahedra.

Key words: Western Carpathians, Jurassic, red nodular limestones, glauconite.

Introduction

The glauconite granules occur in the middle part of red nodular limestones (an equivalent of the Czorsztyn Limestone Fm.) with the stratigraphic span Bathonian - Oxfordian, in the Manín Tectonic Unit, at the locality Manín Gorge near the town of Považská Bystrica, Strážov Mts., (Fig. 1). As the occurrences of glauconite in the typical facies "ammonitico rosso" are very rare (only one mention without further identification from the red nodular Hallstatt Limestone of Norian age, Rieche 1971, p. 94, was registered by us), we decided to describe it in detail.

Geological setting

The profile through the Manín Gorge was thoroughly studied by Borza (1969). The red nodular limestones

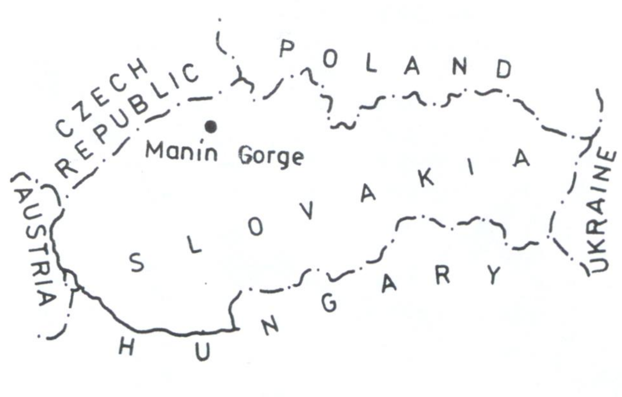

Fig. 1. Situation of the locality.

also studied by us have a thickness of about 11 m. Borza (1969) recognizes among them the following microfacies: 1. m. with filaments, 2. m. with protoglobigerina, 3. m. with radiolarians and globochets. The stratigraphic span of Bathonian to Oxfordian for the red nodular limestones was ascertained by Rakús (1977) on the basis of ammonites. Borza (1969) supposed that the glauconite occurs only in the "filamentous" microfacies; according to our results it is also present in the "protoglobigerina" microfacies with *Colomisphaera fibrata* (Nagy); these first "cadosinas" appeared in Oxfordian (Borza 1984).

The red nodular limestones are thick-bedded with a marked predominance of rosy nodules over the red matrix (Pl. I: Fig. 1). The rock can be designated according to Folk (1959) as intrabiomicrudite. The nodules with various types of microfacies are typical for intraformational carbonate breccias; the nodules were transported as intraclasts for a certain distance. The mixture of clasts proceeding from various stratigraphic horizons is typical for the condensed sedimentation. The nodules with "filamentous" microfacies are embedded within the matrix with "protoglobigerina" microfacies (Pl. I: Figs. 2, 3).

The matrix has a lower content of $CaCO_3$ (Tab. 1) and it is richer in insoluble residue: clay minerals, clastic quartz of silt size, shells of juvenile bivalves. A submarine as well as diagenetic solution (pressure solution) had to take place. The nodules are approximately isometrical, but occasionaly composite nodules containing smaller nodules occur. No disturbance of nodules by boring organisms was observed. They lack S-like narrowed ends which used be formed during the compaction (boudinage). One case of a belemnite rostrum torn to

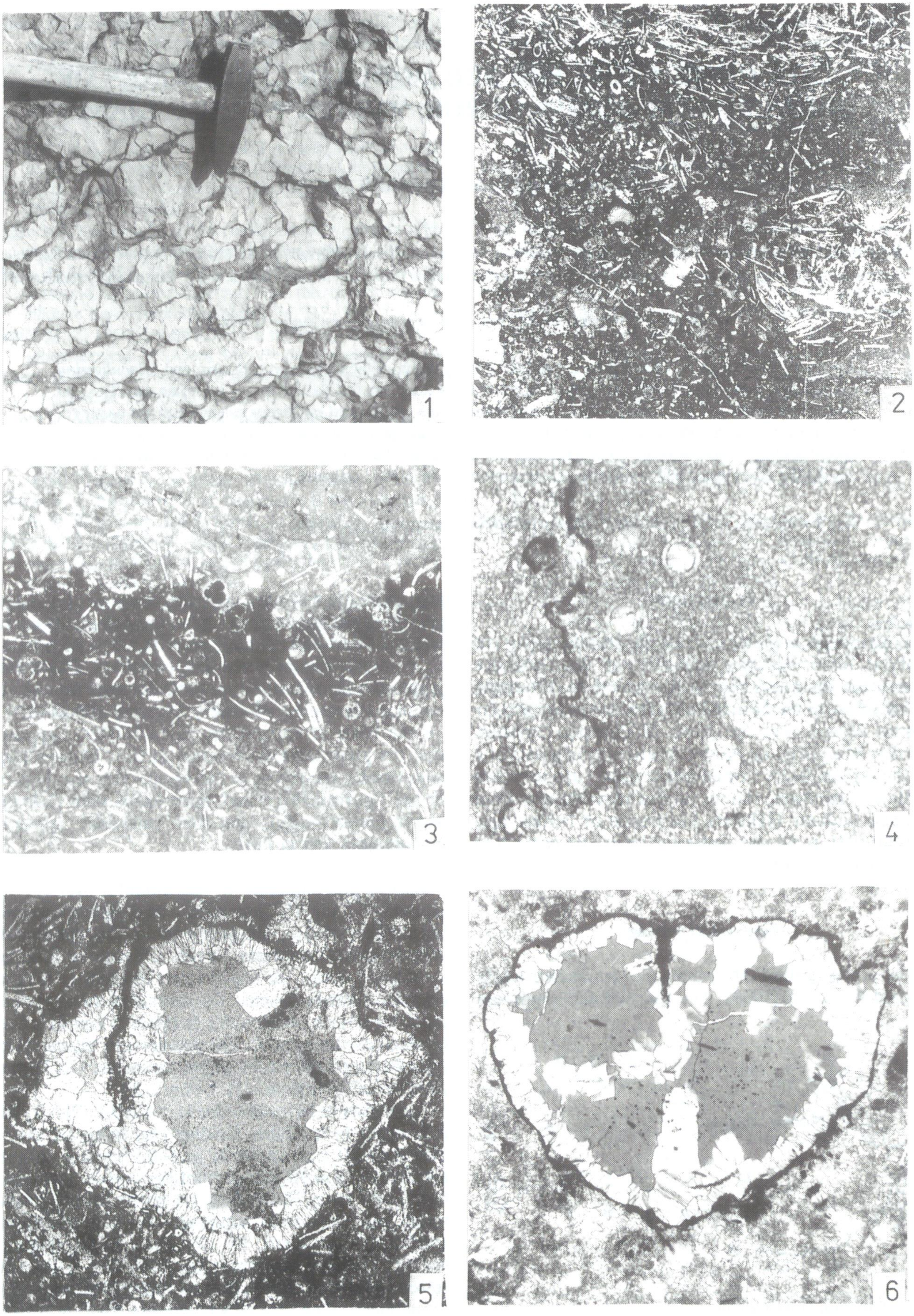
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Table 1: Chemical composition of red nodular limestones.

	CaO %	insoluble residue %
Red nodular limestone-lower part	51.09	5.82
Red nodular limestone-upper part	51.49	4.54
Separated nodule	53.87	1.69
Separated matrix	46.12	12.08

pieces by extension during the compaction with the micrite between its fragments was observed.

The following microorganisms were found in thin sections: foraminifers - *Globuligerina* sp., *Involutina* sp., *Lenticulina* sp., *Spirillina* sp., planktonic algae *Globochaete alpina* Lombard, voids after the dissolved radiolarians and spiculae of silicisponges filled by radial-fibrous aggregates of calcite, crinoidal segments with algal borings, ostracods, rare *Colomisphaera fibrata* (Nagy) - Pl. I: Fig. 4, echinid spines, small gastropods, phosphatic fish teeth, aptychi and juvenile ammonites. The presence of coccolites in the replicas of fracture planes is interesting (Pl. III: Fig. 1). The association is characterized by strong predominance of planktonic and nectonic elements.

Methods

Green glauconite nodules were extracted from the limestone by using 5 % hydrochloric acid at room temperature and sodium acetate buffer (at 70 °C). Macroscopic aggregates were separated from other insoluble remnants by hand using a magnifying glass. X-ray diffraction analysis was conducted by Philips Diffractometer PW-1710 (CuK α radiation, Ni-filter) in the interval 4 - 65 °2 Θ. One part of sample was mixed with pure quartz standard before X-ray diffraction (XRD). Quartz was used as an internal standard for measurement of b - parameter. Oriented specimens were prepared by sedimentation of the suspension (suspended using ultrasonic probe) on glass slides. They were analyzed in air dry state and after saturation with ethylene-glycol (saturated overnight at 60 °C).

Electron micrographs were taken on a transmission electron microscope (TEM) Tesla BS 500 and scanning electron microscope (SEM) Tesla BS 300. Specimens for TEM were prepared by the method of suspension dried on a carbon foil and by replica. For SEM rock chips coated with gold were used.

Plate I. Red nodular limestones with glauconite, Callovian-Oxfordian of the Manín Succession, Manín Gorge near Považská Bystrica. **Fig. 1** - Nodular limestones in outcrop. **Fig. 2** - Nodules (intraclasts) are formed by "filamentous" microfacies without *Globuligerina*; in the matrix *Globuligerina* sp. occurs. Thin section No. 2475, x12. **Fig. 3** - As previous. Thin section No. 2667, x26. **Fig. 4** - *Colomisphaera fibrata* (Nagy) proving the Oxfordian age; a larger circular void after dissolved radiolaria is filled by calcite, a microstylolite is visible. Thin section No. 2667, x145. **Fig. 5** - Glauconite granule with rim formed by radial-fibrous calcite; the rim filled a void formed by dehydratation shrinking. At the periphery of the granule glauconite was partially replaced by calcite rhombs. Thin section No. 17575, x22. **Fig. 6** - As previous, but with dehydratation cracks on which calcite rhombs were formed (veinlets of "string-pearl type"). Thin section No. 2474, x 60.

Study of glauconite aggregates under the optical microscope

The share of glauconite in the horizon with the maximal concentration of glauconite was 13.8 vol. % according to planimetric analysis (counted from 2338 points). The following minerals besides glauconite were identified under the optical microscope: clastic quartz (max. 0.13 mm), hematite pigment, very rare phosphate grains (up to 0.15 mm), exceptionally dolomite rhombs (0.02 - 0.08 mm).

The size of glauconite granules (aggregates) varies between 0.1 - 0.5 mm (maximum 3 mm). In the larger aggregates occasionaly the original "filamentous" structure of the limestone is preserved indicating replacement of the limy sediment (Pl. II: Fig. 2). Juvenile shells of bivalves and foraminifers were replaced by glauconite; they are partly rimmed by Fe-hydroxides. Glauconite is of green colour; oriented aggregates are seen in polarized light (preferential orientation of crystallites with undulatory extinction). Several grains are filled by an opaque pigment (Pl. II: Figs. 3, 4).

Almost all glauconite granules (aggregates) are bordered by rims of fibrous calcite. The larger aggregates possess larger rims (Fig. 2), very small aggregates under 0.18 mm lack the rims.

Pressure twinning of prismatic crystals in the thicker rims was observed; thus might be considered as evidence that the rims were formed before the orogenetic pressures, at least before the Upper Cretaceous. The glauconite aggregates within the solution stringers are always without fibrous rims; solution sutures probably originated before the diagenetic forming of calcite rims.

Along the inward outline, the fibrous calcite rims pass into the calcite rhombohedra pointing to the center of the aggregate (Pl. II: Figs. 5, 6). Tiny calcite rhombs were also formed along the syneretic veinlets within the glauconite (Pl. I: Fig. 6; Pl. II: Fig. 1), in the same way as by veinlets of the "pearl-string type" in the nodular cherts (Mišík 1971, Fig. 61). The glauconite aggregates in the early stage of forming provoked the recrystallization of micrite in calcite rhombs, as can be observed also in the glauconite limestones of Albian age from the locality Štiavnička (Pl. II: Fig. 7). In both cases the calcite rhombohedra do not occur in the surrounding limestone.

Calcite rhombohedra generally absent from the marine limestones with rare exceptions of dedolomitization (calcite pseudomorphs after the dolomite).

(Note: According to the present terminology "filamentous" microfacies is the microfacies with planktonic juvenile shells of *Bositra*, and "protoglobigerina" microfacies is the microfacies with *Globuligerina*).

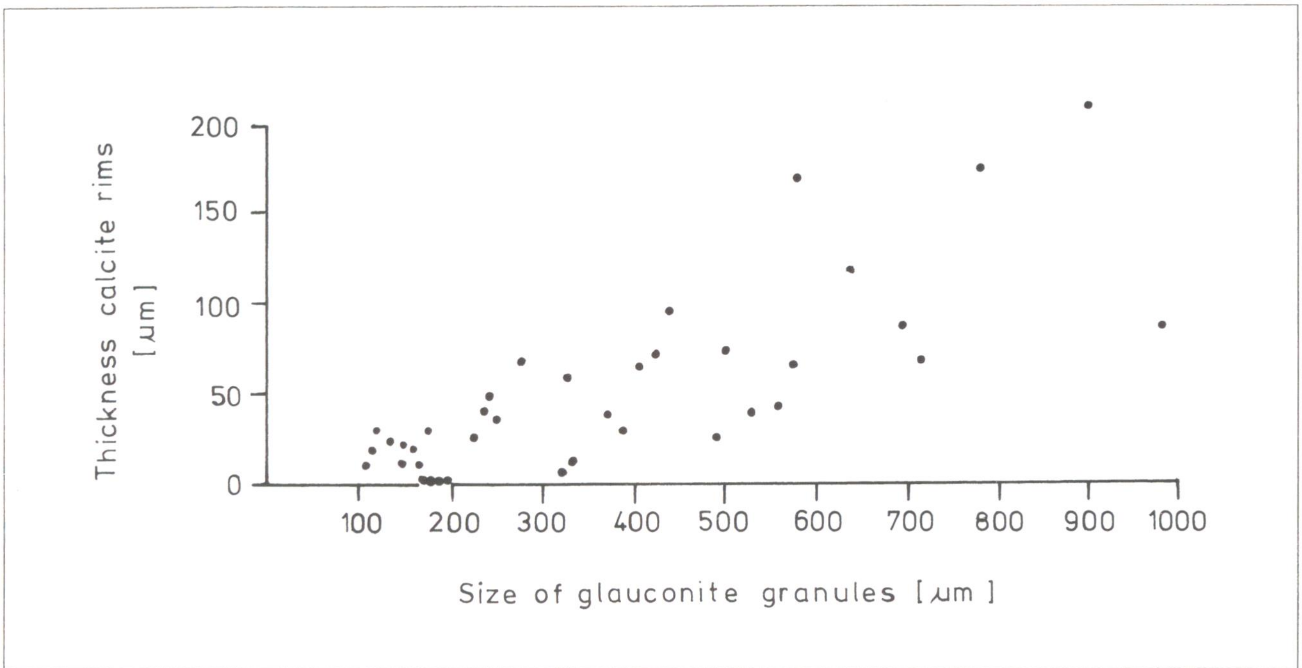

Fig. 2. Relation between the size of glauconite granule and the thickness of corresponding fibrous-calcite rims (in μm).

Mineralogical characteristics of glauconite

The green glauconite aggregates obtained from the limestone were characterized by X-ray diffraction and electron microscopy. The glauconites extracted by hydrochloric acid and acetate buffer were analyzed by XRD separately. The X-ray diffraction patterns of both types did not show any differences either in the position of reflections or in their intensities. So we suppose that the extraction process did not significantly affect the structure of the glauconite.

X-ray diffraction of oriented and randomly oriented specimens confirm that glauconite is the only layer silicate in the extracted green aggregates. Besides glauconite a small amount of quartz was detected. X-ray diffraction patterns of air dried and glycolated oriented specimens did not determine any expandable interlayers in the studied glauconite. The Ir-index (Środoň 1984), which shows the presence of even small amount of expandability was equal to 1.

Randomly oriented specimens were also used for identification of the polytype modification and defects in the structure. The polytype modification 1M of the studied glauconite was determined using 021 and 111 reflections (Fig. 2). The most sensitive reflections for determination of stacking defects are 112 and $\bar{1}12$. Their intensity decreases with the number of defects in the structure (Drits et al. 1993). On the other hand intensities of 200, 201, 131 and 130 reflections are stable even when a high number of defects are present. Comparing our XRD patterns (Fig. 3) with those calculated for different types of structural defects by Drits et al. (1993) we can conclude that the studied glauconite has mean number of structural defects. Most of them are caused by the rotation of layers (n. 60 degrees).

The mean b-parameter (mean of 5 measurements) is 0.906 nm. According to the relation between b-parameter and chemical composition of mica-like minerals (Smoliar & Drits 1988; Drits & Smoliar-Zviagina 1992) studied glauconites are of relatively low content of Fe + Mg in octahedral position.

Plate II. Figs. 1 - 4 - Glauconite granules from the red nodular limestone, Callovian-Oxfordian of the Manín Succession. **Fig. 1** - As Pl. I: Fig. 6. **Fig. 2** - Glauconite granule with remnants of "filaments" - shells of *Bositra* which evidences the replacement of biomicrite by glauconite; a part of the rim of fibrous calcite may be observed. Thin section No. 2765, x43. **Fig. 3** - Glauconite granule with pigment along its periphery. Thin section No. 2475, x17. **Fig. 4** - The same with the pigment in the central part. Thin section No. 2575, x30. **Fig. 5** - Analogic rim from the fibrous calcite grown around a serpentine fragment shrinked during the dehydratation. Pebble of Urgonian limestone of Barremian-Aptian age with dasycladaceans, containing ophiolite detritus, mainly chrome spinels in Paleogene Šambron Conglomerate; Pavlovce. Thin section No. 3894, x43. **Fig. 6** - Other example of the fibrous-calcite rim, formed around a brown granule from syngenetic non-identified clay mineral. Fragment of the Tithonian limestone in the breccia of Upper Cretaceous age; Pieniny Klippen Belt; Raciborska Valley, Orava (leg. R. Aubrecht). Thin section No. 20585, x45. **Fig. 7** - Glauconite grains provoked the calcite recrystallization in their vicinity; they were partially replaced by calcite rhombs. Limestone of the Albian age, Krížna Nappe, Štiavnička, Nízke Tatry Mts. Thin section No. 215, x22.

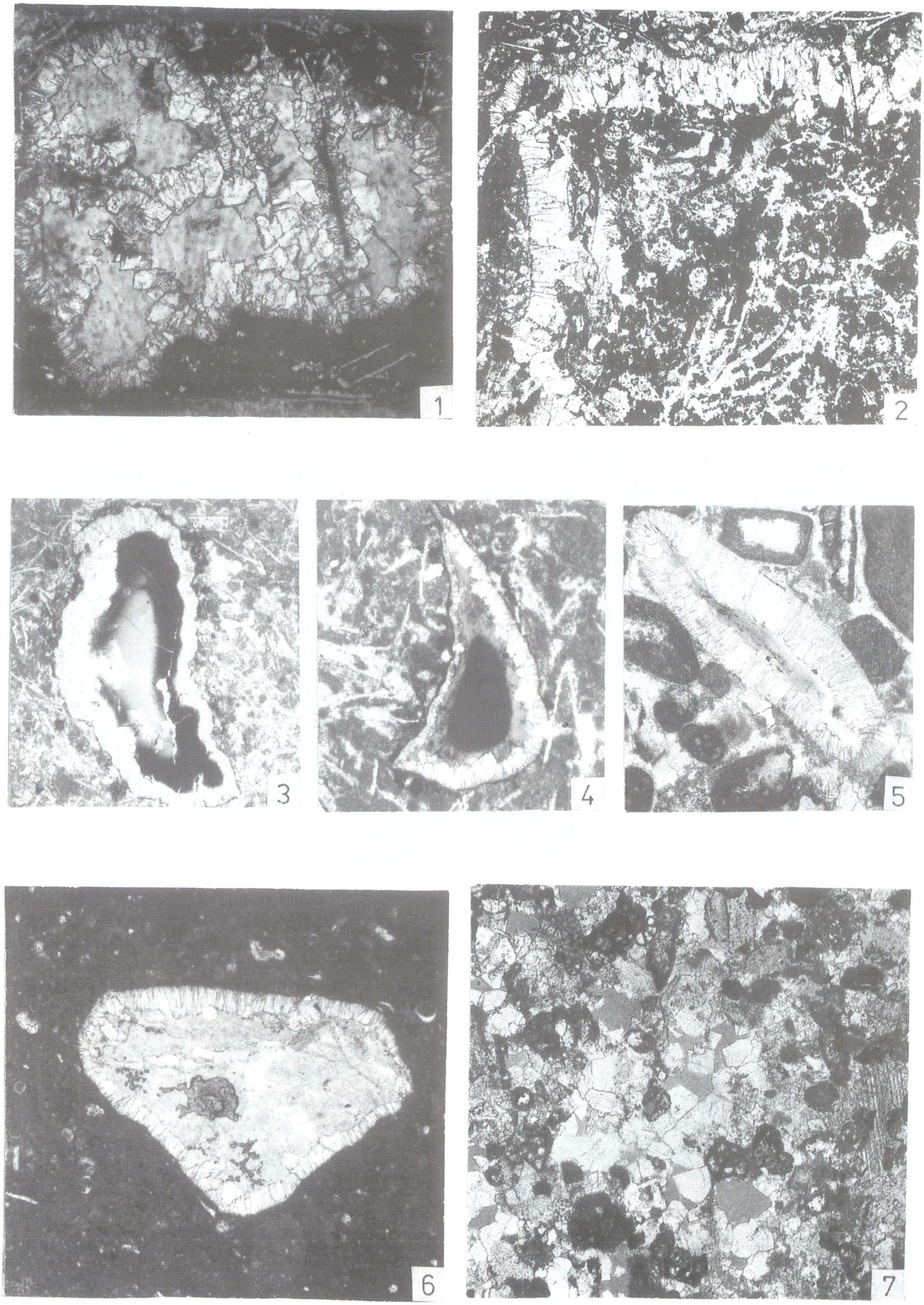
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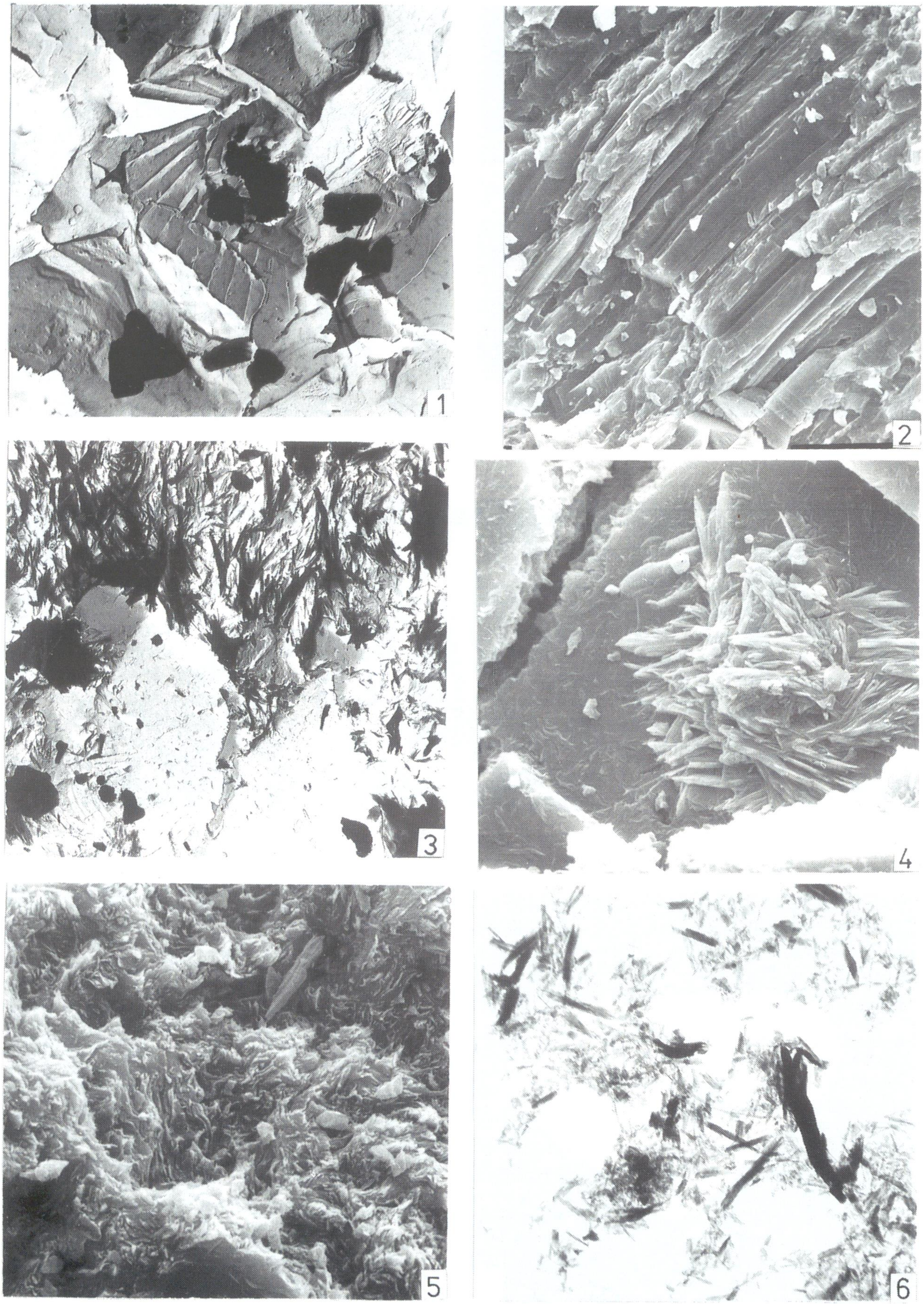
PLATE III



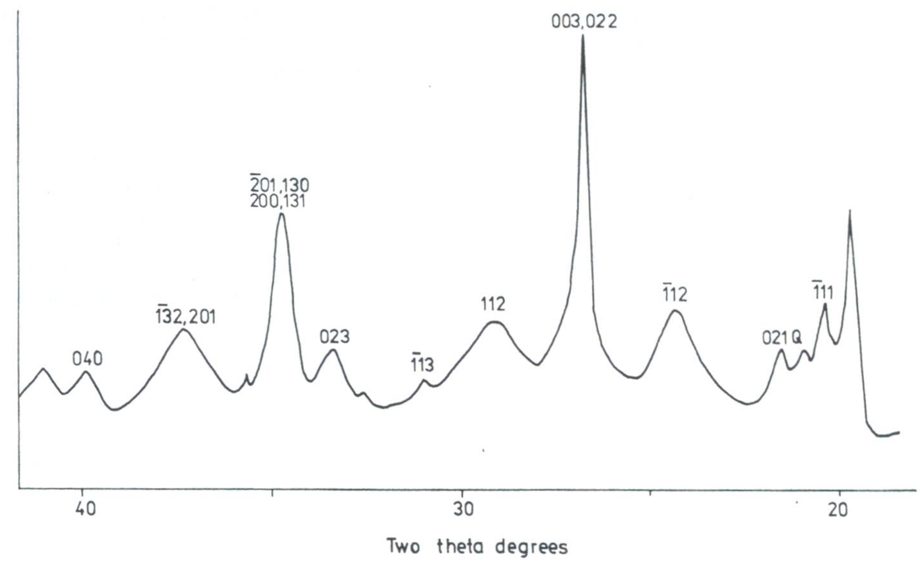


Fig. 3. X-ray diffraction pattern of the separated glauconite.

Electron micrographs obtained by TEM show that glauconite particles are mainly fine laths without significant differences in length and width. SEM micrographs document the existence of glauconitic bundles (Pl. III: Figs. 3, 4), described before by Ireland et al. (1983).

Discussion and results

We do not suppose that glauconite granules were formed at the bottom on the surface of sediments, because the glauconite aggregates do not bear traces of compaction, there are no signs of redeposition and granulometric sorting. The glauconite was not precipitated into the empty spaces, voids. It is absent in the chambers of foraminifers and pores of crinoidal segments. The voids of such form and size as glauconite aggregates do not occur in the facies of red nodular limestones. If they were present, at least a part of them should have been filled by sparite. Glauconite was formed probably by the process of diffuse impregnation.

Plate III. Fig. 1 - Coccolith *Watznauria* sp. in the red nodular limestone with glauconite; Callovian-Oxfodian, Manín Gorge. Replica from the fracture plane, x6800. **Fig. 2** - Part of the fibrous-calcite rim around a glauconite granule; SEM photo, x1500. **Fig. 3** - Sheaf-like aggregates of glauconite in the contact with calcite rhombs. Replica from the fracture plane, x6800. **Fig. 4** - The same on a calcite rhomb, x3000. **Fig. 5** - Glauconite aggregate within a granule, x5000. **Fig. 6** - Glauconite individuals in a suspension.

From the fact that the rims of fibrous calcite were formed only on the larger aggregates and are lacking on the smaller ones (<0.18 mm), it can be deduced, that the formation of rims was caused by the shrinkage, by the volume reduction of dehydratating aggregates. The loosened space was simultaneously filled by fibrous calcite, with fibres oriented perpendicularly to the surface of discontinuity (Pl. I: Figs. 5, 6; Pl. III: Fig. 2). Thin sections oriented perpendicularly to the bedding did not reveal any preferential development of rims in the upper part of aggregate (polarity criterion) what would be expected in the case of rapid shrinkage. In such a case the effect of gravitation would have led to the formation of empty space only on the upper side of aggregate. Radial - fibrous calcite rims in limestones were also formed around the shrinking aggregates of different mineralogical nature (Pl. II: Figs. 5, 6).

The fact that no expandable layers were detected in the structure of glauconite means that it belongs to the group of glauconite micas (according to the Odin & Matter 1981). We also suppose that the glauconite originated from Fe - Si - Al hydrogels in an environment of potassium rather than from smectite or mixed layer illite/smectite precursor. In the case of conversion of smectite or illite/smectite to glauconite we should determine some expandable layers in its structure. The possible origin of mica-like structure from hydrogel was also documented by experiments (Šucha et al. 1994).

In the light of the age of the studied limestones we can expect slow crystallization and dehydration of original hydrogels. This process should not produce too many structural defects.

Glauconite is formed (Odin & Matter 1981) in recent sediments at the depth of 200 - 300 m during condensed sedimentation. These conditions correspond to our interpretation of the sedimentary environment of red nodular limestones from the studied region.

According to data obtained using different methods we suppose that glauconite aggregates were originated by the diffuse impregnation and regrouping of particles.

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