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Impressions of the Biota Associated With Waterfalls and Cascades from a Holocene Tufa in the Zrmanja River Canyon, Croatia

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Abstract

The following types of calcified deposits characterize Holocene waterfall tufas in the Zrmanja river: mossy deposits, algally laminated crusts and algally coated grains. Petrological examination revealed, that abundant organic remains belonging to mosses and algae provide supporting material, over which tufa accretion takes place, leaving well-defined impressions of the biota. Postgenetic features like meniscus, isopachous and drusy mosaic calcite spar cementation, as well as aggradational neomorphism are only rarely present.

1. INTRODUCTION

The term “tufa” (“sedra” in Croatian) refers to freshwater carbonate precipitates from low-temperature springs, lakes, and waterfalls, which contain the remains of macro- and microphytes, invertebrates and bacteria. The term “travertine” refers to thermal and hydrothermal calcium carbonate deposits which lack *in situ* macrophyte and/or animal remains (FORD & PEDLEY, 1996). An increasing amount of work is being done on these rocks (IRION & MÜLLER, 1968; GOLUBIĆ, 1969; CHAFETZ & FOLK, 1984; LOVE, 1985; PEDLEY, 1990, 1992; PENTECOST, 1993; FREYTET & VERRECCHIA, 1998). Recent interest in tufas has been accelerated by suggestions that these carbonates are important archives of palaeoenvironmental and palaeoclimatic information (GOUDIE et al., 1993; PEDLEY et al., 1996; ANDREWS et al., 2000). In particular the global carbon cycle is of special interest in this regard (YUAN, 1997). Additionally, these rocks are potential data repositories for unravelling the question about the modes of calcite precipitation, especially those associated with micro-organisms (MERZ, 1992; SARASHINA & ENDO, 1998; YATES & ROBBINS, 1998; CASTANIER et al., 1999).

Tufa accumulations show widespread development throughout the Dinaric karst region of Croatia where they are associated with thick carbonate sections of Upper Triassic to Cretaceous age (HERAK et al., 1969; POLŠAK, 1979). The spectacular series of tufa dams, lakes and waterfalls of the Plitvice and Krka National Parks are of interest not only to scientists (GOLUBIĆ, 1957; PEVALEK, 1958; MATONIČKIN & PAVLETIĆ, 1963; SRDOČ et al., 1985, 1994; BOŽIČEVIĆ, 1990, 2000; HORVATINČIĆ et al., 2000) but are also of growing interest to tourists. Although the tufa accumulations, which are developed in many parts of the Zrmanja river area, have been the subject of several studies, these were mainly focused on the identification of the present vegetation (MATONIČKIN & PAVLETIĆ, 1961, 1962). There is only one research article on Holocene waterfall tufas in the Zrmanja river canyon, which establishes a model of meteoric diagenesis of tufa deposits by describing and interpreting the relationship between petrographic features and geochemical processes (PAVLOVIĆ et al., 2002). Since relatively little research has been done on these deposits, petrographic analyses have been conducted in order to provide descriptions of sampling localities, original fabric of the tufa and the effects of freshwater on these rocks.

2. GEOLOGICAL SETTING

The study was undertaken in the Zrmanja river canyon which is situated in the northernmost part of Dalmatia (Fig. 1). This area is largely composed of Cretaceous limestones (IVANOVIĆ et al., 1976) while the main portion of the clastic succession consists of Palaeogene clastic carbonates (Promina beds), Neogene clayey marls and Holocene river deposits (FRITZ et al., 1978). The morphology of the Zrmanja canyon evolved through deformation in the Eocene and Oligocene, which produced compressional structures striking NW-SE (FRITZ, 1972). The largest tributary of the Zrmanja is the Krupa river, and tufa formation readily occurs downstream from their confluence which is situated within the settlement of Sastavci. Faster precipitation

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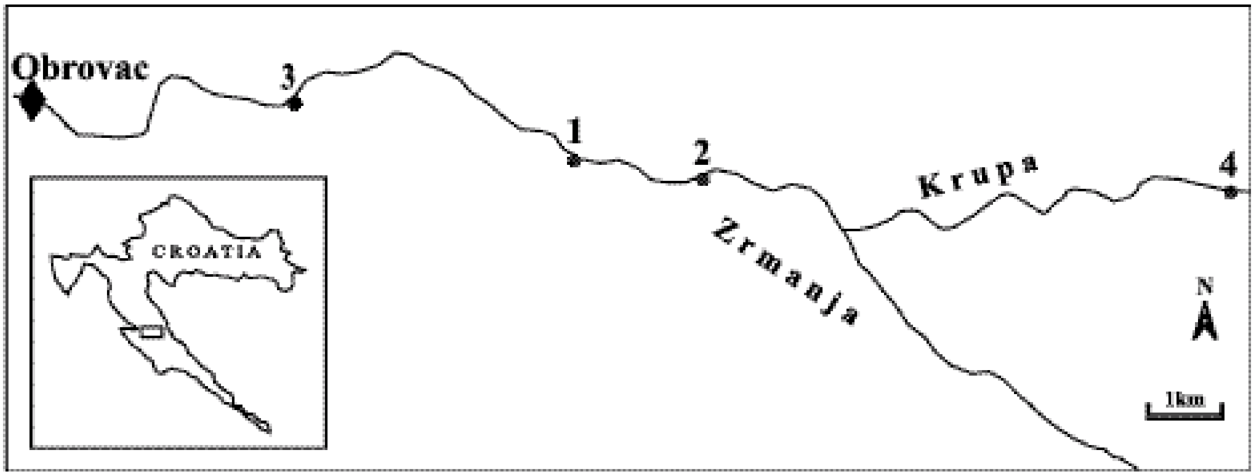

Fig. 1 Location map of the Zrmanja river canyon showing an expanded view of the study area (waterfalls: 1 - Berberi buk, 2 - Ogari buk, 3 - Jankovića buk; cascade: 4 - Krupa). Obrovac marks a downstream direction.

rates are favoured downstream, owing to increased saturation levels with respect to calcite as well as increased water flow and temperature of water (MATONIČKIN & PAVLETIĆ, 1961). Due to river incision into earlier deposited tufa, fossil tufa profiles, up to 10 m in height, are found along the river banks (FRITZ, 1972). The investigated deposits were formed during Holocene times to the present day, with the main precipitation period occuring during the Atlantic period, i.e. 5800-3200 yr B.P. (ŠEGOTA, 1968).

3. METHODS

Field-work was conducted around 3 waterfalls on the Zrmanja river, and at a small cascade on the Krupa river where tufa precipitation is presently active (Fig. 1). Recent precipitates were sampled from the river bed (in some instances from the crest of waterfalls/cascade), where a variety of macrotypes were collected. The fossil tufa samples were collected in profiles along the flanks of the Zrmanja. At each sample point full site descriptions were made, backed up with photographs. All samples were air dried and macroscopic descriptions and photographs of representative hand specimens taken. Due to their crumbly fabric it was necessary to impregnate a representative suite of samples under vacuum with epoxy resin in order to obtain standard thin sections for study using a petrographic microscope.

4. SAMPLING LOCALITIES

The investigated tufa deposits have the form of phytoherm build-ups which correspond closely with the descriptions of CHAFETZ & FOLK (1984) and PEDLEY (1990) for the waterfall or cascade environmental model of cool freshwater tufas. They are most commonly wedge-shaped with the thickest parts relating to locations of maximum turbulence such as at locations where waterfalls/cascades occur. Both inorganic (CO_2 degassing) and organically (the excretion of highly adhesive mucopolysaccharides) mediated precipitation is enhanced at these sites, though the relative abundance of each type is yet to be ascertained (EMEIS et al., 1987; LORAH & HERMAN, 1988; MERZ-PREISS & RIDING, 1999).

The streambed of the Jankovića buk (Fig. 2) waterfall (approximately 3-4 m high), which is very shallow and densely owergrown by an algal mat, has an undulatory appearance due to convex surfaces separated by narrow troughs. It is a habitat that is submerged or at least continuously kept wet and therefore heavily colonized by cyanobacteria which facilitate binding and/or precipitation of calcium carbonate onto their sheaths, thereby often forming hemispherical stromatolitic cushions. Certain species occur only under specific hydraulic conditions and their local relief can cause a rise of their own local water table level by upstream ponding, while disruption of flow enhances the degree of turbulence at the substrate/water interface. These more turbulent situations are favourable for the development of mosses which represent the next stage of a vegetational succession characteristic of tufa waterfalls (MATONIČKIN & PAVLETIĆ, 1960).

The flanks of the Berberi buk (Fig. 3) and Ogari buk (Fig. 4) waterfalls (approximately 7-8 m high) are abundantly lined by perennial higher plants (trees) which provide an ideal habitat for the development of the so called “vegetation of shade” that is extensively described by MATONIČKIN & PAVLETIĆ (1961). This vegetation of shade, densely established on waterfall faces, is represented by ecologically distinctive species of overhanging mosses which form small dams and decorative “curtains” with cavernous areas inside and underneath the tufa accumulations. Both waterfalls, in contrast to the Jankovića buk waterfall, represent progressive stages of tufa development due to the con-

Fig. 2 Jankovića buk waterfall cascading over Cretaceous limestone which is densely overgrown by an algal mat whereas mosses represent small, isolated patches at the sites of turbulent water flow.

Fig. 3 Overview of a heavily vegetated tufa dam at Berberi buk waterfall. Vigorous water flow is associated with macrophyte hummocks (mosses).

siderable growth and diversity of supporting plant material.

At the face of the Krupa cascade (Fig. 5), up to 0.5 m high, the deposit thickens both in a down- and upstream direction with regard to the streambed. In a downstream direction, along the streambed lie numerous coated grains, the overall dimensions of which are up to 15 cm in diameter.

5. ORIGINAL FABRIC

On the basis of macroscopic characteristics, such as the type of encrusted substrate (i.e. a framework of encrusted plant remains and the kind of plants which participate in rock formation), and porosity type, the studied tufas are similar in structure and composition to deposits reported by IRION & MÜLLER (1968) and LOVE (1985). Accordingly, three major morphologies of tufas can be distinguished in this active system: 1) encrusted mossy deposits, 2) algally laminated crusts, and 3) algally coated grains. Nevertheless, an attempt at classifying samples has proven to be a problem. Investigated deposits tend to exhibit a great diversity of structures, textures, morphologies and constituents, differing very much from deposit to deposit.

Since aquatic mosses are ubiquitous at sites of water turbulence, they occupy a substantial part of the tufa waterfalls and constitute the bulk of the studied deposits. Due to the macroscopic dimensions of these plants, their moulds (Pl. 1/1) are readily visible in the rock compared to algal morphologies. The overall framework of the deposits is provided by elongated, parallel stems whereby the 0.1-0.3 mm diameter holes (stem moulds) are formed, the orientations of which range from vertical to horizontal. Occasionally, up to 2 cm long cavities are present. Most of the specimens are extremely friable, and brown to light brown in colour. In thin-section, encrustations consist of microcrystalline low-magnesian calcite (PAVLOVIĆ et al., 2002) composed of peloidal micrite that grow upon all exposed surfaces resulting in a highly porous (up to 75% porosity) fragile structure (Pl. 1/2). Encrusting crystals very often surround the mosses in a concentric pattern that closely fit the morphology of their stems. These are responsible for the preservation of well-defined moulds after plant decay (Pl. 1/3). The same arrangement is produced on the protonema (Pl. 1/4) which represent the first stadium of the growth of mosses (PAVLETIĆ, 1968). This kind of precipitation is attributed to the photosynthesis-respiration plant cycle (GOLUBIĆ, 1973) but frequently is enhanced by prokaryote-microphyte biofilms which colonize the mosses (PEDLEY, 1992). The female plants can produce a sporophyte plant composed of a foot, seta and capsule; the latter is a distinguishing feature between genera and species (PAVLETIĆ, 1968). With progressive encrustation, the mosses begin to decay turning reddish-orange (Pl. 1/5) and finally black (in plane light).

Algally laminated crusts frequently form stromatolites in the deposits. They consist of alternating laminations paralleling the substrate, with individual laminae

Fig. 4 A typical waterfall site (Ogari buk) showing the large cavity (centre) developed behind the overhangs. A series of moss-covered cascades develop on the upstream side of waterfall.

Fig. 5 Overview of the Krupa cascade (up to 0.5 m in height) that is largely devoid of macrophytes. Submerged algally coated grains are situated on the downstream side of the cascade.

ranging up to 4 mm in thickness (Pl. 1/6). Such bacterioherms are almost totally lacking mosses and higher plants. They are undulatory at both large and small scales, and alternate with horizons containing small lenticular openings caused by degradation processes or faunal (burrowing) activity. The crusts mainly display dense, micritic features but porous, friable deposits are also likely to occur. On a microscopic scale, these rocks are characterized by thin internal micritic and microsparitic laminations (Pl. 2/1) as a result of continuing encrustation by algal filaments which are approximately up to 0.005 mm in diameter. Most of these filaments are intertwined or parallel. It is possible to interpret a dense lamina (Pl. 2/2), composed of micrite-encrusted filaments, as a consequence of rapid spring growth and, a more porous lamina caused by summer/autumn, decreased algal growth (IRION & MÜLLER, 1968; LOVE, 1985; JANSSEN et al., 1999). These investigators have suggested that this laminated fabric should be explained by seasonal variation in growth of the plants and especially cyanobacteria and algae. Some algal colonies form hemispherical to subspherical masses of radiating filaments coated with micrite (Pl. 2/3). Complex diagenetic recrystallizations can lead to subhedral or euhedral sparite crystals (Pl. 2/4) which form fanlike or radial palisadic structures (KENDALL & BROUGHTON, 1978; BRAITHWAITE, 1979; CHAFETZ et al., 1985; FREYTET & VERRECCHIA, 1998, 1999). It is explained by the fact that many small nuclei, as a result of high degrees of supersaturation in the vicinity of metabolising cells, can coalesce primarily along the *c* axis with little lateral growth and generate the large columnar crystals. However, some of these spar crystals are almost certainly produced by obligatory calcifying cyanobacteria, especially members of the *Rivulariacea* (PEDLEY, 1992). In this case the mechanism of growth of calcite crystals is interpreted in the scope of biological mediation related to metabolism.

Since tufa-forming environments are characterized by the highly complex interplay between organic and inorganic processes, it is possible to find that the dominance of mosses and algae vary greatly and are intermixed in differing proportions. Some specimens (Pl. 2/3), classified as mossy deposits according to their structure, have conspicuously low porosity due to the fact that calcite is associated with abundant algal and microbial communities attached to the moss stems and leaves; this feature is reported by many investigators (e.g. PENTECOST, 1987; WINSBOROUGH & GOLUBIĆ, 1987; PEDLEY, 1992). Also, a large proportion of cyanobacterial biomass can host scattered occurrences of mosses (Pl. 2/1). It can be said that the intimate association of procaryotes, macrophytes, microphytes and fauna actively create their microenvironment in order to keep up with individual ecological requirements (DRYSDALE, 1999). For these reasons simultaneous build-up and decomposition of carbonates can produce varied and often complex patterns of encrustation (Pls. 1/2, 2/1).

Algally coated grains are also common. These take the form of oncoids formed from various particles which may be coated in the streams (Pl. 2/5). Many nuclei are clasts of Cretaceous limestone up to 15 cm in diameter, while micritic envelopes developed due to the process of biogenic carbonate precipitation as described by SCHNEIDER (1977). The carbonate substrate (limestone) had been attacked by endolithic microorganisms the activity of which has left recognizable boring patterns (Pl. 2/6). The following microbial colonization of the surface of the nucleus produced concentric banding with the cortices similar in thickness to the laminations seen in the algal crusts. In most cases, the upper portion of a clast has a soft, bumpy surface while the bottom of the clast has a hard, smooth surface. In addition, the cortices are thinner along the base of clast due to the inability of the larger grains to roll. In thin section, the cortical laminations consist of two alternating layers (Pl. 2/2): (1) elongate spar crystals, cross cut by V-shaped clumps of filamentous cyanobacterial "bushes", and (2) individual subparallel cyanobacterial filaments calcified by micrite. This feature is almost identical to that recorded by LOVE (1985).

6. EFECTS OF FRESHWATER ON TUFA

A low degree of diagenetic alteration of primary tufa fabric is one of the main characteristics of investigated Holocene tufas. This is due to the presence of an insoluble residue, which greatly retards textural alteration, and due to the fact that the studied rocks are young tufas (PAVLOVIĆ et al., 2002). Consequently, there is very little recrystallization or carbonate cement development.

Occurrences of diagenetic cementation are present in samples either characterized by a combination of large cavities and/or a low insoluble residue content (Pl. 3/1, 3/2) or by sampling sites related to places with vigorous water flow (Pl. 3/3). Meniscus texture (Pl. 3/2), which is a common feature in the vadose zone (CHAFETZ et al., 1985), is composed of anhedral and/or rhombohedral crystals, generally clear in appearance, ranging in size from 0.01 mm to approximately 0.05 mm. Isopachous and drusy mosaic cements are commonly associated with the phreatic zone (CHAFETZ et al., 1985). Some pores are lined with equant rhombohedral or bladed crystals of isopachous cements (Pl. 3/3) up to 0.1 mm in length and up to 0.05 mm in width. Others are filled with drusy fabric (Pl. 3/1) displaying an increase in crystal size (up to 0.1 mm) away from the substrate or cavity wall. We ascribe large, well-ordered spar crystals (Pl. 3/1) to slow, inorganic precipitation inside of the macrophyte boundary layer where water flow is reduced; an in-depth description of this occurrence is provided in PEDLEY (1992). This study has shown the complex cementation pattern that is characteristic for non-marine settings, indicating a range of microenvironments in which formation occurs. These are in agreement with the work of CHAFETZ et al. (1985).

After formation, some of the algally laminated crusts can undergo aggradational neomorphism (a type of recrystallization) that results in laminated, coarsely crystalline, neomorphic crusts. The specimen which is ascribed to this process is heavier, harder, less porous and more massive with regard to the porous, light tufa (Pl. 3/4). We believe that diagenesis commences inside of V-shaped algal bushes (Pl. 2/2) which are encased within a micritic or sparry calcite phase; the process is explained in detail by LOVE & CHAFETZ (1988). BRADLEY (1929, in LOVE & CHAFETZ, 1988) attributed the cause of the process to ammonia from decomposing algae. This sparitization occurs at the expense of the overlying micritic crystals (Pl. 3/5) and gives rise to the disappearance of the original micritic phase and organic filaments. With time, it results in continuous layers composed almost entirely of coarse, columnar crystals. In the literature, different hypotheses are put forward to explain such sparite crusts, i.e. the question as to whether these deposits represent diagenetic and recrystallized features or physicochemical precipitates remains unresolved (LOVE & CHAFETZ, 1988; PEDLEY, 1992; JANSSEN et al., 1999; FREYTET & VERRECCHIA, 1999). Also, this polycyclic isopachous fringe sequence is explained by biological mediation associated with a procaryote-microphyte biofilm producing peloidal micrite and inorganic precipitation resulting in pallisade spar (PEDLEY, 1992; FORD & PEDLEY, 1996). PAVLOVIĆ et al. (2002) favour neomorphism, as explained by LOVE & CHAFETZ (1988), based on the overall geochemical evidence.

In close proximity to the large pores the coarsening of crystal sizes in micrite is common because of enhanced meteoric diagenesis (Pl. 3/6).

7. CONCLUSION

Phytoherm deposits abound in the studied sites, and show preserved organic structures as well as well-defined impressions of their shape when in life position. The fairly rapid development of tufa build-ups, at the Ogari buk and Berberi buk waterfall sites, is greatly enhanced by the vigorous growth of macro- and microphytic vegetation. Based on macroscopic observation, the predominant types of encrustation are: (1) encrusted mossy deposits, (2) algally laminated crusts, and (3) algally coated grains. Encrustations on mosses are composed of peloidal micrite which often mimic their morphology. Algal encrustations are characterized by thin alternating micritic and microsparitic/sparitic laminae. With increasing age the deposits show postgenetic transformations which result in meniscus, isopachous and drusy mosaic cement growths that are encountered primarily in open-textured fabrics. Specimens belonging to algally laminated crusts have undergone aggradational neomorphism which resulted in the development of a dense crust composed of laminae containing coarse, columnar crystals.

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PLATE I

1 Hand specimen of a typical tufa-encrusted mossy deposit displaying a high degree of porosity and a lace-like structure. Jankovića buk waterfall. Sample 3/1.

2 Thin-section photomicrograph (crossed nicols) of a mossy tufa showing micritic encrustations of micro- and macrophytes. Berberi buk waterfall. Sample 1/2.

3 Thin-section photomicrograph (crossed nicols) of a transverse section through a mossy tufa displaying moulds of moss stems encrusted by micritic and microspar layers. Krupa cascade. Sample 4/4.

4 Thin-section photomicrograph (plane light) of a mossy tufa showing moulds of protonema encrusted by micritic aggregates. Jankovića buk waterfall. Sample 3/7.

5 Thin-section photomicrograph (plane light) of a mossy tufa displaying remains of a moss stem. Krupa cascade. Sample 4/4.

6 Hand specimen of a typical porous, algally laminated crust. Jankovića buk waterfall. Sample 3/3.

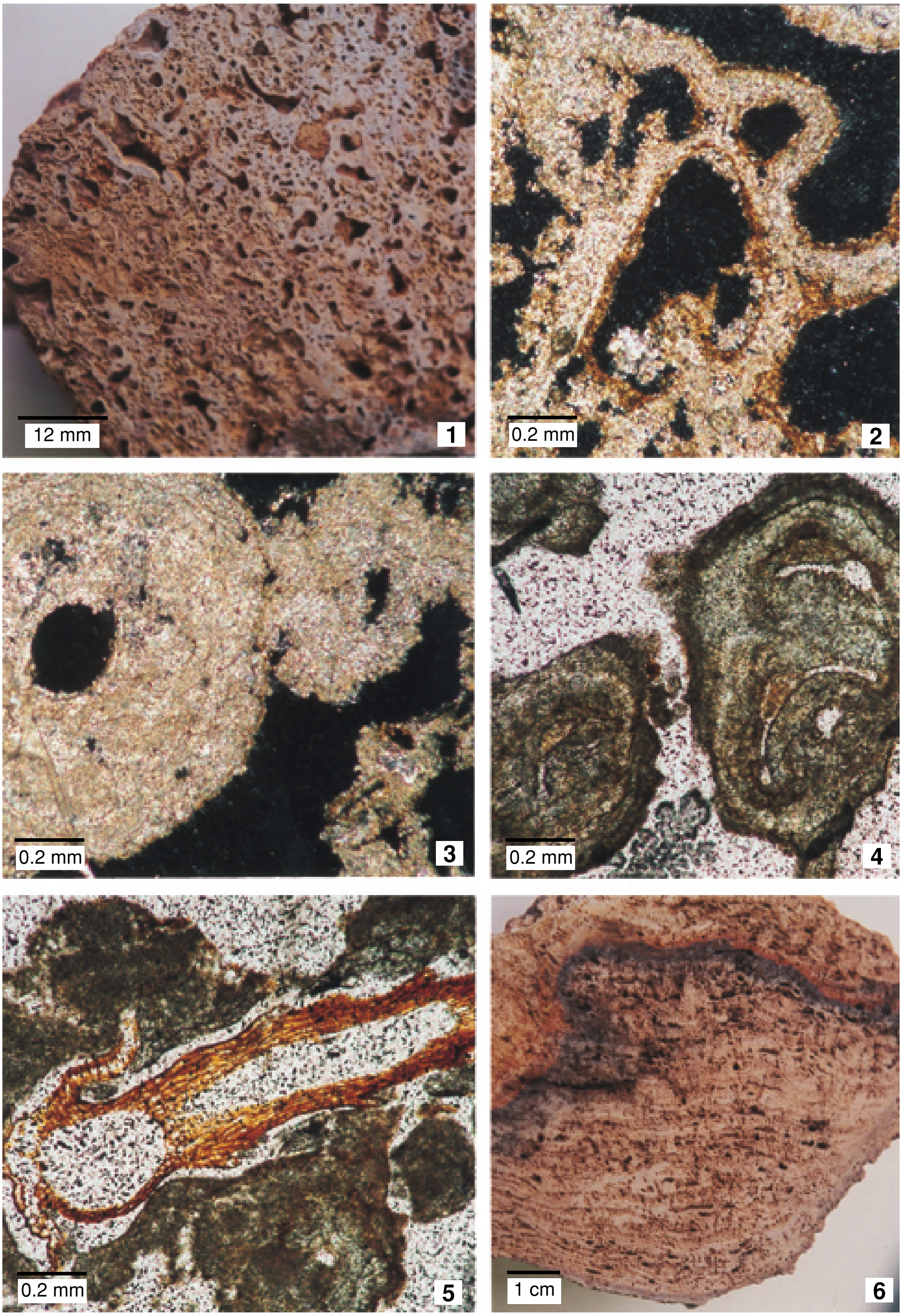
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PLATE II

1 Thin-section photomicrograph (crossed nicols) of an algally laminated crust showing well developed seasonal growth-layers. Upper side shows an encrusted moss stalk. Jankovića buk waterfall. Sample 3/3.

2 Thin-section photomicrograph (plane light) of an algally coated grain. Lower side shows “bushy” algal filaments encased in elongate crystals (visible only under crossed nicols) of spar. Upper side shows a porous layer composed of parallel filaments encrusted by micrite. Krupa cascade. Sample 4/2.

3 Thin-section photomicrograph (crossed nicols) of a transverse section through a subspherical algal colony; the hollows are the moulds of the filaments. Ogari buk waterfall. Sample 2/6.

4 Thin-section photomicrograph (crossed nicols) of branching algal colony (*Oocardium*?) showing that several filaments, branching from the base upwards, are calcified in a bladed monocrystal. Ogari buk waterfall. Sample 2/4.

5 Hand specimen of an algally coated grain with a nucleus of Cretaceous limestone. Cortices are another version of algally laminated crusts. Krupa cascade. Sample 4/2.

6 Thin-section photomicrograph (crossed nicols) of an algally coated grain where the lower side represents a limestone fragment with boring tunnels of an endolithic alga. Krupa cascade. Sample 4/2.

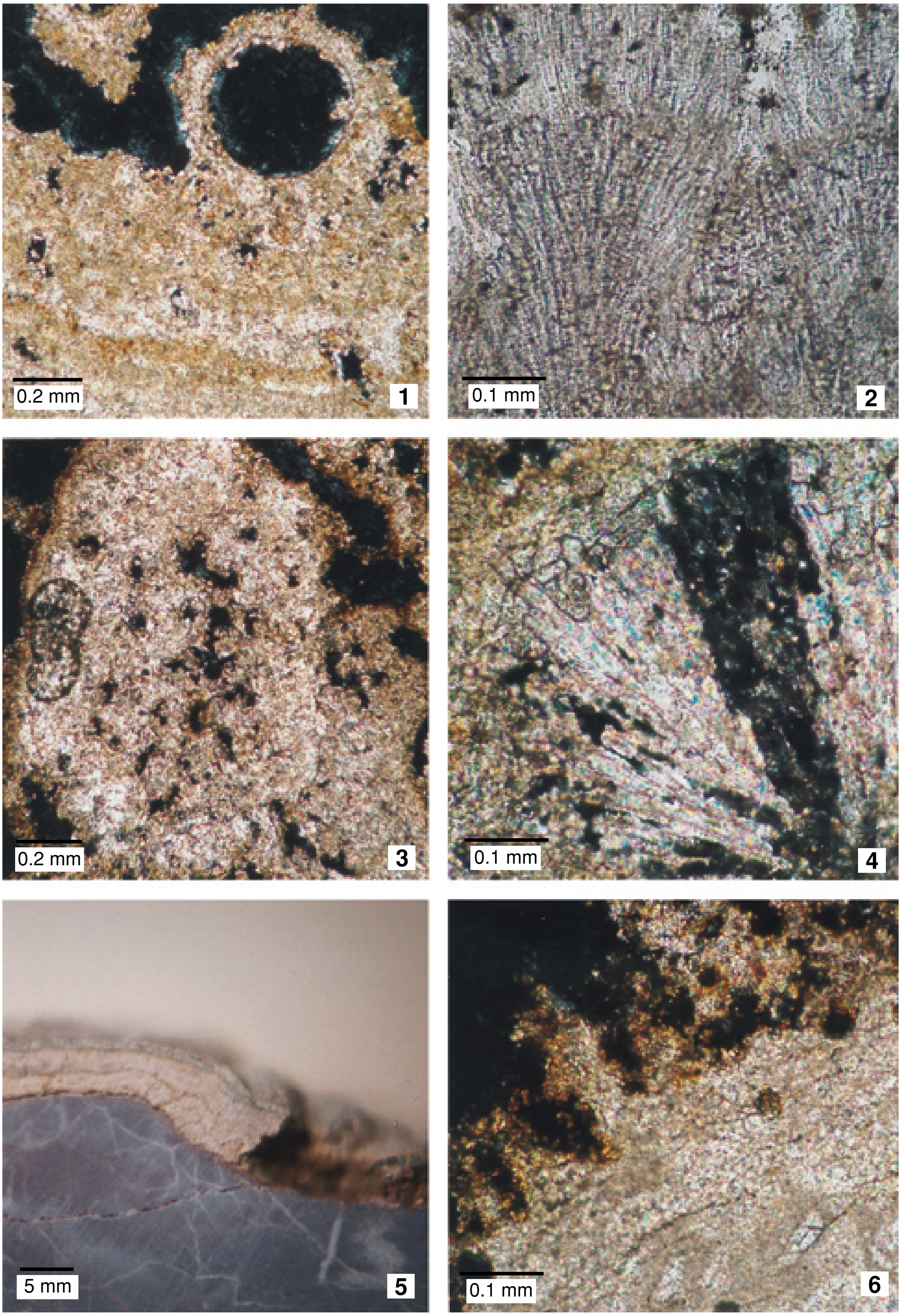
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PLATE III

1 Thin-section photomicrograph (plane light) of drusy mosaic composed of euhedral calcite crystals that increase in size toward the centre of the cavity. Jankovića buk waterfall. Sample 3/7.

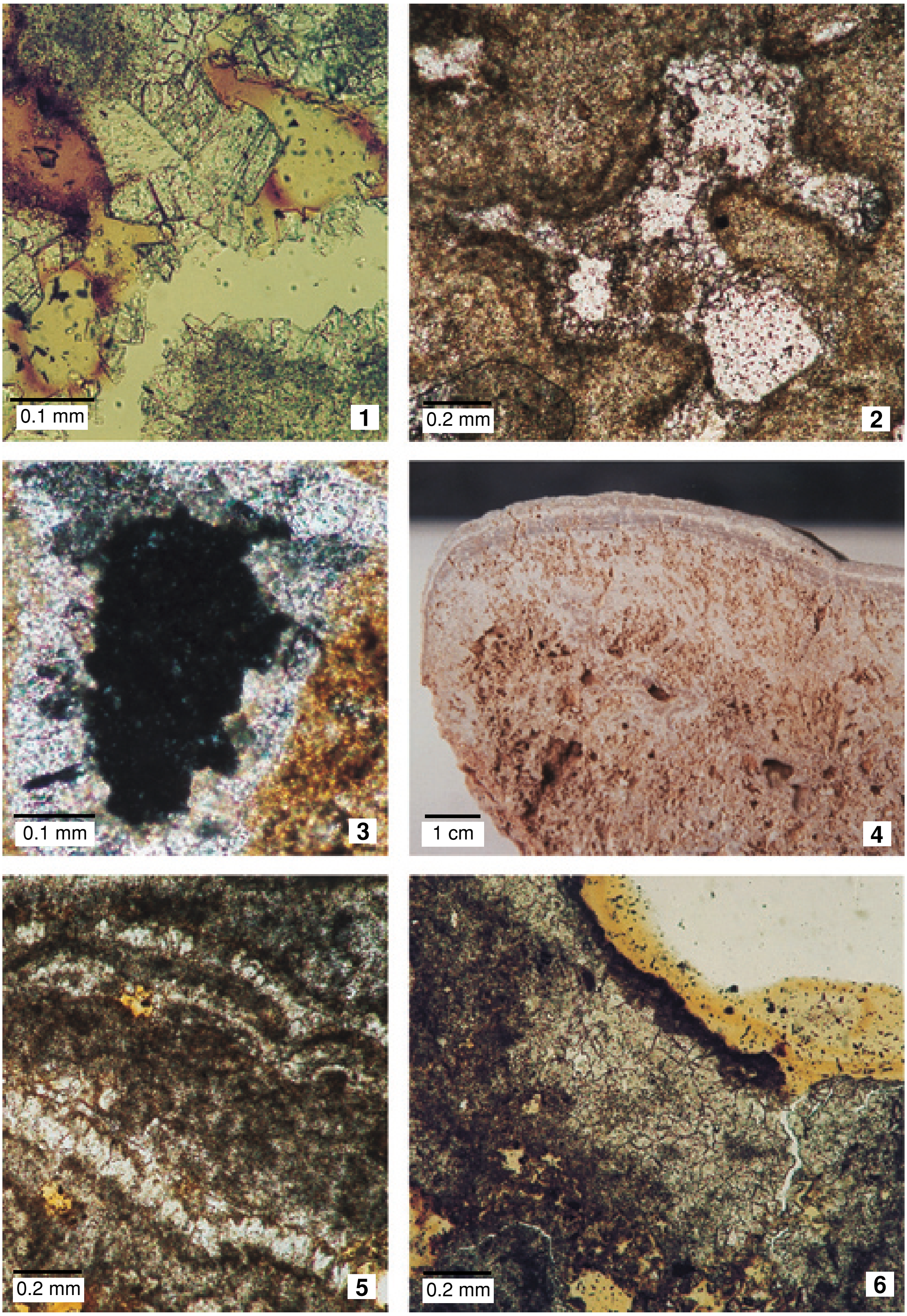
2 Thin-section photomicrograph (plane light) showing clear, rhombohedral crystals composing meniscus cement. Jankovića buk waterfall. Sample 3/7.

3 Thin-section photomicrograph (crossed nicols) showing isopachous rim of equant and bladed spar crystals. Berberi buk waterfall. Sample 1/2.

4 Upper side of this hand specimen represents stromatolitic encrustation showing progressive diagenesis, enveloping an encrusted moss substrate. Jankovića buk waterfall. Sample 3/6/1.

5 Thin-section photomicrograph (plane light) of polycyclic spar/micrite couplets. Spar crystals extend upward through micritic material by aggradational neomorphism. Jankovića buk waterfall. Sample 3/6/1.

6 Thin-section photomicrograph (plane light) shows micritic groundmass. The part which is closely associated with the cavity has been recrystallized due to enhanced circulation. Jankovića buk waterfall. Sample 3/1.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