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Travertines and calcareous tufa deposits: an insight into diagenesis

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ABSTRACT

Travertines and calcareous tufa are porous deposits formed by interactions between ambient precipitation of calcium carbonate and resident organisms under different temperature regimes. The distinctions between travertine as thermal spring deposits and calcareous tufa (Kalktuff) as deposits in the springs and rivers at ambient temperatures are fluid. Both represent end points in bio- and physico-chemical calcification processes across a broad gradient of temperature, mineral composition and ion saturation levels. Ecological preferences of micro- and macroorganisms in travertine depositional systems result in the re-distribution of water flow, modification of the landscape and its ecology. The resulting sedimentary structures include new environmental settings with different and diversified biota. They also include different microenvironments of diagenesis with different timings of the processes involved. Conditions in modern ambient temperature travertines of the Plitvice system of lakes and waterfalls are compared with the similar, ancient system of Rocchetta a Volturno, in the central Apennines. Diagenetic alterations are described and illustrated starting with biologically identified primary deposits.

Keywords: carbonate, diagenesis, freshwater, karst, micrite, precipitation, sparite, tufa, travertine

1. INTRODUCTION

The term travertine has been used for centuries for porous building stone, desirable for its structural quality especially for the construction of vaults and arches (PENTECOST, 2005). The term derives from the Latin *lapis tiburtinus* in reference to the town Tibur, today's Tivoli, near Rome, Italy. The term was also used to designate inscriptions in stone of that origin. The porous stone of Tivoli is still being quarried today, most of it originating from thermal springs of the area. The use of the name in geology has often been associated strictly with thermal spring deposits, whereas its ambient water counterpart is usually referred to as calcareous tufa (German: *Kalktuff*, Croatian: *sedra*). This distinction is difficult to maintain, because hydrothermal springs, range in temperature, and so do the processes of mineral precipitation. As thermal waters cool, carbonate precipitates change from predominantly aragonitic to calcitic and they become rapidly associated with a different microbiota of increasing diversity. Travertine as building stone includes both hot spring and ambient temperature deposits. Thus, for ecological as well as historic reasons, we prefer to use the term travertine for a range of sedimentary processes along the gradient of different temperatures, as has been the practice in the studies of the ambient temperature system of the Plitvice Lakes (SRDOČ et al., 1985). Deposition of travertines and calcareous tufa in the region occurred at different times during interglacial and postglacial periods and remained preserved in different stages of development (GOLUBIĆ, 1969). A review of travertine and tufa deposits of the world, listing occurrences in 22 European countries, is given by FORD & PEDLEY (1996), and they are common in the karstic region of Croatia (e.g. PRIMC-HABDIJA et al., 2001; PAVLOVIĆ et al., 2002). Travertines and calcareous tufa are considered excellent indicators of past climate conditions (e.g. PEŃA et al., 2000), an interest that has been recently triggered by the concerns about climate change. Stable isotope and trace element analyses address these topics (LOJEN et al., 2004; KELE et al., 2006; ANZALONE et al., 2007). Diagenetic alterations of travertine deposits depend on microenvironmental influences and constitute a background relevant to the interpretation of the isotopic record (SRDOČ et al., 1983; ANDREWS et al., 1997). This work studies the formation and early diagenesis of mineral products in biologically influenced sedimentary processes by recent-to-fossil comparisons, with examples from the Plitvice travertine depositional system and from fossil travertine deposits of the river Volturno, in the Central Apennines (GOLUBIC et al., 1993).

2. MATERIALS AND METHODS

Live mosses, algae and cyanobacteria were collected in the cascades of the Plitvice Lakes system, and observed and identified using light microscopy. Their relation to carbonate deposits was studied using Scanning Electron Microscopy (SEM, Jeolco, MBL, Woods Hole, MA) of critical point-dried specimens. Live materials were decalcified in dilute hydrochloric acid and studied by light microscopy. Fossil deposits were collected in the Plitvice National Park and in fossil travertine deposits in the valley of the river Volturno, Italy. Following macroscopic identification at the site of deposition, samples were selected using an incident light dissecting microscope. Selected samples were analyzed by SEM with subsamples prepared as petrographic thin sections and studied by light microscopy (Zeiss Universal) using transmitted light, DIC illumination and cross-polarized illumination. Samples were studied and the results presented in order to illustrate the advancement of diagenetic alteration processes.

3. RESULTS AND DISCUSSION

3.1. The geomorphology of travertine deposits

The main distinction between thermal and ambient water travertine deposits is in the porosity. In thermal deposits, where precipitation is rapid, the porosity is produced by the trapped gas and by micrometer sized organisms embedded into the deposit. Additional microstructure is produced by crystal growth (PENTECOST, 1990). Ambient temperature systems attract, in addition to microorganisms, also mosses, insect larvae and plants, which shape the deposit leaving imprints and cavities of corresponding size. Both systems commonly produce a calcareous deposit, characterized by an even distribution of water-flow and formation of pools behind carbonate barriers. Both systems result in differentiation between lotic (running water, rapids), and lentic (relatively still water), environmental settings along streams and rivers. In thermal systems, carbonate precipitation predominates, guided by differential degassing, evaporation and cooling, favouring precipitation where the water is in direct contact with the atmosphere. The microorganisms are present but their contribution to the shapes of the deposits appears to be limited (PENTECOST, 1990 *vs.* CHAFETZ & FOLK, 1984 and CHAFETZ & GUIDRY, 1999). The diversity and size of organisms increases with the lowering of temperature to ambient levels, and their role in carbonate deposition increases toward the establishment of chemical equilibrium in surface waters (MERZ, 1992; FRANČIŠKOVIĆ-BILINSKI et al., 2004). In thermal systems, the pools range from millimetre to metre scale, arranged step-wise down the slope, supported by smooth semicircular carbonate walls, over which the water overflows in a thin, evenly distributed film (GUO & RIDING, 1999, figs. 13, 17). In ambient temperature systems the formation of pools and barriers is less regular, but they are constructed by the same principle of differentiated carbonate deposition. The scale of participating organisms and of the resulting deposits is larger, and the timing is extended and subject to changes in seasons and meteorological conditions.

The valley (*thal*) of the river that deposits calcareous tufa is modified by the selective preference of calcifying rheophilic algae and mosses for growth in rapids, which are also the sites of maximum exchange of gases with the atmosphere. The growth of organisms, combined with carbonate deposition, produces a porous rapidly hardened substrate, which tends to partition the water flow. This results in the lateral displacement and fan-like distribution of both the deposit and the flow of water, ultimately extending across the river, forming a dam with a pool of water behind. This development has a regulatory effect as the water loses its erosional power, further promoting deposition and vertical growth of dams. The lakes grow larger by competition in barrier accretion in which the growth of lower barriers floods those upstream. Once formed, the pooled water bodies became effective traps of eroded material (GOLUBIĆ, 1967, 1969). Gradually, the river is transformed into a series of distinct lakes and waterfalls, and the initially inclined river bed is altered into a series of terraces. Similar systems developed during Pleistocene and early Holocene throughout southern Europe (e.g. PEŃA et al., 2000), but few remained active.

Different stages in the progression of this development can be observed in the Plitvice system of alternating lakes and waterfalls (Plate 1, Fig. 1). Impressive waterfalls (Pl. 1, Fig. 2) are the exception rather than the rule in this development, which normally tends to subdivide the water passages and distribute them in a net-like fashion over the entire barrier, a condition which supports the growth of higher plants and trees. Yet, the barriers may become unstable and collapse, changing the water passages abruptly. Massive waterfalls may be created by occasional erosional events or, more often, by humans, in order to guide the water to their water mills or to maintain waterfalls for a tourist attraction.

The shallow flat-bottomed ponds between smaller barriers, initially support rapid water exchange and create conditions in which carbonate accumulates in microbially coated grains and forms laminated nodules or oncoids (GOLUBIC

& FISCHER, 1975; PEDLEY, 1990; HÄGELE et al., 2006). Within the Plitvice system, oncoids are sporadically present along shallow flat shorelines of Lake Kozjak, and also as large fields in slow flowing widened areas of the river Slunjčica at Rastoke (Pl. 1, Fig. 3). They are dominated by cyanobacteria and microscopic algae. Such shallow ponds deepen over time through the vertical growth of barriers between them (Pl. 1, Fig. 4) and then accumulate fine carbonate sand, which supports aquatic plants such as *Myriophyllum spicatum* L. with charophytes on the shallower pond margins.

Some water passages elevate their bed while maintaining the flow on top of a carbonate ridge. These, so called "cat walk" deposits (German: *Kalkrinnen*) are often products of small, carbonate supersaturated springs that emerge on slopes (Pl. 1, Fig. 5). This represents another depositional feature that is similar in both ambient temperature and hot water deposits (see GUO & RIDING, 1999). Carbonate precipitates a certain distance from the spring as soon as the carbonate equilibrium shifts in favour of precipitation. There is a preference of moss growth and associated deposition of carbonate in the spray at the margins of such water flows. Consequently, the creek bed is elevated while the margins prevent lateral overflow. Over time, the "cat walk" flattens in the upper ranges while it steepens distally. The lateral overflow and displacement occurs with a delay so that the deposits ultimately widen to produce semi-conical tufa structures called "*crone"* or "*cranier"* in French, and *"Hangtuff"* in German.

The Plitvice system of lakes and waterfalls developed in a valley overlying the Triassic dolomites, which narrows downstream into a canyon carved into Cretaceous limestone (GOLUBIĆ & GRGASOVIĆ, 2007). The upper lakes are wider and the ponds occupy different levels. The fossil sites at Rocchetta a Volturno occur on slopes of an even wider valley and developed, accordingly, in the form of an extended set of terraces with steeper slopes and waterfall facies on their outer margins. Similar systems have been described in Antalia, Turkey (GLOVER & ROBERTSON, 2003).

3.2. The constructive role of aquatic mosses

Aquatic mosses such as *Cratoneurum commutatum* (HEDW.) ROTH, *Eucladium verticillatum* (WITH.) BRUCH & SCHIMPER, *Bryum pseudotriquetrum* (HEDW.) P. GAERTN., B. MEY & SCHERB. and *Didymodon tophaceus* (BRID.) JUR. are known as travertine-forming organisms. They thrive in the water spray in waterfalls where they become encrusted by carbonate. By their growth preferences, the mosses guide the precipitation and modify the flow of water (Pl. 1, Fig. 6). However, the carbonate encrustation takes place on older leaflets and on the moss stems rather than on young actively growing leaflets (Pl. 1, Fig. 7), which suggests that there is no direct relationship between moss photosynthesis and carbonate deposition. Instead, mosses are stimulated to grow at their tips so as to escape being cemented in carbonate. In contrast, the carbonate precipitate is associated with a biofilm of microorganisms, which overgrows the moss with age. Some carbonate deposited in the moss cushions is allochthonous, i.e. precipitated upstream and then trapped by the moss. Carbonate precipitation starts on crystallization nuclei provided by the microbial biofilm of cyanobacteria, diatoms and microscopic chlorophytes, such as the desmid *Oocardium stratum* (Pl. 1, Fig. 10). Similar microbial biofilms coat the branches and leaf litter trapped in the waterways (Pl. 1, Fig. 7).

Encrusted by carbonate, the moss cushions form porous sponge-like carbonate sediment that retains the shape of the moss and fossilizes instantly, often incorporating other plant material (Pl. 1, Fig. 8). As the calcification continues, the mosses respond by growing out of the deposit. In the race that ensues between moss growth and calcification, the latter is shaped and directed by the growth of mosses which, in turn, follow the water currents, cascades and spray. The porous spongy consistency of moss thalli provides the architectural framework for the travertine deposit. The environmental requirements of rheophilic aquatic mosses promote their settlement in rapids and cascades, where they become encrusted by carbonate. Such biologically controlled deposition is contrary to the pattern of inorganic deposition of particulate matter. In addition, the presence of mosses in travertine deposits organizes rock porosity at scales ranging from mm-size spaces between moss leaflets and stems to cm- and metre-scale cavities and caves formed under cascades and waterfalls. The environmental consequence of moss participation is the formation of a voluminous travertine structure from relatively small amounts of carbonate mineral, which would otherwise form compact crusts, similar to cave stone (GOLUBIC, 1973). Due to the rheophily of aquatic mosses and microorganisms, carbonate accumulates in rapids rather than in pools and depressions where it is deposited as fine particulate matter (calcilutite). Fossil travertine of both thermal and ambient temperature systems has been used in architecture since ancient times as seen in the ruins of Pompeii and in the Doric Greek temples of Magna Grecia, in present southern Italy (Pl. 1, Fig. 9).

The landscape modification by the combined activity of aquatic mosses, eukaryotic microorganisms such as *Oocardium stratum* (Pl. 1, Fig. 10), and calcifying cyanobacteria (Pl. 1, Fig. 11) has important ecological consequences, as new niches and opportunities for growth arise that did not previously exist in the river. The water behind travertine dams accumulates as lakes with their own communities of plankton, benthos and littoral, which are alien to fast flowing rivers. Vaults of travertine that support, (and are shaped by) waterfalls, overhang and enclose cave spaces beneath them (Pl. 1, Fig. 2), with new habitats provided with trickling water and a humidity-saturated atmosphere, able to support a luxurious microflora of cyanobacteria and algae specialized to photosynthesize under dim illumination, e.g. *Scytonema julianum* (KÜTZING) MENEGHINI, *S. myochrous* (DILLW.) AGARDH (Pl. 1, Fig. 11) and *Petalonema alatum* BERKELEY (Pl. 1, Fig. 12). The spongy porous deposit becomes a home to bacteria as well as to numerous minute invertebrates that thrive on the organics produced in the system and are carried by waters trickling through the porous deposit. These developments derive from the growth preferences and adaptive capacity of aquatic mosses (Pl. 2, Fig. 1), which are in that sense the real architects of cold water travertine deposits (ARENAS et al., 2000). Mosses fossilize well and identify past environmental

PLATE 1

Calcareous tufa formations and their microbiota

1 View of the two lowermost lakes of the Plitvice system of Korana River, Kaluđerovac and Novakovića Brod, separated by a low barrier.

2 Water falls down the tall travertine barrier in the upper parts of the Plitvice system, "Mali prštavac" waterfall. Note the overhanging tufa enclosing caves under the water arches.

3 Shallow ponds with high water exchange rates in a part of the water-flow network of the River Slunjčica, a tributary of the Korana (Rastoke village), supporting a "pavement" of oncoids. Insert: two of the oncoids, the right one cut open to show the laminated internal texture. Scale bar is 1 cm long.

4 A series of small tufa barriers with cascades, separating shallow ponds, lower lakes.

5 "Cat walk"- type calcareous deposit in a small carbonate super-saturated spring located on a hill slope.

6 Luxurious cushions of the moss *Cratoneurum commutatum,* growing in the water spray and participating in the even distribution of water along the barrier. Scale bar is ca 20 cm long.

7 A leaf of *Alnus glutinosa* trapped in the cascade and overgrown by globular *Oocardium* colonies. Scale bars in figs 7, 8 and 9 are 1 cm long.

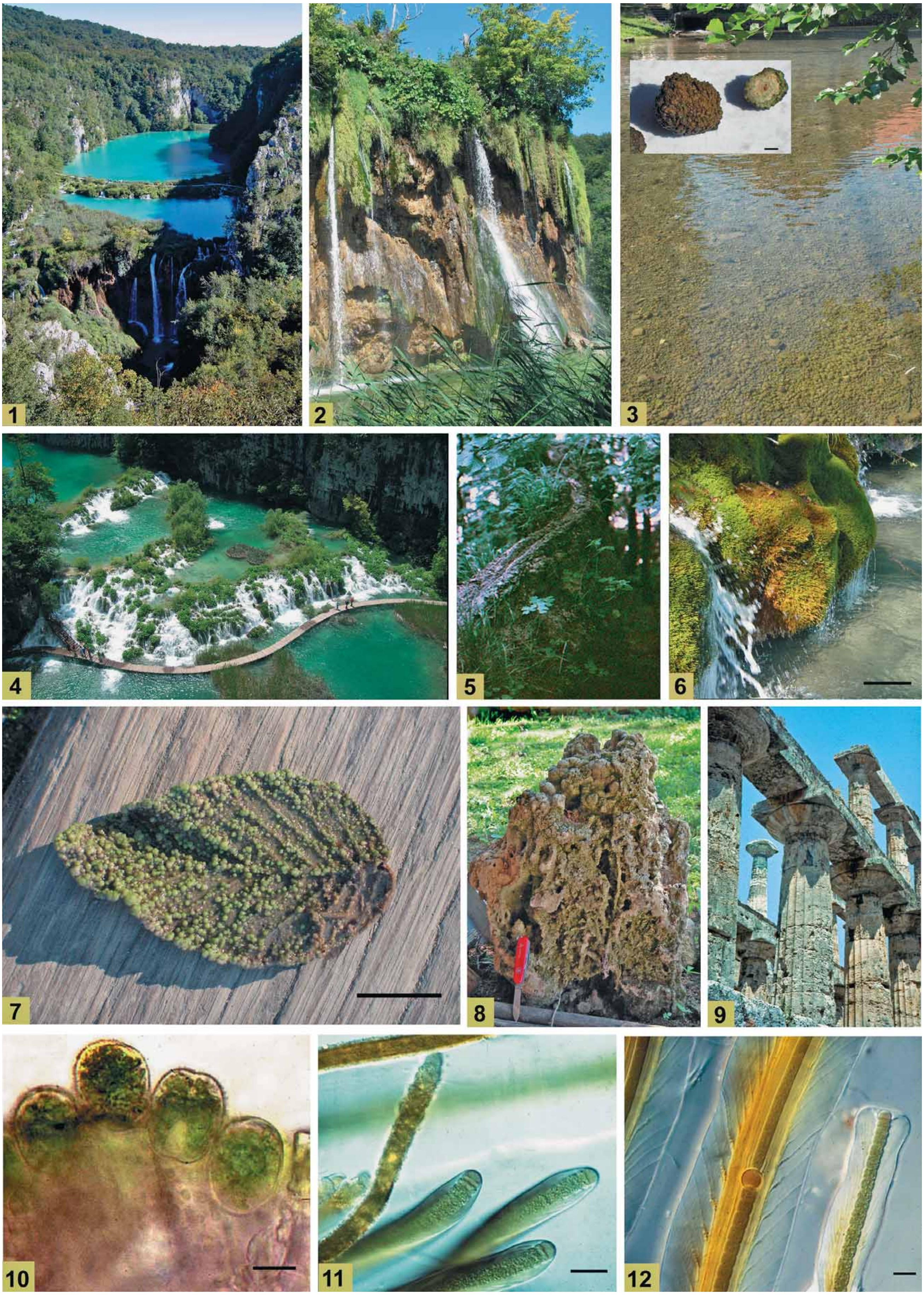
8 Fossil calcareous tufa with cavities and incorporated branches of trees fallen into the lakes.

9 Doric temple in Paestum, southern Italy, built of ambient water travertine that preserves aquatic mosses.

10 Cells of *Oocardium stratum* inserted in the calcified tubes, forming a single layer of cells on the surface of each colony.

11 Two species of *Scytonema* (Cyanobacteria). The smaller one on the upper left is calcified *S. julianum* next to the larger uncalcified *S. myochrous* below.

12 The nitrogen fixing cyanobacterium *Petalonema alatum* forms soft gelatinous colonies in the moist cave entrances underneath the waterfalls. Note the differently pigmented nitrogen-fixing heterocyst in the centre. Scale bars in figures 10, 11 and 12 are 10 μm long.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changes such as seasonal rhythms or the lateral displacement of depositional regimes (Pl. 2, Fig. 2), often preserving the taxonomic identities of ancient travertine builders (Pl. 2, Fig. 3).

3.3. The role of cyanobacteria and micro-algae

A closer look at the moss leaflet surfaces reveals a biofilm of cyanobacteria and diatoms in close association with calcite crystals (Pl. 2, Fig. 4). In addition to aquatic mosses, the other most-important organisms involved in the formation of ambient water travertine are cyanobacteria and eukaryotic algae, which form biofilms and promote calcification (Pl. 2, Figs. 5–7). Without their contribution, precipitation of calcium carbonate would still occur, but the precipitate may not be retained in rapids, but transported downstream instead. Experiments with exposed copper grids that are toxic to microorganisms and do not support biofilm development also remain uncalcified (SRDOČ et al., 1985). Calcification on exposed slides shows a positive linear correlation with the rates of periphyton growth (PRIMC-HABDIJA et al., 2001). Species-specific differences in the degree of calcification and in the shape of the resulting calcium carbonate crystals have been documented in cases of freshwater (OBENLÜNESCHLOSS & SCHNEIDER, 1991) as well as marine cyanobacteria (GOLUBIC & CAMPBELL, 1981). Similar cases of biological crystal specificity have been documented in ambient water travertines (e.g. GOLUBIC et al., 1993). While some cyanobacterial species calcify, other species remain uncalcified, although growing under the same conditions and in close proximity to each other (Pl. 1, Fig. 11).

In order to investigate the role of microphytes in the process of tufa deposition in the Plitvice Lakes National Park area, qualitative and quantitative analyses of periphyton were carried out between 1985 and 1990 (PLENKOVIĆ et al., 2002). The connection between carbonate deposition and periphyton was tested by experimental exposure of microscope slides. Glass slides were submerged in streaming water and exposed for 30, 60, and 90 days. Seven locations with different intensities of natural tufa deposition were chosen along the Plitvice Lake system. Temperature, pH and current were monitored simultaneously. Growth of periphyton was analyzed, and 191 species were determined with the highest diversity being shown by diatoms (139 species). The dominance of diatom species was observed at all locations (especially in winter), irrespective of changes in physicochemical properties of the water and the intensity of $CaCO_3$ precipitation. A particularly intensive precipitation of microcrystalline calcite was found in the presence of cyanobacteria: *Chamaesiphon incrustans* GRUNOW, *Homoeothrix varians* GEITLER, *Hydrococcus rivularis* MENEGHINI, and diatoms: *Achnanthes affinis* GRUNOW, *A. microcephala* GRUNOW, *A. pyrenaica* HUSTEDT, *Synedra vaucheriae* KÜTZING, *Cymbella affinis* KÜTZING, *C. microcephala* GRUNOW, *Gomphonema olivaceum* KÜTZING, *G. olivaceum* var. *calcareum* CLEVE, and *G. parvulum* GRUNOW. In addition to physicochemical and geological factors, the qualitative composition and density of the microphyte community appeared to be of major importance in the formation of tufa. However, recent massive developments of different benthic diatoms in the Plitvice Lake system associated with an increase in nutrients correlate instead with a decline in calcification intensity, especially in smaller pools on top of the barriers (unpublished observation).

Calcite precipitation by diatoms (Pl. 2, Fig. 6), is associated more directly with cell products than their photosynthetic activity, which is less evident with cyanobacteria where the calcification occurs on extracellular sheaths enveloping the cells (Pl. 2, Fig. 6, insert). Diatoms are ubiquitous epiphytes on mosses (Pl. 2, Fig. 7), but are themselves overgrown by smaller microorganisms such as bacteria (Pl. 2, Fig. 7, insert). Crystal growth takes place around gelatinous stalks produced by the cells of the diatom *Gomphonema olivaceum* var. *calcareum* CLEVE, and are arranged in stromatolitic laminae through pulses of diatom growth (WINSBOROUGH & GOLUBIC, 1987). This relationship between a microbial product and crystal nucleation is consistent with the concept of organomineralization *sensu* TRICHET (1967) and DÉFARGE & TRICHET (1993). Initiation of calcite precipitation on moss leaflet surfaces without the presence of microbial epiphytes, but associated with organic templates of apparent microbial origin, has been recently described by TURNER & JONES (2005). This particular pattern of "dendritic" calcite precipitate has been described earlier and associated with a *Schizothrix* sp. in the Everglades, Florida (MERZ & ZANKL, 1993). We found the same crystallization pattern associated with the sheaths of the subaerial cyanobacterium *Geitleria calcarea* FRIEDMANN, which inhabits the semi-enclosed caves in the travertine barriers, beneath the waterfalls (Pl. 2, Fig. 8). The crystallization follows the mineral lattice of calcite, but favours sharp crystal edges over the plates, which are completed later (Pl. 2, Fig. 9).

Dominant assemblages of cyanobacteria and diatoms are present in different natural habitats along the system according to their specific adaptations and growth preferences. The exclusive domain of cyanobacteria is on travertine cones under the waterfalls, which receive the direct impact of falling water. These microorganisms are structurally supported by carbonate deposition in and around their extracellular sheaths and envelopes. The associated carbonate deposit is more compact than that forming around mosses, with a fine, micrometer-scale porosity provided by the filaments of cyanobacteria. The most common among these carbonate-encrusted cyanobacteria are *Phormidium incrustatum* (NÄGELI) GOMONT. We have followed the early stages in encrustation of this organism in the Plitvice travertines (Pl. 2, Fig. 6, insert and Fig. 10), as well as early and late diagenetic changes (see below).

Other cyanobacteria that show different degrees of calcification in the Plitvice system are *Schizothrix fasciculata* (NÄGELI) GOMONT, and the moderately encrusted *Phormidum favosum* (BORY) GOMONT, *P. uncinatum* GOMONT and *Hydrocoleum homoeotrichum* KÜTZING, These organisms are common in rapidly flowing channels over and around travertine barriers. Similar habitats show frequent growth of hemispherical colonies of *Rivularia haematites* (DE CANDOLE) AGARDH, hardened by the dense zonal deposition of calcite grains. A specific difference in carbonate precipitates in this and other freshwater species of *Rivularia* has been documented by OBENLÜNESCHLOSS & SCHNEIDER (1991).

High rates of calcification, as well as a species-specific modification of precipitates, are shown by chlorophytes, especially by the desmid *Oocardium stratum* and the xanthophyte *Vaucheria geminata* (VAUCH.) DE CANDOLLE. These cases have been selected in the present study of diagenesis (see below).

Although subject to numerous investigations, the deposition of calcareous tufa in karstic waters remains incompletely explained. The problem stems largely from different interpretations of the biogenic vs. abiogenic components which are responsible for calcification and the formation of travertines. To approach this question in a constructive fashion requires realization of the complexity of the process, and its sequential development. The environmental conditions such as pH, carbonate chemistry and saturation levels of solutions change as a part of this process and so do the nature and proportion of biogenic vs. abiotic influences. An average carbon atom engaged in this process, passes through the phases of (a) carbonate chemistry, (b) nucleation, crystal organization and growth, and (c) accumulation and build-up of carbonate sediment. Each of these phases may be responding to a different balance of biogenic vs. abiotic forces, and they may influence each other sequentially (GOLUBIC, 1973; EMEIS et al**.**, 1987).

Carbonate deposition is a process at the intersection of inorganic and organic carbon cycling, which ranges in scale from molecular to global (GOLUBIC et al**.**, 1979; GOLUBIC & SCHNEIDER, 1979). The supersaturation of karstic springs, which is the prerequisite for carbonate precipitation, is largely biogenic by enrichment with respiratory CO_2 in soils. The precipitation of carbonate that follows the emergence of these waters is part of the adjustment of the preceding biogenic carbonate dissolution. The extensive fossil tufa deposits of Roccheta a Volturno, used here in the current Recent-to-fossil comparison, are no longer actively accumulating, since the slopes of the watershed have been deforested and the soils washed out (D'ARGENIO et al., 1995). The barriers of the Plitvice Lake system are still in the process of active accretion (ZWICKER & RUBINIĆ, 2005), within its densely forested watershed largely protected by its National Park status.

A predominance of "abiotic" influences on carbonate precipitation (e.g. CHEN et al., 2004), is expected at a relatively short distance from the spring, as part of the re-adjustment of excessive (respiratory) CO_2 transported in the ground waters to the pCO_2 of the atmosphere. It is promoted by increase of the air-water interface in waterfalls (ZHANG et al., 2001). In the hard calcite-saturated waters of the Plitvice Lakes system, locally strong aeration promotes considerable calcium carbonate precipitation.

The predominance of biogenic influences on carbonate chemistry through microbial photosynthetic activity is expected later in the water flow, after equilibrium with the atmosphere has largely been reached (MERZ-PREISS & RIDING, 1999; FRANČIŠKOVIĆ-BILINSKI et al., 2004). The microbial biogenic influences on crystal nucleation and construction of minerals are separate from the carbonate chemistry (FREYTET & VERRECCHIA, 1998), and operate at a much finer scale than the sedimentary processes under the influences of aquatic mosses, the latter producing the macro-architecture of travertine deposits.

4. DIAGENESIS IN TRAVERTINE DEPOSITS

Diagenesis of travertine deposits starts early and proceeds unevenly. It is initiated contemporaneously with travertine barrier building, as calcification instantly fossilizes the biological structure. Further diagenesis is conditioned by the very porosity of the deposit. As water seeps through the travertine, the gravitational field determines its passage, so that some conduits are in frequent use, while other parts of the porous sediment are avoided and remain unaffected. As in soils, the interstitial waters in travertine barriers collect respirational CO_2 and may dissolve some of the carbonate deposit, which subsequently precipitates when equilibrium with atmospheric pCO_2 is re-established (GOLUBIĆ, 1969, 1973). The process is similar to the deposition of stalactites in caves: it produces a coating of compact crystalline carbonate over travertine that becomes superficially indistinguishable from cavestone (Pl. 1, Fig. 8, smooth surfaces). At a microscopic scale, minute details in the travertine deposit become dissolved or re-arranged, gradually losing original texture and biogenic signature. As part of the same process, other places within the travertine structure remain unchanged. This condition permits comparison between different stages of the diagenetic process, which have been arrested and preserved by the changes of water passage.

Preserved thalli of interglacial and early Holocene *Cratoneurum commutatum* remain preserved and recognizable in the caves of the waterfall facies of the Roccheta a Volturno deposits (Pl. 2, Fig. 11). Similarly, the stromatolitic laminae of alternating chironomid housings and zones of *Oocardium stratum,* testify to seasonal changes on the travertine slopes at the same fossil site (Pl. 2, Fig. 12), as discussed by GOLUBIC et al. (1993, 1995), and documented by stable isotope measurements (ANZALONE et al. 2007).

4.1. Diagenesis of the micrite deposit of *Phormidium incrustatum* (cyanobacteria)

Diagenetic alterations in sites exposed to direct water impact show considerable variation, as shown in calcified colonies of the cyanobacterium *Phormidium incrustatum* (Pl. 3, Fig. 1). When active, filaments of *P. incrustatum* are composed of sheathed trichomes, about 4 μm in diameter. The trichomes are surrounded by a firm sheath of extracellular polymers (EPS), which are the locus of intensive calcification. Filaments are often arranged parallel to each other, forming upright bundles that jointly resist the water impact. The bundles build colonies in the form of lens-shaped cushions, two to three cm in diameter, slightly inclined in the direction of water flow (Pl. 3, Fig. 2). In petrographic thin section under unpolarized and polarized transmitted light, the outlines of these filaments appear dark due to the densely arranged grains of micritic calcite (GOLUBIC et al., 1993, pl. 2, figs. 5, 8). In sections perpendicular to the direction of bundles, the filaments seen in cross section are similarly outlined by primary micrite, whereas the spaces between bundles are filled with sparry calcite (Pl. 3, Fig. 3). Fractured samples along the bundles as seen by SEM, (Pl. 3, Fig. 4), reveal uniformly distributed calcified tubes of empty sheaths preserved as micritic linings.

PLATE 2

Aquatic mosses and biofilms, the main architects of calcareous tufa

1 *Cratoneurum commutatum* dominates the cascades of the Plitvice system. Scale bar is ca 5 cm long.

2 Fossil moss, *Bryum pseudotriquetrum,* forming distinct, apparently seasonal laminae on the travertine slopes at Rocchetta a Volturno, central Apennines.

3 Well preserved fossil moss plantlets of *Eucladium verticillatum* near calcareous waterfalls at Tivoli, Italy. Scale bar is 1 cm long.

4 Critical-point dried moss plantlets under Scanning Electron Microscope (SEM). Note the dense overgrowth of microorganisms forming an epiphytic biofilm. Scale bar is 100 µm long.

5 The tip of a moss leaflet coated by microbial biofilms dominated by *Leptolyngbya* (cyanobacteria), and sessile eukaryotic green algae and diatoms. Scale bar is 10 µm long.

6 Detail of the biofilm, dominated by pinnate diatoms and associated carbonate precipitates. Insert: heavily calcified tube formed by the cyanobacterium *Phormidium incrustatum*. Scale bar is 10 µm long, also for the insert.

7 Tip of a different moss leaflet densely covered by *Synedra* (Bacillariophyta), Insert: heterotrophic bacteria overgrowing the diatom. Scale bar is 50 µm for the leaflet and 20 µm for the insert.

8 Calcified sheaths of the cyanobacterium *Geitleria calcarea* and *G. floridana* growing subaerially in the semi-enclosed caves under the waterfalls.

9 Detail of the sheaths shown in fig. 8, illustrating distinctive fibrous growth of the calcite crystals. Scale bar is 1 µm long.

10 Early growth stages of *Phormidium incrustatum* (Cyanobacteria) with heavily calcified sheaths (see insert in fig. 6). Scale bar is 50 µm long.

11 Fossil lithified moss (*Cratoneurum commutatum*) comprising a cave ceiling in the waterfall facies of Roccketta a Volturno. The details are sufficiently well preserved to identify the fossil organism.

12 Interglacial stromatolitic travertine on the slope facies of Rocchetta a Volturno showing seasonal deposition of *Oocardium stratum,* alternating with housings of chironomid larvae. *Oocardium* settles every June, following chironomid maturation.

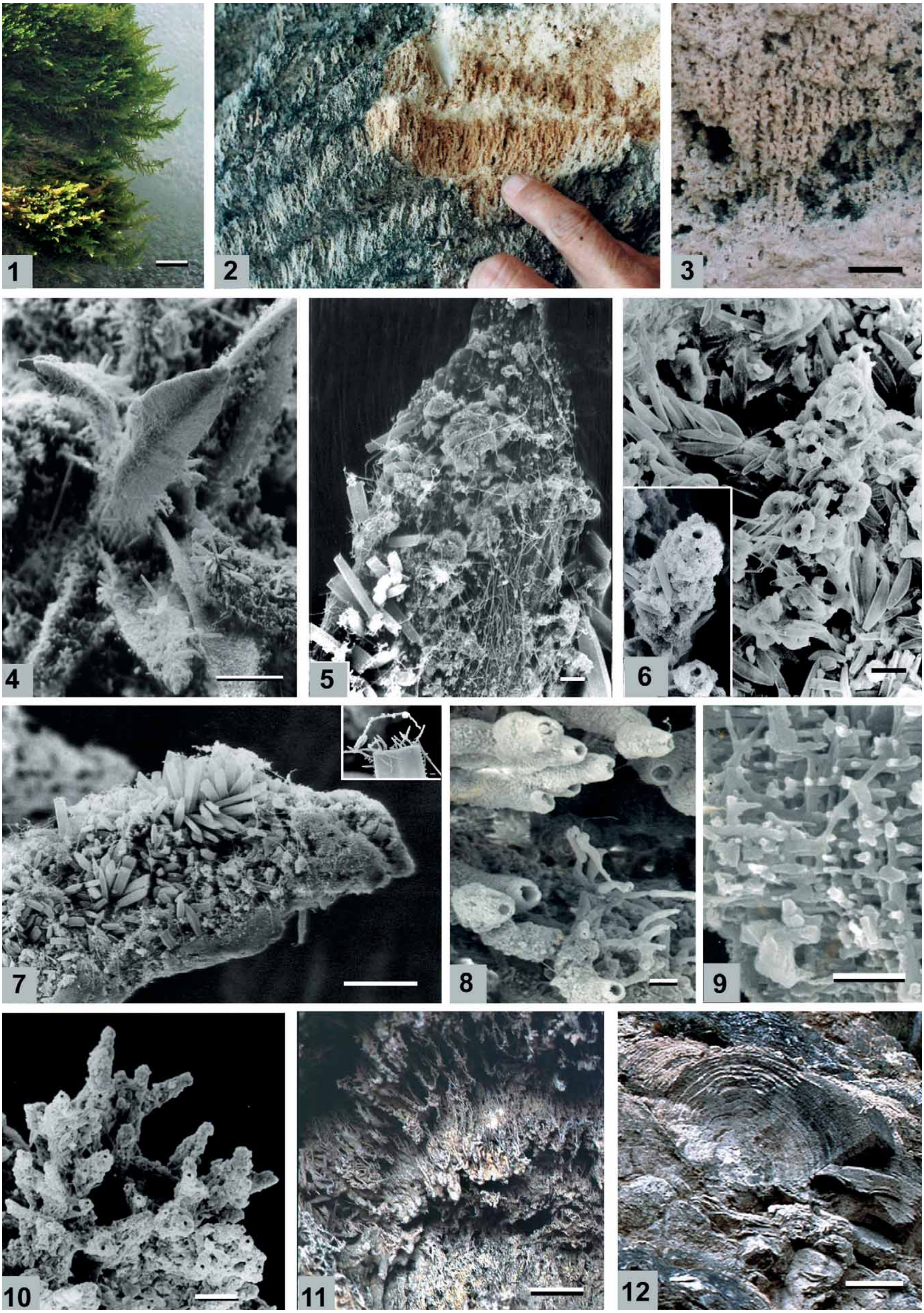
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PLATE 3

Diagenesis of a calcareous deposit of *Phormidium incrustatum*

1 Calcified cushions of *Phormidium* populations which dominate areas with a strong impact of falling water. The flow of water and orientation of the cyanobacterial filaments are toward the observer. Scale bar is 5 cm long.

2 Section through the cushions of *Phormidium* in side view; the direction of water flow is from left to right. Scale bar is 1 cm long.

3 Petrographic thin section perpendicular to the filament orientation. Note dark micritic outlines of cyanobacterial sheaths and large sparitic fill of the interfilament spaces. Scale bar is 20 μm long.

4 Longitudinal fracture through a bundle of *Phormidium* filaments preserved as calcified tubes. Scale bar is 20 μm long.

5 Early stages of diagenesis of *Phormidium* travertine. Note that the recrystallization starts in the interior of the bundles and progresses outward. Peripheral filament imprints are perfectly preserved whereas the interior appears as a solid carbonate block. Scale bar is 100 μm long.

6–8 Advanced diagenetic alteration of *Phormidium* travertine. Scale bars are 50 μm long

6 Petrographic thin section through an altered bundle of *Phormidium*. Note the pseudostromatolitic lamination stained by bands of concentrated iron precipitate alternating with clear zones.

7 The same frame in cross polarized transmitted light shows the uniform optical orientation of the entire column as a single crystal.

8 Large monocrystalline palisades originated from bundles of *Phormidium* filaments. Fig. 8 represents further development of the stage shown in fig. 5 above.

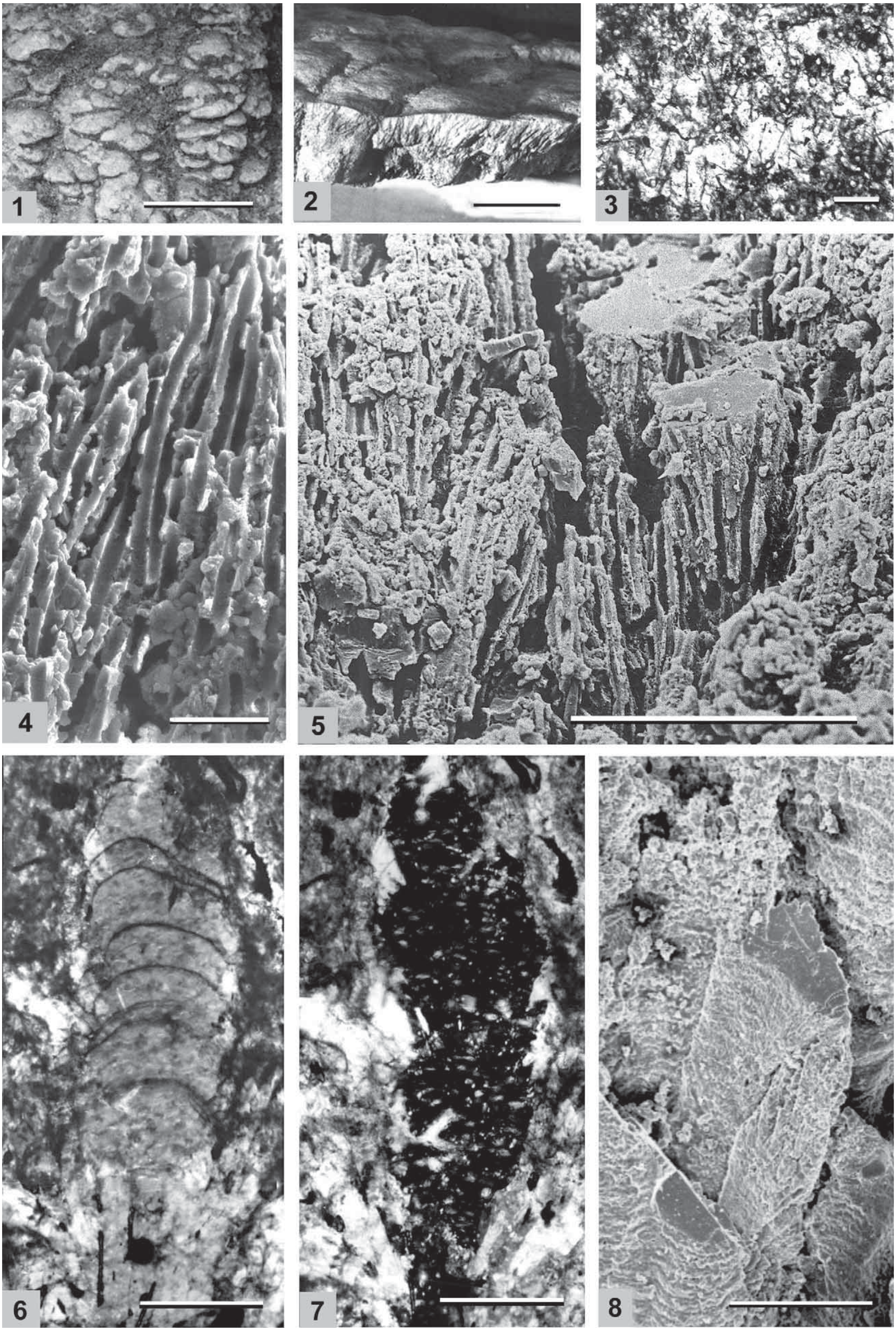
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PLATE 4

Calcareous deposition by *Oocardium stratum* and *Vaucheria geminata*

1 Detail of a micro-reef produced by *Oocardium* showing monocrystalline calcareous tubules that branch with each cell division of the desmid. Scale bar is 50 μm long.

2 Petrographic thin-section through an upright colony of *Oocardium* in cross polarized light. Note that crystal orientation is the same for each clonal population of the alga.

3 Similarly fractured upright colony seen by SEM. Scale bars in figs. 2 and 3 are 100 μm long.

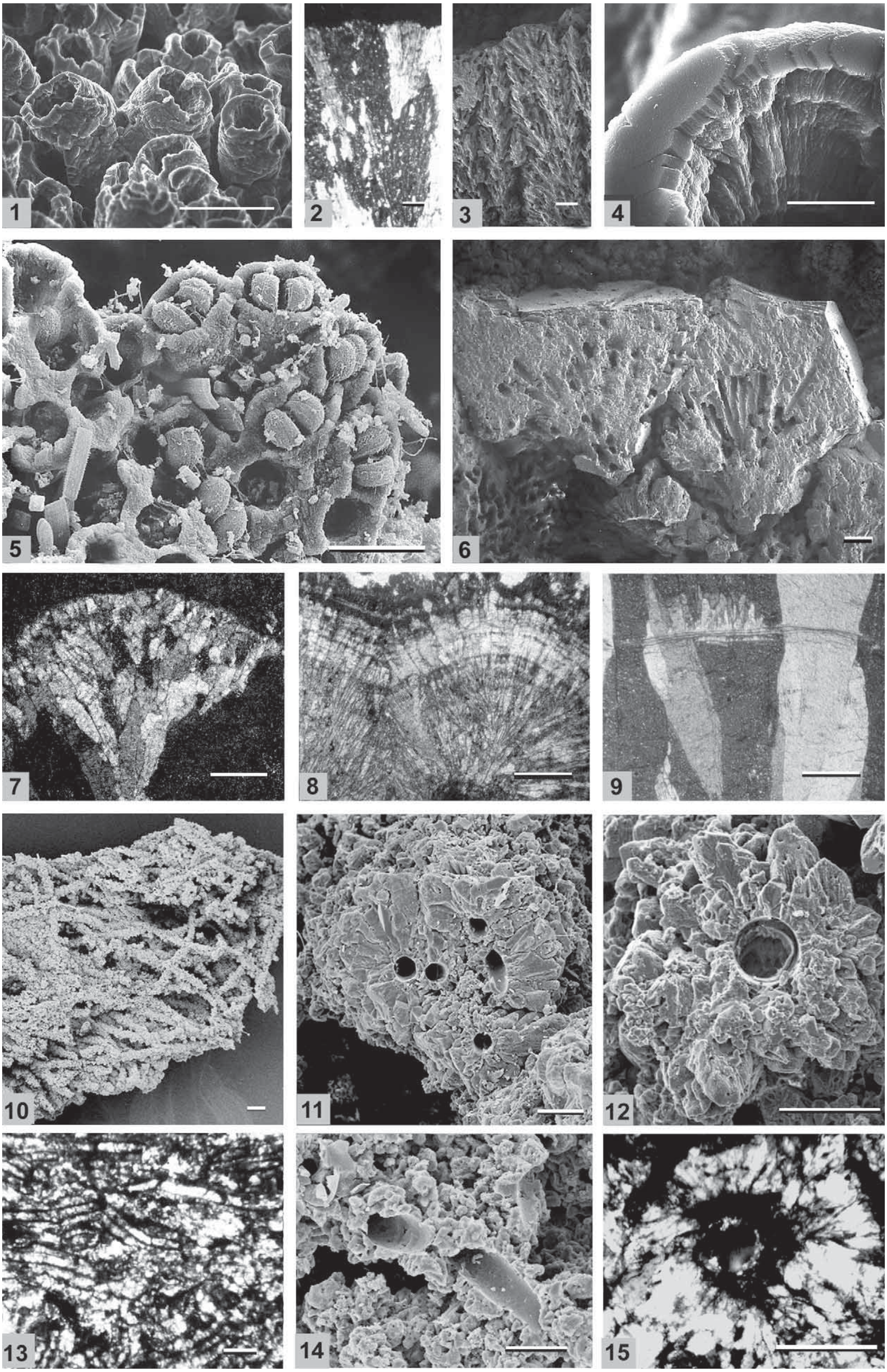
4 Detail of the rim of the *Ocardium* calcareous tube following hypochlorite treatment to remove organic components. Note the orientation of the cleavage pattern is consistent with a single calcite crystal and the cylindrical imprint of the organic tubule. Scale bar is 5 μm long.

5 Critical-point dried clonal colony of *Ocardium stratum* showing cells in the state of division inserted into calcareous tubes. Scale bar is 30 μm long.

6 Early diagenetic alteration of an *Oocardium* calcite grain. Note the euhedral outline of the grain, while its interior contains the original tubules. Scale bar is 50 μm long.

7–9 Three advanced stages in diagenetic alteration of an *Oocardium* colony. Scale bars in these figures are 1 mm long. Note the gradual increase in the average size of calcite grains, while their upward divergence remains preserved.

10–15 Calcified filaments of *Vaucheria geminata*; Fig. 10 – SEM view of the calcified network of *Vaucheria* filaments; Fig. 11 – A fractured group of heavily calcified filaments; Fig. 12 – A single filament of *Vaucheria* with the residue of the cell wall visible inside the calcified tube. Note the radial arrangement of microspar grains encrusting the filament. Scale in Figs. 10–12 is 100 μm long; Fig. 13 – Petrographic thin-section of diagenetically altered *Vaucheria* filaments; Fig. 14 – SEM of broken *Vaucheria* travertine obliquely cutting the calcareous tubes; Fig. 15 – Petrographic thin-section of a calcified *Vaucheria* filament in cross section. Scale bars in Figs. 13–15 are 50 μm long.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Diagenetic changes of *Phormidium incrustatum* deposits are accompanied by gradual recrystallization, within which the size of calcite grains increases. This process usually starts in the centres of filament bundles and spreads toward the bundle periphery. This stage is shown in Pl. 3, Fig. 5, where the left side of the image contains bundles unaffected by recrystallization, whereas two bundles to the right are cleaved and show compact interiors, while the periphery of each bundle preserves individual tubules of the original biogenic imprint. In later stages of diagenesis, observed in those parts of the same sample that were affected by serving as a water conduit, the original biogenic signature is completely erased (Pl. 3, Figs 6–8). In plain transmitted light, a petrographic thin section along the bundle shows pseudostromatolitic structure with rhythmic lamination of iron enrichment lines (Pl. 3, Fig. 6). The same section in cross-polarized light (Pl. 3, Fig.7) reveals that the entire pseudostromatolite is comprised of a single crystal grain. The diagenetically altered *Phormidium incrustatum* bundles as shown by SEM (Pl. 3, Fig. 8), are converted into large calcitic palisades with external outlines of the original bundles smoothed but still recognizable.

This observed diagenetic sequence is invariably trends towards an increase in the average carbonate grain size, whereas the preserved micritic carbonate identifies the parts of the original mineralogy. There was no evidence of secondary micritization in this process.

4.2. Diagenesis of primary sparite of *Oocardium stratum* (Chlorophyceae)

Diagenesis of fossil *Oocardium* tufa has been reported and discussed by GOLUBIC et al. (1993). The present study compares the process with other biogenically modified primary precipitates. The desmid *Oocardium stratum* is a common constituent of ambient temperature travertines. Its life cycle, growth patterns and ecology have been studied since the 1930s (WALLNER, 1933, 1934). In the Karstic region of Croatia, it was first observed by Ivo Pevalek, an early explorer of the Plitvice system, and later found in the travertine deposits of the river Krka (PAVLETIĆ & GOLUBIĆ, 1956). Its taxonomic status was subsequently clarified by GOLUBIĆ & MARČENKO, (1958). The characteristic calcified light green colonies (Pl. 1, Fig. 7) of *Oocardium* form contiguous microscopic reefs (GOLUBIC et al., 1993, pl. 3). The extracellular polymers produced by this unicellular green alga form a ring around the cell, which starts calcifying by organizing a single calcite crystal that conforms to the shape of the organic ring. As the production of the polymer continues, the cell is lifted from the substrate, carried by a calcified tube. As the cell divides, the tube branches (Pl. 4, Fig. 1), while continuing the orientation of the monocrystalline lattice. Ultimately, the entire clonal colony produces a single calcite spar crystal, as evident by cross-polarized light microscopy (Pl. 4, Fig. 2) compared with SEM images (Pl. 4, Fig. 3). The combined biological and mineralogical characteristic of the mineral is illustrated in Pl. 4, Fig. 4, showing uniform orientation of calcite cleavage lines, combined with the round shape of the organic tubule. An entire clonal colony with its mineral product is shown in the SEM of a critical-point-dried preparation (Pl. 4, Fig. 5).

Diagenetic alteration of these primary spars starts by recrystallization of the external parts, from where it proceeds toward the interior. The exterior of altered spars (Pl. 4, Fig. 6) gains a rhombohedral morphology typical of pure calcite, whereas the interior still preserves the tubular imprint of the original *Oocardium* tubules. The same has been shown in petrographic thin sections (GOLUBIC et al., 1993, pl. 4, figs. 4–10). Advanced stages of diagenetic recrystallization are illustrated in Pl. 4, Figs. 7–9. Note that these three figures are at the same low magnification. The recrystallization resulted first in the complete loss of the internal tubular structure, retaining only "clonal" crystalline identities in the form of wedge-shaped grains (Pl. 4, Fig.7). The next step resulted in re-organization of the grains toward a radial symmetry with pseudostromatolitic zonation (Pl. 4, Fig. 8). This stage has certain morphological properties similar to those shown in the diagenetic sequence of *Phormidium incrustatum* (compare with Pl. 3, Fig. 5) suggesting convergent diagenetic modification starting from different original precipitates. This convergence is further supported by the next stage (Pl. 4, Fig. 9).

4.3. Diagenesis of microsparites of *Vaucheria geminata* (Xanthophyceae)

Large colonies of the filamentous xanthophyte (Heterocontae) *Vaucheria geminata* are regularly calcified, forming large spongy travertine deposits that compare in volume with mosses (Pl. 4, Fig. 10). The organism is characterized by tubular filaments without cross walls which occasionally branch. Reproductive organs are carried on short side branches. In travertine depositing systems, the cell walls of *Vaucheria* filaments are rapidly covered by calcite crystals, which continue to grow outward until they reach a fairly uniform size, intermediate between *Phormidium* micrite and *Oocardium* sparite (Pl. 4, Figs. 11, 12). The petrographic thin section images (Pl. 4, Figs. 13, 15) agree well with the SEM images. This type of encrustation apparently results from competing growth of synchronously seeded calcite grains, in which only the initial nucleation is under the control of the cell wall composition (Pl. 4, Fig. 14), whereas further growth of crystals continues under supersaturation of interstitial waters, competing for space. The average size of grains gradually increases from the cell wall surface outward (Pl. 4, Figs. 12, 15). By comparing different stages in diagenetic alteration, we again observed the same pattern of grain size increase following recrystallization as in other examples, although the initial stages are species-specific and quite different from each other.

5. CONCLUSIONS

The formation of thermal and ambient water travertines have the following properties in common: even distribution of water and modification of the flow into pools separated by walls of carbonate deposit. In the ambient temperature tufa of the Plitvice system, carbonate precipitation shows differences specific to particular microorganisms, whereas the travertine barriers are constructed by mosses. Diagenetic alteration of primary precipitates starts contemporaneously with carbonate deposition, but depends on the later access of water. In the porous calcareous tufa, diagenesis is uneven, and primary precipitates remain locally preserved.

Diagenetic changes are derived from recrystallization of primary precipitates and from secondary coating of the structures by cave-stone type deposits. Diagenetic recrystallization leads convergently toward an increase in the average carbonate grain size. No evidence of secondary micritization processes was found.

The present study has identified several active environments within the Plitvice travertine system that correspond to lithofacies assemblages described from Quaternary travertines in the central Apennines (FERRERI, 1985; D'ARGENIO & FERRERI, 1987), reviewed by GOLUBIC et al. (1993). Lithofacies assemblages of lentic environments described as (1) Calcareous sands with travertine intercalations, are observed in the Plitvice system in smaller deeper ponds separated by barriers that are arranged in terraces between larger upper lakes. (2) Phytoclastic calcarenite and phytohermal travertine with phanerogam fragments characterize shallow lentic conditions (quiet waters). Within this lithofacies assemblage, we have identified an oncolitic setting (Pl. 1, Fig. 3). A further four lithofacies associations refer to habitats and biota in lotic (fast flowing) environments with an increasing slope angle, as a consequence of accretion of travertine barriers. The most conspicuous feature is the stromatolitic type of lamination, which characterizes (3) Phytoclastic packstone-grainstone and stromatolitic travertine organized in lensoid and tabular bodies. Within this lithofacies, we have studied modern *Oocardium* in association with "bibliolitic" travertine, (layered carbonate-encrustged phanerogame leaf litter), on the edges of *Cratoneurum* facies. In the Plitvice system this environment is localized in parts of the barrier with gradual slope. (4) Phytoclastic rudstone with microhermal and stromatolitic travertine with moss cushions and (5) Micro-phytohermal and stromatolitic travertine with grasses are the two most widespread environments dominating on all the barriers of the Plitvice system. Within the above environmental context, the present study has uncovered the taxonomic identity of one of the fossil deposits reported by GOLUBIC et al. (1993, p. 236, pl. 2, fig. 8) as *Vaucheria geminata* (Pl. 4, Figs. 10–15).

The sequences of the travertine lithofacies combinations described above, when superimposed in a vertical sedimentary section do not reflect a change in climatic conditions. Instead, they are consequence of the lateral displacement of waterways and sedimentary environments, which are part of the normal depositional processes in travertines. A model illustrating these processes has been proposed (GOLUBIĆ, 1969; GOLUBIC et al., 1993) and was more recently documented by deep ground penetrating radar analysis (PEDLEY et al., 2000).

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