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ORGANIC COMPONENTS AND DIAGENETIC PRODUCTS IN THE TRAVERTINE DEPOSIT AT VILLERS-DEVANT-ORVAL (S. BELGIUM)

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(3 figures and 3 plates)

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ABSTRACT. The travertine deposit at Villers-devant-Orval (S. Belgium) formed during the Preboreal till the Boreal. In the first terrace studied in this paper, five lithostratigraphic units were distinguished, based on the presence of gravel, loam, peat and fine, medium grained and coarse travertine. Within the latter, encrusted branches and algal and cyanobacterial filaments are the most important organic components. Vadose diagenesis of the deposit is indicated by the presence of needle-crystals, fiber calcite crystals and dendrites. Meteoric phreatic diagenetic products occur as gothic-arch calcite crystals and euhedral crystals, which cement the pores.

KEYWORDS: travertine, algal and cyanobacterial filaments, diagenesis, needle-like calcite crystals, gothic-arch calcite crystals

SAMENVATTING. Organische componenten en diagenetische producten in de travertijnafzetting te Villers-devant-Orval (Zuid-Belgïe). De travertijn- of kalktufafzetting te Villers-devant-Orval (Zuid-Belgïe) vormde zich gedurende het Preboreaal en het Boreaal. In het eerste terras, dat hier bestudeerd werd, werden 5 lithostratigrafische eenheden onderscheiden op basis van grind-, leem- en veenlagen in de fijn-, medium- en grofkorrelige travertijn. De belangrijkste organische componenten van deze laatste zijn geïncrusteerde takken en algaire en cyanobacteriële filamenten. Naaldvormige kristallen, "fiber" calciet kristallen en dendrieten duiden op vadose diagenese van de afzetting. Gothische-boog kristallen en euhedrale kristallen vormden zich als cementen tijdens meteorisch freatische diagenese.

SLEUTELWOORDEN: travertijn, algaire en cyanobacteriële filamenten, diagenese, naaldvormige kristallen, gothische-boog kristallen

1. Introduction

Travertines have already been the subject of several investigations. Some important localities were studied in Italy (e.g. Folk *et al.,* 1985; Golubic *et al.*, 1993; Violante *et al.*, 1994), in the USA (e.g. Love & Chafetz, 1988) and in former Yugoslavia (e.g. Stoffers, 1975; Emeis *et al.*, 1987). Also the Belgian travertine deposits have been studied by several authors (e.g. Symoens *et al.,* 1951; Symoens, 1957; Geurts, 1976; Vervoort, 1984; Van Frausum, 1987). These latter studies mainly focused on the geomorphology, the palynology and age determinations. An investigation of the carbonate itself based on petrography and geochemistry has never been executed, except recently on some of the Belgian deposits (e.g. Treignes and Annevoie-Rouillon, Janssen & Swennen, in press; Janssen *et al.*, 1999).

In this paper, petrographical data on the fossil travertine deposit at Villers-devant-Orval (south Belgium) are presented. After a short introduction about setting and age, some particular diagenetic components and travertine textures will be discussed. The aim of this paper is to document that diagenetic products are common in travertine deposits.

2. Methodology

Samples of the travertine deposit at Villers-devant-Orval were taken from three of the eleven bore holes, that were placed within the first travertine terrace by the Belgian Geological Survey in 1968 and 1969, namely bore holes 1 (Pl. 217 E, 426 A), 4 (Pl. 217 E., 437 A) and 6 (Pl. 217 E, 437 C) (Fig. 1 and Paepe *et al.*, 1970). After macroscopic and binocular investigation, a more detailed study was carried out on selected samples by conventional transmitted light microscopy of thin sections. Because of their high porosity, the samples were first impregnated by blue resin before thin section preparation. To examine detailed textures on small broken rock samples, a JEOL-JSM 6400 Scanning Electron Microscope (SEM) was used. SEM operating conditions were 15 to 40 kVolt acceleration voltage, 2.10^{-7} to 10^{-9} A probe current, magnifications of 10 to 15,000 times and working distances of 39 to 8 mm. Mineralogical identification was carried out on a Philips PW 1130 X-ray diffractometer. Scanning conditions were Cobalt K_α-rays, 30 kVolt and 20 mA current, divergence slit of 1°, receiving slit of 0.1 mm and scatter slit of 1°. Scanning rate was 1° / min.

3. Geological setting and age

Villers-devant-Orval is situated in the province of Luxembourg in southern Belgium (Fig. 1A). The travertine deposit is formed in the Ruisseau du Williers, which forms at this location the border between Belgium and France (Fig. 1B).

In this Ruisseau du Williers, two successive travertine terraces alternating with travertine and peat deposits have been recognized (Fig. 1B-C). In both travertine terraces, nine bore holes were placed by Heinrich (1967) to determine the construction of the deposit. In 1968 and 1969 the Belgian Geological Survey has additionally executed eleven bore holes in the first travertine terrace and travertine-peat deposits (Paepe *et al.*, 1970; Souchez & Paepe, 1972; Paepe & Souchez, 1973). The main aim of the latter investigation was the study of one of the most important travertine deposits in Belgium, including radiocarbon dating, palynological investigation and determination of the precipitation rates of the travertines. Later, Geurts (1976) studied the palynology and the evolution of the palaeo-climate on an additional bore hole.

Despite the fact that within the travertine deposit large lateral variations occur in composition, travertine type, thickness and presence of peat layers, five lithostratigraphic units were distinguished within the 11 bore holes (Fig. 2). The substrate on which the travertine formed, consists of a calcareous sandstone, the so-called Luxembourg sandstone of Liassic age (Paepe *et al.*, 1970). However, these five units are not always easily distinguishable in the bore holes. Sometimes, their boundaries are not at all visible and can not be determined. The age of the different units was deduced from radiocarbon dating of intercalated peat layers

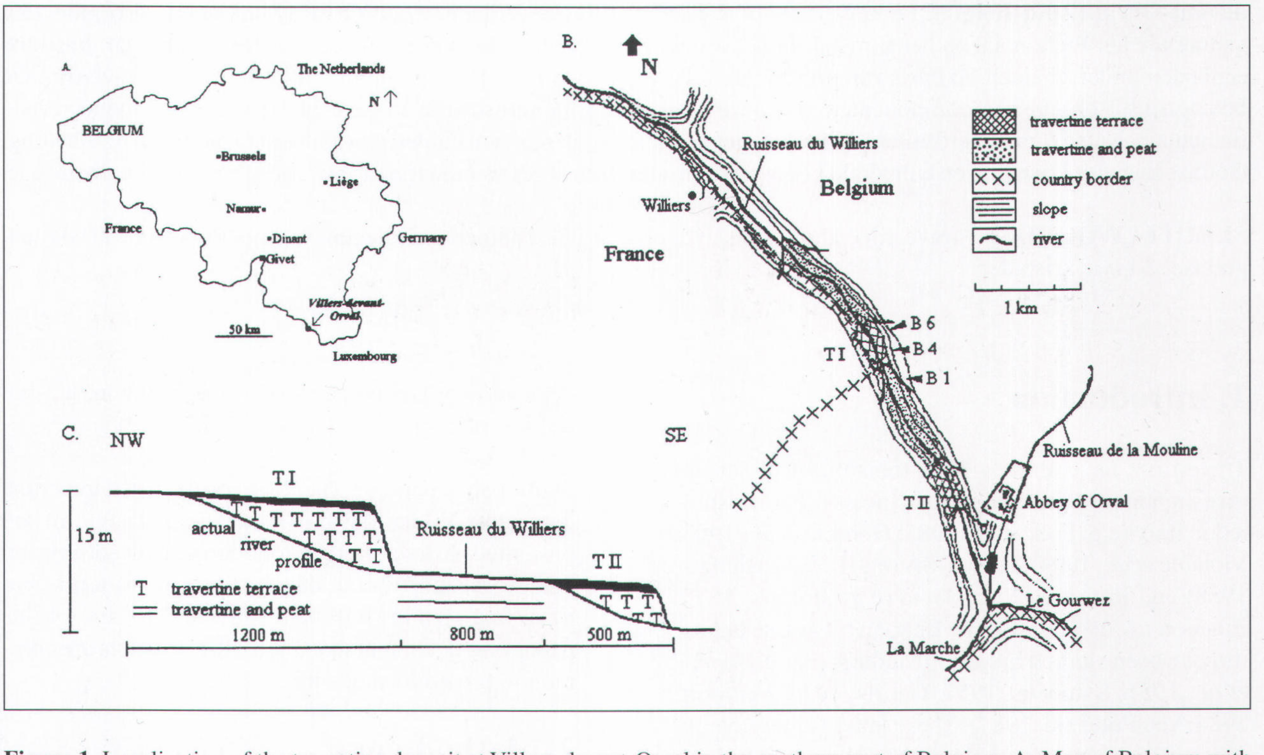


Figure 1. Localization of the travertine deposit at Villers-devant-Orval in the southern part of Belgium. A: Map of Belgium with the location of Villers-devant-Orval. B: Detailed map of the valley of the Ruisseau du Williers between Williers and the abbey of Orval. Both travertine terraces (T I and T II) and the exact locations of the three studied bore holes (B1, B4 and B6) are indicated. C: Cross section along the Ruisseau du Williers with indication of both travertine terraces (T I and T II) with intermediate travertine and peat layers (after Heinrich, 1967).

(Paepe & Souchez, 1973). The lower unit A is mainly composed of basal gravel and is Allerød or Bølling in age. The B unit, Preboreal in age, consists of the lower loamy travertines and peat layers. Subsequently, pure travertine (unit C) is present, that consists of fine travertine and thick layers of coarse travertine with many prints and remains of plants (e.g. branches and leaves). This pure travertine formed during the Preboreal and the Boreal. Precipitation continued during the Boreal with the formation of the upper loamy travertines and peat (unit D). Finally, the unit E consists of peat and travertine deposits. According to the ^{14}C-ages of the peat layers, this unit is Subboreal in age (Paepe *et al.*, 1970). The latter unit, however, is only present in bore holes 9 and 11, which were not studied here. It can be deduced from the radiocarbon ages of the intercalated peat layers that travertine of Atlantic age is not present. This points to a hiatus in deposition during this period, indicating incision of the river in its own former deposited travertine precipitates (Paepe & Souchez, 1973). However, Geurts (1976) mentions that, according to palynological data, deposition still continued during the Atlantic and that incision of the river only took place after this period.

4. Travertine textures and building components

In the here studied representative bore holes 1, 4 and 6, three dominant travertine types were distinguished. These in fact build up the upper described travertine units B, C and D (Fig. 2). Unit A consists of basal gravel and no travertine is present here. The first type consists of "fine homogeneous travertine" without any obvious macroscopic structure. The second type, the "medium grained travertine", has a more granular appearance since it is composed of carbonate grains of 0.5 to 2 mm in diameter. Finally, the "coarse travertine" consists of large fragments and structures and is mainly formed by encrustation of branches and higher plants. Precipitation around individual smaller branches causes the formation of tubes with central opening. These tubes are generally 2 to 4 cm in length and up to 5 mm in diameter. The structure of the branches is still visible in broken tubes. Encrustation of a whole set of branches forms a variant of the coarse travertine, the so-called "hard travertine".

A more detailed study based on binocular, thin section and SEM investigation of the travertine samples allowed the differentiation of different organic building components, crystal morphologies and travertine textures.

4.1 Organic components

Several organic components, such as branches, algal and cyanobacterial filaments, shells and shell prints and leaves, were determined. Most important are the branches and the algae and cyanobacteria. The branches form passive substrates on which the travertine precipitated, while the algae and cyanobac-

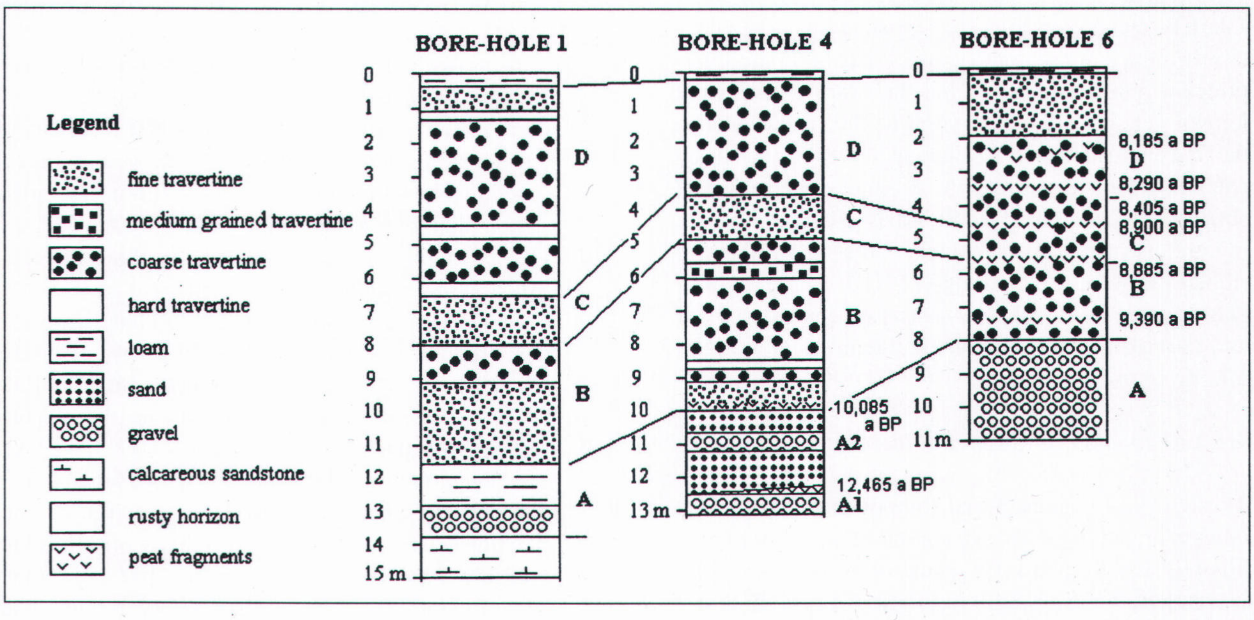


Figure 2. Profiles of the here studied bore holes 1, 4 and 6 in the first travertine terrace at Villers-devant-Orval. The profiles are reconstructed based on the travertine samples that were provided by the Belgian Geological Survey. Four of the five recognized lithostratigraphic units (A to D), as well as the radiocarbon ages of the intercalated peat layers are given, based on Paepe *et al.* (1970). Unit E is not indicated in this figure, because it only occurs in bore holes 9 and 11.

teria are encrusted by $CaCO_3$. Petrographical and geochemical data indicate an active biological influence of these microorganisms on carbonate precipitation (Janssen & Swennen, in press; Janssen *et al.*, 1999). However, the exact contribution of the algae and cyanobacteria has not yet been determined.

4.1.1 Encrusted branches

Most of the wood, branches and leaves that are present in the medium grained and coarse travertine are totally encrusted by $CaCO_3$. In broken samples of tubes and hard travertine, often parallel ridges can be recognized. This structure is formed by negative prints of the surfaces of the wood and branches, which themselves have disappeared due to organic decay. The original presence of these branches, leaves and stems of plants is also indicated by rounded and narrow long openings in the deposit (Pl. 1A) and small black remains of organic material between the calcite crystals. The organic material thus is not replaced by the $CaCO_3$. It is encrusted by these carbonate crystals before disappearance. Under binocular and in thin section, several parts can be distinguished within the encrustation (Pl. 1A-B). Around the central openings, which are left by the stems and leaves, large transparent sparry calcite crystals represent the first encrustation. These crystals are mainly oriented perpendicular to the original organic substrate. Subsequently, a denser zoned deposit, consisting of an alternation of light and dark brown micritic layers (each around 0.1 mm in thickness) is present. The crystals often are elongated and radially oriented. The spaces between the more dense deposit around the organic materials are then filled by a dark brown porous micritic deposit, which often contains rounded dense micritic balls. The latter are interpreted as pseudo-pelloids, but the exact origin is not known yet. In sections parallel to the former stems, the first encrustation forms elongated transparent sparry calcites, which accentuate the original ribbed external structure of the plants. Also the tubes with central opening are encrustations of branches, that leave negative ribbed prints in the opening (Pl. 1B). The carbonate encrustation here mainly consists of encrusted algal and cyanobacterial filaments and dense dark balls of micrite or pseudo-pelloids.

4.1.2 Algal and cyanobacterial filaments

The algal and cyanobacterial components usually form upward branching bushes of encrusted filaments. These bushes are dominantly present within the fine travertine, where small laminated aggregates are formed by successive layers of these bushes. Often, the aggregates possess a rusty color. Algal and cyanobacterial crusts are also present as radial deposits around branches. The encrusted filaments form micritic tubes and small towers with central openings (Pl. 1C). The inner dimensions of these openings vary between 5 to 10 μm, the outer dimensions are in the order of 15 to 20 μm in diameter. The encrustation consists mainly of massive deposits of anhedral calcite crystals. Between the filaments, the deposit is very porous. It is in these pores that the below described crystal morphologies have been recognized.

4.2 Crystal morphologies

Many different crystal morphologies, such as blocky (Pl. 3A-C), platy (Pl. 3A), anhedral, rounded (Pl. 3B), elongate (Pl. 3C), euhedral and coarse crystalline crystals have been recognized in the travertine deposit at Villers-devant-Orval. These crystal morphologies are very common in travertine deposits (e.g. Janssen & Swennen, in press; Janssen *et al.*, 1999). XRD analysis showed that all these crystals consist of low-Mg calcite. Apart from these crystals, also some crystal morphologies, which are much less common in travertines were recognized. These needle-like crystals and gothic-arch calcite crystals, are discussed in this paper.

4.2.1 Needle-like calcite crystals

The so-called needle-like calcite crystals form one of the most dominant crystal morphologies in the travertine deposit at Villers-devant-Orval. These carbonate crystals are characterized by a length : width ratio greater than 6 : 1 and consist of low-Mg calcite. Based on crystal form and structure, three different classes of needle-like crystals can be differentiated (Fig. 3).

a) The individual needle crystals are the most frequent morphology (class 1). They occur in all travertine types (fine, medium grained and coarse travertine). The needles consist of small single bars and they range from less than 1 μm up to 20 μm in length. Their diameter is less than 1 μm (Pls. 1D & 3A). Based on their dimensions, long small needles and short wider needles can be distinguished (Fig. 3). The needles are usually straight and have rounded or irregular crystal terminations. Normally they have smooth surfaces, which become irregular due to anhedral calcite growth upon the needles. Apart from the individual needle crystals, also networks can occur (Pl. 1D). In these networks usually a few groups of crystals with similar orientation can be distinguished. Often two dominant orientations perpendicular to each other are present. Well developed lattices can form in such a way. The needle crystals mainly occur in pores and holes within the travertine. They also occur on the surfaces of very large calcite crystals or they can be grouped tightly and parallel to each other.

b) A second and less common class of needle-like crystals are the so-called dendrite calcite crystals (class 2). These are crystals with a tree-like outline with a primary stem and primary branches. The stems are usually several µm long and less than 1 µm in diameter. The branches are smaller than 1 µm. These dendrite calcite crystals only develop locally.

c) The third type of needle-like crystals are the so-called needle fiber calcite crystals (class 3). These crystals are composed of parallel aligned small elongate crystals or rods that are glued or cemented together. The length of these fibers ranges from a few µm up to 100 µm and the width varies around 1 µm (Pl. 1E). The fibers mainly occur within the fine laminated travertine, that consists of several layers of upwards branching bushes of cyanobacterial filaments. Between these layers, flat surfaces with a rusty color are present. It is on these surfaces that the fiber crystals develop. The orientation of the fibers can either be random or tangential and their packing is tight or loose (Pl. 2A-B). Individual crystals are usually straight with flat crystal surfaces, but broken or curved and even twisted fibers have been recognized. An irregular bump often characterizes the termination of the individual fiber crystals (Pl. 2C). Normally, the fibers can be covered by an anhedral $CaCO_3$ that appears either in the form of a continuous layer (Pl. 2C) or as an irregular deposit on and between the fiber crystals (Pl. 2D). The former causes an irregular surface of the fibers. In the latter case, the fibers are cemented together and the original form of the fiber crystals is obscured by the anhedral $CaCO_3$ deposit.

Based on the number of the parallel aligned needle crystals composing the fibers, the following classification has been worked out (Fig. 3):

a) 1-lobed fibers that are small single needles with a semi-circular section.

b) 2-lobed fibers that are composed of two parallel needles with semi-circular section (Pl. 2C). Usually, those two needles are cemented together by an intermediate smaller part.

c) 4-lobed fibers that consist of four semi-circular calcite needles grouped by two and parallel to each other. In the center between the four needles an intermediate part may be present. Consequently,

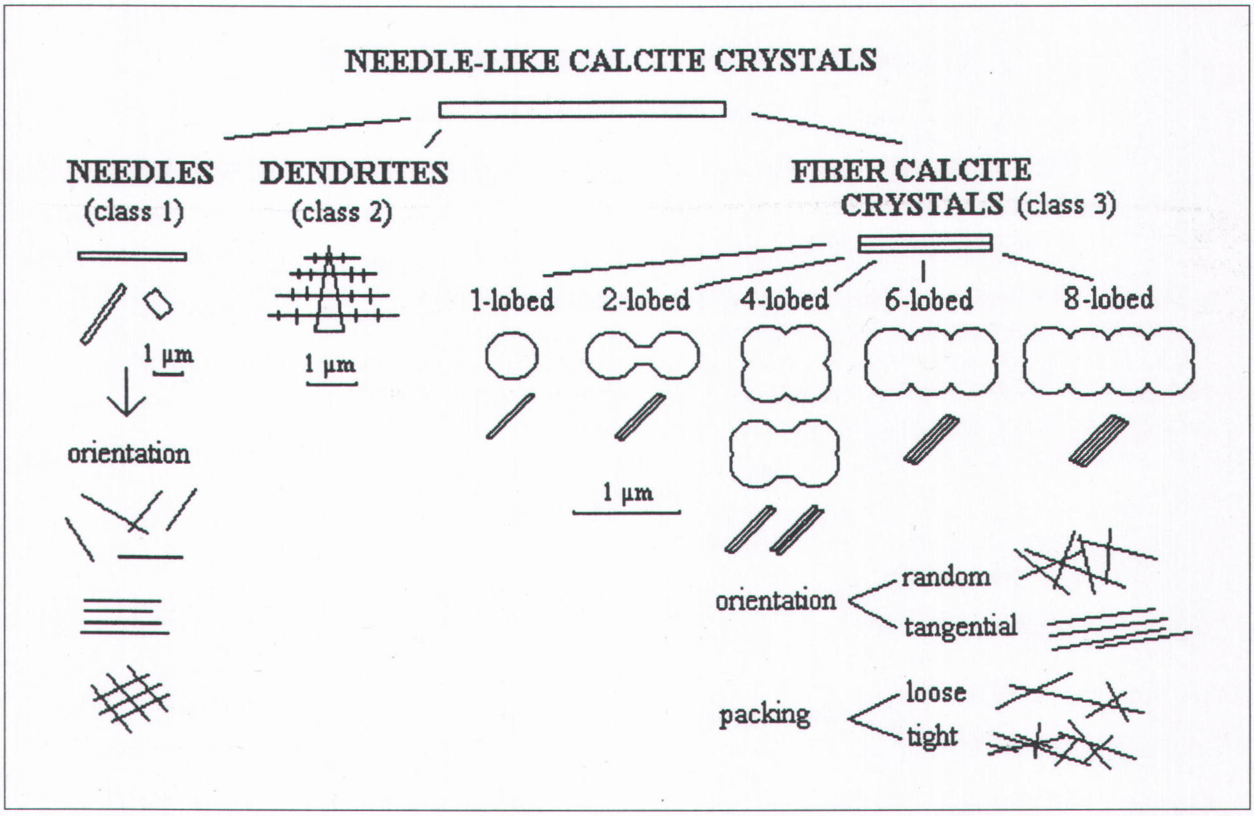


Figure 3. Classification of the needle-like calcite crystals, that were recognized within the travertine deposit at Villers-devant-Orval. Class 1 needles consist of long small needles and short wider needles and they have a random or a parallel orientation. These needles also occur as well developed lattices. Class 2 dendrites only develop locally. Class 3 needle fiber calcite crystals can be subdivided into 1-, 2-, 4-, 6- and 8-lobed fibers. Their orientation can be either random or tangential and their packing is loose or tight.

PLATE 1

A-B: Photomicrographs of thin sections of $CaCO_3$ encrustation around branches, stems and leaves. A: Different parts can be distinguished: (1) central openings left open after decay of the organic material; (2) large transparent sparry calcite crystals, forming the first encrustation; (3) a dense zoned deposit of alternating light and dark micritic layers and (4) a porous brown deposit in between. Scale bar is 1 mm. B: Knotty carbonate deposit around a central branch, forming tubes with central opening. Here the encrustation is formed by dense dark micritic balls or pseudo-pelloids and zoned light-dark micritic layers. Scale bar is 250 µm.

C-D-E: Scanning electron microscopy photomicrographs of some organic components and crystal morphologies in the travertine deposit at Villlers-devant-Orval. C: upward branching bushes of encrusted cyanobacterial filaments forming tubes with central opening. Scale bar is 100 µm. D: Needle calcite crystals forming a porous open network in a pore. Scale bar is 10 µm. E: Needle-fiber calcite crystals composed of parallel-aligned needles. Scale bar is 1 µm.

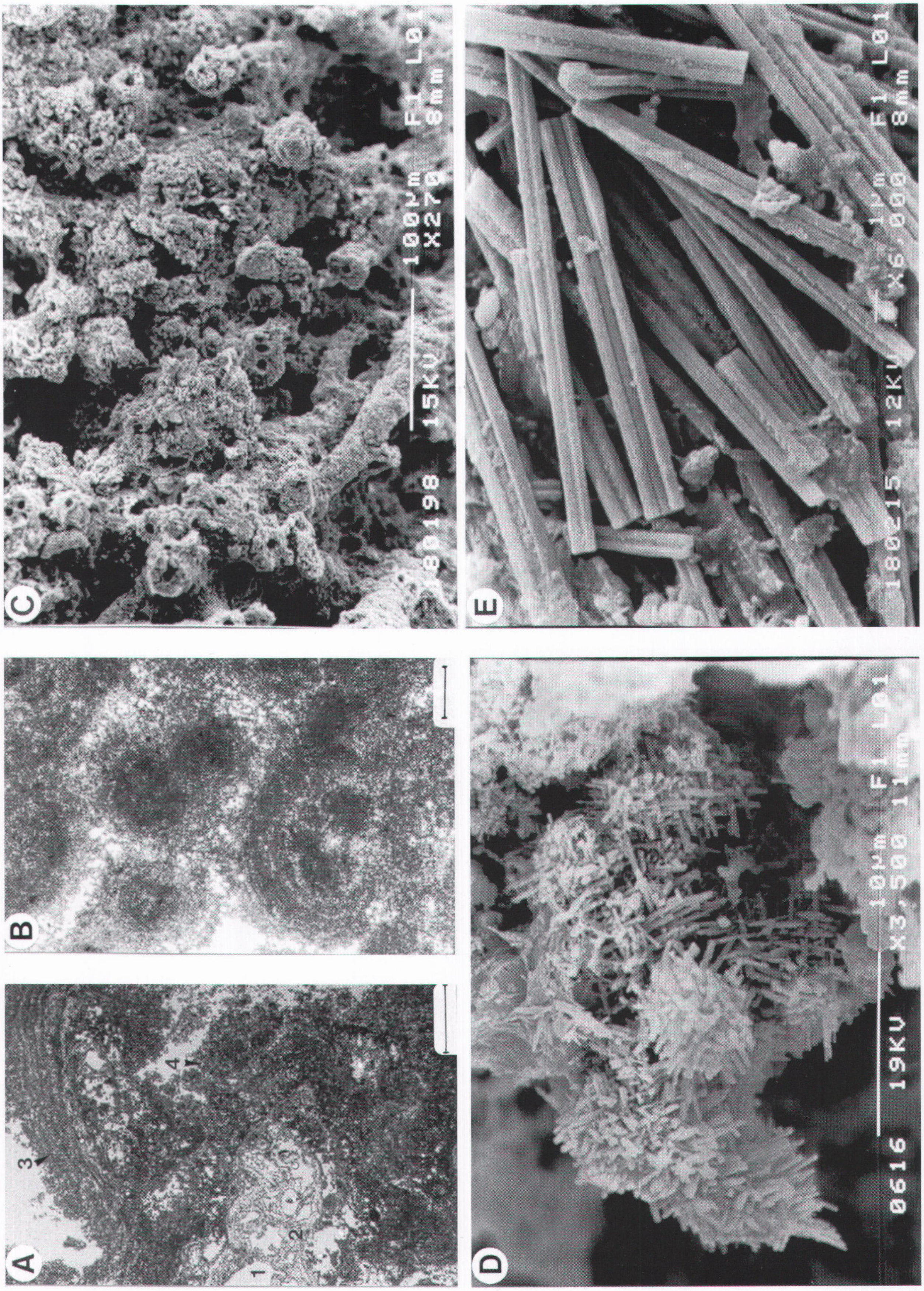
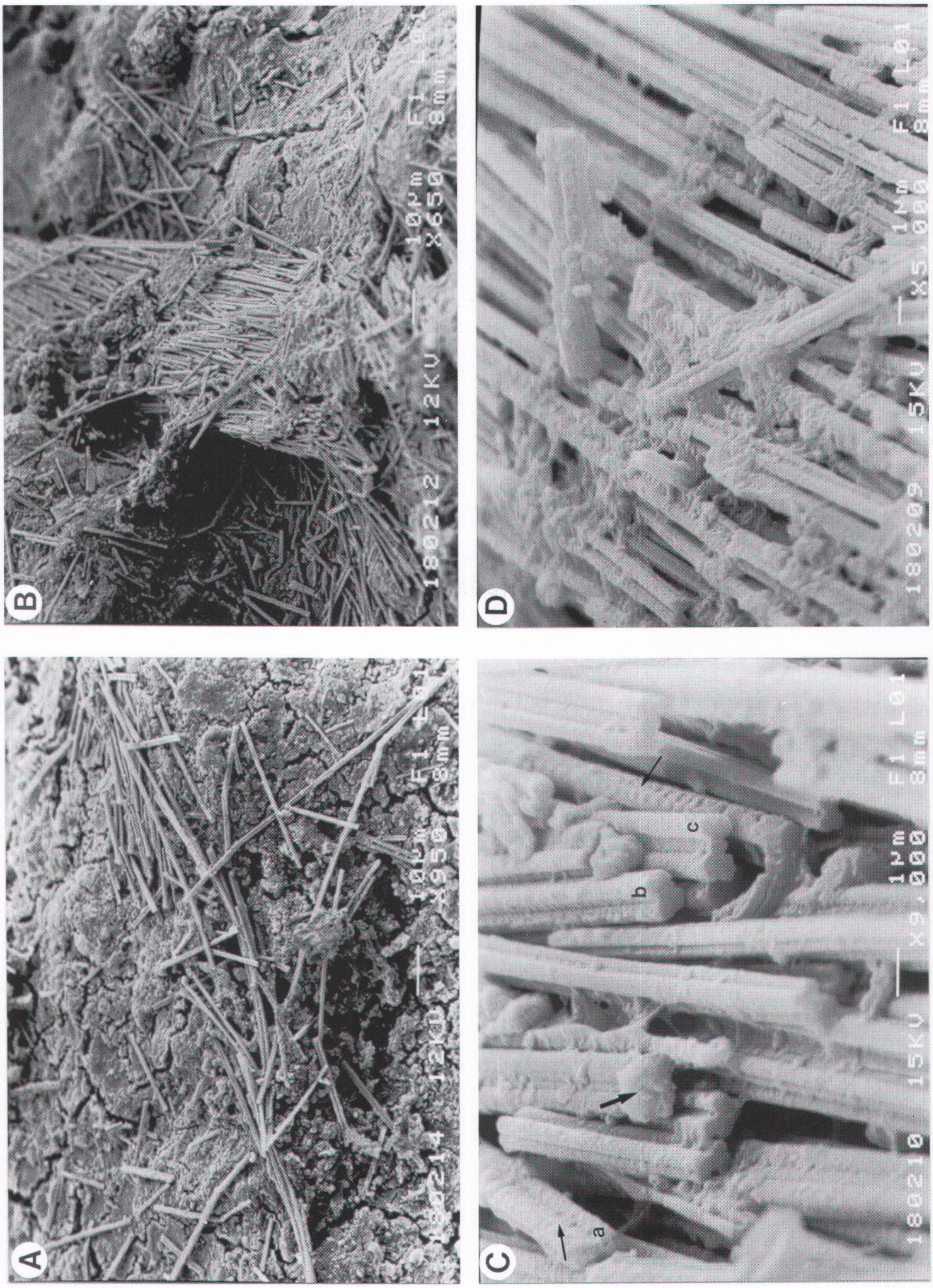

A
B
C
D
E

PLATE 2

A-D: Scanning electron microscopy photomicrographs illustrating needle-fiber calcite crystals occurring on a rusty surface between two cyanobacterial layers. A: Random orientation and B: Tangential orientation. Scale bar is 10 µm. C: Detailed picture of the fiber calcite crystals, with anhedral $CaCO_3$ covering the fiber crystals (small arrow) and an irregular bump characterizing the crystal terminations (bigger arrow). Based on the number of the composing needles, different fiber calcite crystals are distinguished, such as 2-lobed (a), 4-lobed (b) and 4-lobed fibers with an intermediate part (c). Scale bar is 1 µm. D: An irregular anhedral $CaCO_3$ deposit covers the crystals and obscures the original outline of the fibers. Scale bar is 1 µm.


A
B
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a
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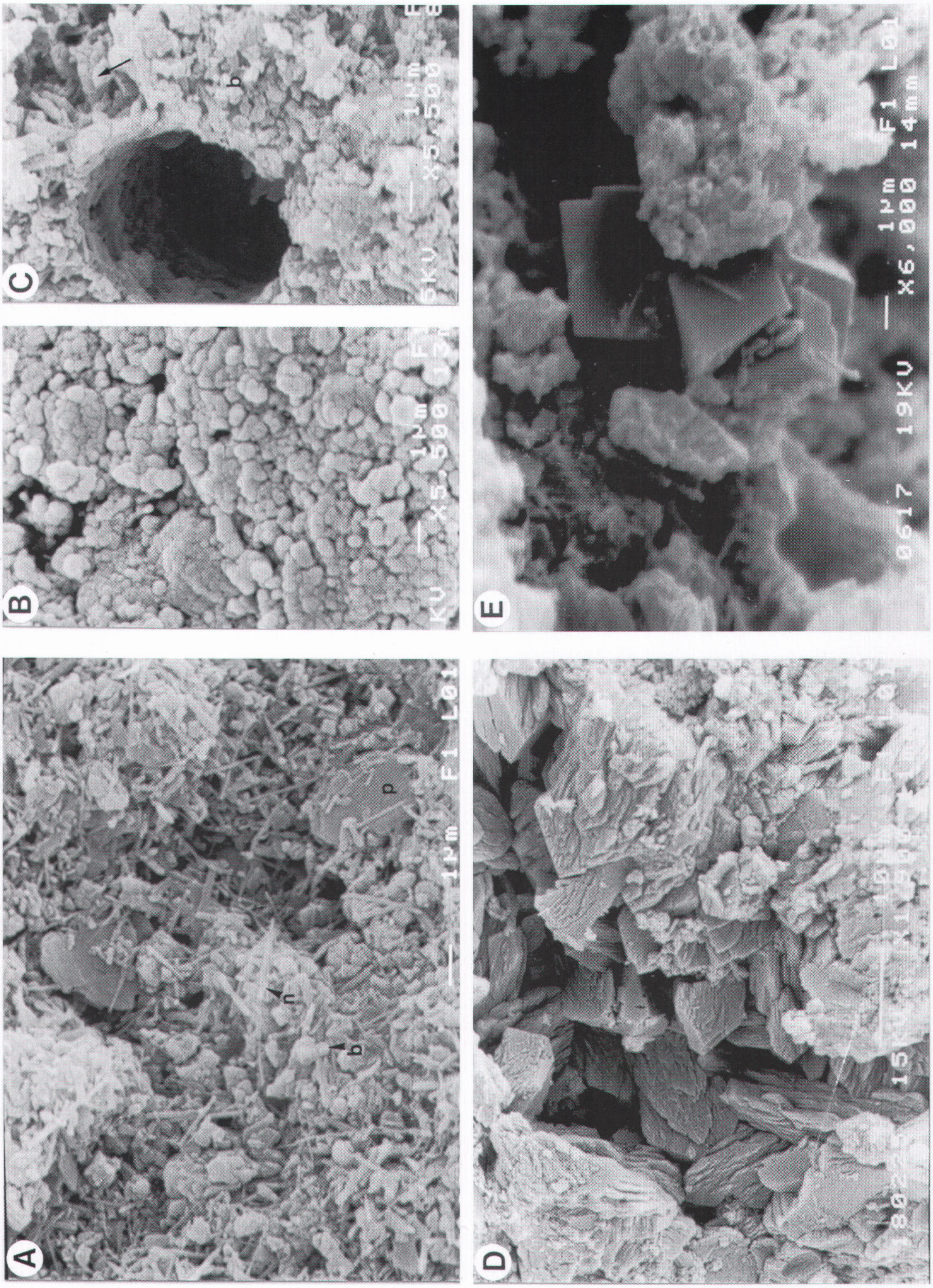
PLATE 3

A-B: Scanning electron microscopy photomicrographs illustrating the porous travertine deposit, consisting of different types of common calcite crystals. A: individual needles (n), blocky crystals (b) and platy crystals (p). B: rounded crystals. C: The encrustation around a cyanobacterial tube is formed by blocky crystals (b) and radially oriented elongate calcite crystals (arrow). Scale bar is 1 µm.

D-E: Scanning electron microscopy photomicrographs of uncommon calcite crystals formed as cements within the pores of the deposit. D: Gothic-arch calcite crystals. Scale bar is 10 µm. E: Euhedral calcite crystals. Scale bar is 1 µm.


A
B
C
D
E
0617 19KV — X6,000 14mm
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two types of 4-lobed fibers can be differentiated (Pl. 2C), namely fibers with and without an intermediate part.

d) 6-lobed fibers that are composed of two parallel groups of three needles glued together. The cements between the individual needles are not well defined and an intermediate part is not present.
e) 8-lobed fibers that consist of two parallel groups of four needles glued together.

It is obvious that in this classification only fibers consisting of multiples of two needles are present and 3-, 5- or 7-lobed fibers have not been recognized.

Similar needle-like calcite crystals have already been mentioned in literature, where they are mainly described from pedological environments, such as calcareous soils and calcretes (e.g. Verges *et al.*, 1982; Callot *et al.*, 1985; Phillips & Self, 1987; Jones & Kahle, 1993; Verrecchia & Verrecchia, 1994). As far as we know, needle crystals such as those described in this paper, have never been described in travertine deposits before.

Within the literature, calcite crystals with a length : width ratio of 6 : 1 or more are determined as fiber calcite crystals. Every tree-like crystal that has a primary stem, primary branches and in some cases secondary branches, is called a dendrite. Two distinct morphological groups of needle crystals occur within soils and calcretes (e.g. Phillips & Self, 1987). The first morphological group consists of very small single rods with a diameter of 0.1 µm or less and a length of about 1 µm. These crystals are called micro-rods. The second group consists of larger sized needle crystals that are referred to as needle fiber calcite crystals. These needle fiber crystals are 2 to 100 µm long and have a diameter of 0.5 to 2 µm. Within this second morphological group there are two subgroups. The first subgroup is the most common and consists of smooth rods that are formed by a variable number of parallel aligned and cemented single rods. The second subgroup is formed by elongated fibers with serrated edges.

Based on these two morphological groups, two classification systems for fiber and dendrite calcite crystals are proposed. A first classification is based on shape (distinction between fiber and dendrite crystals), disposition (random or tangential orientation) and packing (tight or loose) and is proposed by Jones & Kahle (1993). Further subdivision of the fiber crystals on the basis of the crystal form consists of hexagonal, composite, ribbon and rhomb chain fibers. In cross section, 2, 4 or 6 distinct lobes can be differentiated. The second classification is proposed by Verrecchia & Verrecchia (1994). These authors make a differentiation between monocrystalline and polycrystalline rods. The former consist of small micro-rods (M type), smooth paired rods (MA type) and serrated paired rods (MB type). The MA type is further subdivided based on the number of parallel aligned rods within the fiber crystal. The MA 1 type consisting of two cemented rods is the elemental crystal form. The polycrystalline rods are composed of chains of small platelets forming a needle-like crystal.

Needle fiber calcite crystals appear to be very sensitive to both destructive and constructive diagenetic modification (Jones & Kahle, 1993). In the former case, dissolution and breaking down of the fibers forms smaller rods. In the latter case, epitaxial growth around the fibers can enclose the original crystals and fill the spaces between parallel and random fibers.

The needle-like calcite crystals that occur within the travertine deposit at Villers-devant-Orval are very similar to those described from calcretes and calcareous soils. As is mentioned earlier, within the travertine, two common types of needle crystals are recognized, which are comparable to the two morphological groups described in the literature. The small needle crystals (class 1) correspond to the micro-rods, while the needle-fiber crystals (class 3) are similar to the smooth paired rods. However, no serrated rods were recognized in the here studied travertine deposit.

At Villers-devant-Orval, precipitation of anhedral $CaCO_3$ on the needle crystals can occur. This carbonate precipitation is similar to the epitaxial growth of $CaCO_3$ on the fiber crystals that is mentioned by Jones & Kahle (1993). The presence of this anhedral deposit on the fibers indicates that diagenetic modification occurred after formation of the fibers. Furthermore, this diagenesis could be one of the reasons that needle fiber calcite crystals have not been recognized more often in travertine deposits.

Based on the occurrence of needle-fiber calcite crystals within pedogenic environments, a vadose diagenetic origin can be assumed for the needle like calcite crystals (e.g. Phillips & Self, 1987; Jones & Kahle, 1993). Furthermore, both inorganic fysico-chemical precipitation and biologically influenced precipitation are invoked as possible mechanisms for the needle calcite crystal formation. In the former case, very high supersaturation of the solution is often accompanied by intense evaporation and CO_2-outgassing (Given & Wilkinson, 1985). This causes fast and differentiated growth of the crystals (Verges *et al.*, 1982) parallel to their c-axis. In this direction growth is controlled by the availability of the CO_3^{2-}- ions and is not limited by dehydration of the Ca^{2+}. Furthermore, organic compounds or other ions can inhibit crystal growth in a specific direction.

Since needle crystals are, however, commonly associated with plant roots, algae, fungi or bacteria (Klappa, 1979; Folk *et al.*, 1985), a biological origin for these crystals is possible. Here, absorption of organic compounds inhibiting lateral crystalline growth is often reported. Alternatively, crystals can develop inside microorganisms.

Detailed research on the needle crystals in soils showed that the two above described morphological groups of needle crystals are formed by two different biological processes (Callot *et al.*, 1985; Phillips & Self, 1987; Verrecchia & Verrecchia, 1994). On the one hand, the small single micro-rods are in fact calcified bacteria, while, on the other hand, the larger needle fiber calcite crystals are formed due to internal precipitation of $CaCO_3$ within fungal filaments (hyphae or mycelian strands). These fungi feed on organic matter that is present within the fossil travertine deposit. Because of the high Ca^{2+}-concentrations outside of the fungal filaments in comparison with the inner part of the cell, Ca^{2+}-ions are transported passively into the cell. In order to remove these Ca^{2+}-ions from the fungal cell, the organisms actively precipitate the Ca^{2+} as $CaCO_3$ crystals. The morphology of the crystals is determined by the outline of the fungal cell, so that a fiber crystal consisting of two parallel aligned rods is formed. The fiber crystals that consist of multiples of two rods are probably due to linkage of fibers that are formed within adjoining hyphae. The irregular terminations of the fibers may have been the sites of attachment or nucleation within the hyphae. Due to decomposition and disappearance of the fungal hyphae, the fibers within the filaments are released, forming bundles or irregular meshes. Later epitaxial growth of plates and rhombs on the crystal surfaces, causes formation of the serrated paired rods (Verrecchia & Verrecchia, 1994).

The observations from the travertine deposit at Villers-devant-Orval confirm both the vadose diagenetic and the biologically influenced origin for the needle crystals. In the Belgian example, needle-like calcite crystals have only been recognized in fossil deposits, where precipitation activity has ceased. Furthermore, based on their geomorphological position, it is likely that the deposits have undergone vadose diagenesis for a considerable time period. The samples containing the fibers are taken from this present-day vadose zone in the travertine deposit. In recent still active travertine deposits, the needle crystals have not been recognized (Janssen & Swennen, in press; Janssen *et al.*, 1999). The small single needles (class 1) occur on the surfaces of larger calcite crystals, between calcite crystals and in the pores between the denser deposit of larger crystals (Pl. 3A). This points to needle crystal formation after precipitation of the larger crystals and the creation of the pores. In the latter, the crystals form porous networks that bridge the walls (Pl. 1D). Furthermore, the needle crystals are recognized in print-cavities of wood, shells and leaves as well as in voids left by algal and cyanobacterial filaments. It is obvious that this precipitate only could have formed after encrustation and disappearance of the central filament. The fiber crystals (class 3) occur on rusty colored oxidized surfaces between two layers of cyanobacterial filaments. They are seldom recognized within the cyanobacterial bushes.

Since the fiber calcite crystals (class 3) within the travertine deposit show the same characteristics as the fibers described from calcretes and soils, it is most likely that these needle crystals have a similar fungal origin. Since fungal hyphae were not recognized within the travertine, this can not be proven directly. However, it is possible that these organisms have disappeared due to organic decay and that only the fiber crystals remain visible within the deposit. Furthermore, no indications of cyanobacterial or algal origin of the fiber crystals were found. A close association between these components and the needle-like crystals is not obvious. The crystals mainly form in pores and voids between the calcite crystals and the algal and cyanobacterial filaments. The fiber calcite crystals are mainly present between two cyanobacterial layers. Since here cyanobacterial evidences are absent, their influence is considered to be limited. These observations show that biological precipitation in relationship with cyanobacteria or algae is not likely.

The smaller single needle crystals (class 1) can be compared with the micro-rods described from soils and calcretes. However, the needles within the travertine deposit are longer than the soil crystals and no bacterial bodies were recognized. The exact origin of these small needles thus remains unsure. In our opinion, they are not fungal in origin, because of the differences in crystal morphology with the above described fiber crystals. Furthermore, no evidence is seen for algal or cyanobacterial origin. The most plausible origin for these needles remains bacterial precipitation.

4.2.2 Gothic arch and euhedral calcite crystals

The so-called gothic-arch calcite crystals (named after Folk *et al.*, 1985) form another morphology of beautiful uncommon calcite crystals that have been recognized in the travertine deposit at Villers-devant-Orval (Pl. 3D). These large crystals of about 10 to 40 µm in length, 10 µm wide and with a thickness of 2 to 3 µm, are characterized by triangular faces that converge to one point. This causes the so-called gothic-arch outline of the crystals. Another characteristic feature is that the main face of the crystal is covered with smaller successive slabs possessing similar gothic-arch shapes, while the smaller face is completely flat (Pl. 3D). The gothic-arch crystals occur in larger pores within the fine homogenous and the medium grained travertine. They always grow towards the center of the pore. Here also, these crystals have not yet been recognized in the recent, still active travertine deposits in Belgium. Both arguments of growth position and formation time of the crystals in the deposit can be used to support a diagenetic origin for these crystals. Similar gothic-arch crystals are mentioned by Folk *et al.* (1985) in hot-spring travertine deposits in Italy as steep rhombic crystals having a series of flat iron-like slabs added to rhombic faces. The authors also put forward a hypothesis for the formation of the crystals. Because in a S-rich environment a SO_4^{2-}-group can take the place of a planar CO_3^{2-}- group in the calcite, the carbonate sheets bent upwards forming the gothic-arch crystals. In this study, however, the SO_4^{2-}-concentrations of the river water from which the travertine precipitated, are relatively small to negligible. Consequently, the hypothesis of Folk *et al.* (1985) can not be used here. Probably the gothic-arch calcite crystals formed due to rapid precipitation from highly supersaturated waters. The fact that they fill up pores from all directions supports a phreatic meteoric diagenetic environment.

It is assumed that in places where supersaturation and precipitation rates are smaller, the gothic-arch crystals will be absent. Instead rhombohedral calcite crystals, that are called euhedral calcite crystals in this study, form in the pores of the deposit (Pl. 3E). These crystals also form as cements during meteoric phreatic diagenesis.

5. Conclusion

Petrographical investigation of the travertine deposit at Villers-devant-Orval showed that this deposit, which formed during the Preboreal until the Boreal in the Ruisseau du Williers, is built up by encrustation of higher plants, such as branches and leaves, and algal and cyanobacterial filaments. The former occur as calcitized tubes and hard travertine. The algal and cyanobacterial filaments often form upwards branching bushes. The encrustation of the organic compounds consists of calcite crystals with many different morphologies.

After active travertine deposition ceased, the deposit was diagenetically modified. Organic decay caused the disappearance of the algae and branches forming holes and pores. Furthermore, needle-like calcite crystals (needles, needle fiber calcite and dendrites) and gothic-arch crystals formed next to the more classical euhedral calcite crystals. These crystals testify of a vadose and meteoric phreatic setting. Such needle-like calcite crystals, especially the fiber calcite crystals, are most likely here for the first time described in travertine deposits.

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