

PETROGRAPHY AND GEOCHEMISTRY OF THE TRAVERTINE DEPOSIT AT TREIGNES (S. BELGIUM)

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ABSTRACT. Active as well as paleo-travertine precipitates at Treignes (S. Belgium) have been studied from a petrographical and a geochemical point of view. ¹⁴C dating gave an age of about 8,600 y.B.P. for the lower part of the seven meter thick profile. Within the recent travertine deposits, precipitates on inorganic and organic structures can be differentiated. Six morphotypes (ball, knotty, prickly, branched, cauliflower and granular precipitates) make up these structures. Algal filaments, bacterial filaments and diatoms are omnipresent. Within the paleo-deposit, three dominant morphotypes have been recognized (fine tufa, aggregates with towerlike and knotty precipitates and tubes). However, here nearly no organic features have been determined, most likely due to organic decay. Instead, acicular calcite cements of vadose and blocky cements of meteoric phreatic origin are often present. Bulk trace element distribution in the profile allows to differentiate a lower succession with moderate Fe and Mn contents and an upper part with comparable high contents as encountered in the recent precipitates. This difference has been interpreted to relate to the positioning of a paleo-ground-water table. $\delta^{13}\text{C}$ values of the precipitates (between -9.11 and -11.77 ‰ PDB) clearly show that, apart from atmospheric-related CO₂, mixture with a depleted CO₂ source occurred, which is interpreted in terms of photosynthetic activity of algae and bacterial processes. If precipitation occurred in equilibrium to the present-day water of the «Fonds de Ry» ($\delta^{18}\text{O} = -7.32$ ‰ PDB) the calculated precipitation temperature is 12° C for the carbonates ($\delta^{18}\text{O}$ values between -5.48 and -6.78 ‰ PDB). A slight difference in stable carbon and oxygen isotope composition exists between recent and paleo-deposits with recent precipitates being the most depleted. This difference is explained in terms of diagenesis. Diagenetic alteration makes it necessary to be very careful in determining palaeoclimatic signals based on stable isotope analysis.

KEY-WORDS: Travertine textures, algal and bacterial filaments, stable isotope geochemistry, trace element geochemistry, diagenesis.

RESUME. Les dépôts de travertin actif et fossile à Treignes étaient étudiés du point de vue pétrographique et géochimique. La datation en ¹⁴C de la partie basale du profil donne un âge d'environ 8,600 ans B.P. Dans les dépôts récents, des précipitations sur des structures organiques et inorganiques peuvent être différenciées. Ces structures sont construites par six types morphologiques. Des filaments algaires et bactériens et aussi des diatomées y sont présent. Dans les paléo-dépôts, trois types morphologiques peuvent être reconnus (du tuf calcaire fin, du calcaire grossier et des tubes). Ici les structures organiques ont presque disparu, du fait de la décomposition de la matière organique. Au contraire, des ciments de calcite aciculaire et euhédrale d'origine vadose et phréatique sont présent. La distribution des éléments en trace dans le profil montre la présence de concentrations modérées de Fe et Mn dans la partie inférieure et des concentrations comparables à celles des dépôts récents pour la partie supérieure. Cette différence peut être reliée à la position d'une paléo-nappe phréatique. Les valeurs de $\delta^{13}\text{C}$ des carbonates (entre -9.11 et -11.77 ‰ PDB) traduisent un mélange du CO₂ atmosphérique avec une source appauvrie en ¹³C. Cette dernière source est probablement reliée à l'activité photosynthétique des algues et des bactéries. Si l'on admet que la précipitation des carbonates ($\delta^{18}\text{O}$ valeurs entre -5.48 et -6.78 ‰ PDB) s'est faite en équilibre avec l'eau du Fonds de Ry ($\delta^{18}\text{O} = -7.32$ ‰ PDB), une température de précipitation de 12°C peut être calculée. La différence entre les compositions des isotopes stables des dépôts récents et fossiles peut être expliquée par les phénomènes de diagenèse observés dans les dépôts fossiles. La plus grande prudence dans l'interprétation paléoclimatique basée sur cette méthode isotopique doit donc être observée.

MOTS-CLES: Textures de travertin, filaments algaires et bactériens, géochimie des isotopes stables, géochimie des éléments de trace, diagenèse.

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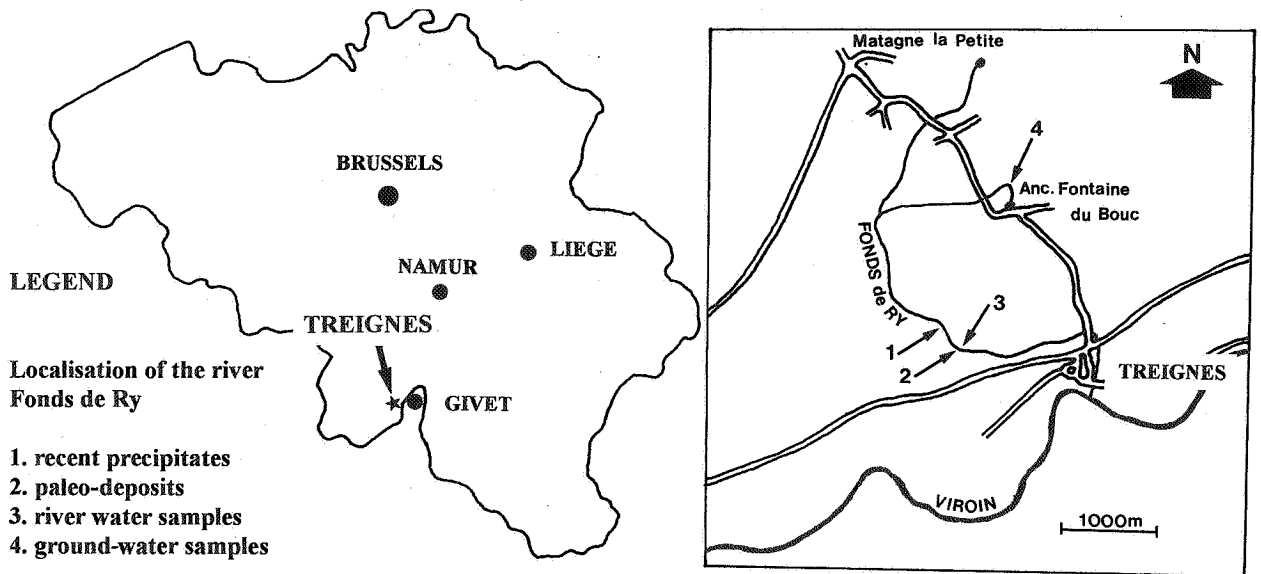


Figure 1. Localisation of the travertine deposit at Treignes.

1. INTRODUCTION

Travertines are carbonate rocks that form due to CO_2 outgassing in rivers and lakes. This outgassing can be the consequence of turbulence within waterfalls and rapids or can be related to the photosynthetic absorption of CO_2 by organisms (plants, algae, bacteria, ...). However, which mechanism is the most important is still a matter of debate. Several authors put forward arguments to show that biological influence is neglectable against pure inorganic precipitation (Couteaux, 1969; Lorah & Herman, 1988; Hoffer-French & Herman, 1989, ...). Others, however, provide valid data that biological interferences may cause carbonate precipitation (e.g. Adolphe, 1981; Folk *et al.*, 1985; Casanova, 1986; Winsborough & Golubic, 1986; Castanier, 1987; Freydet & Verrecchia, 1989; Golubic *et al.*, 1993; ...), while still other authors point to the combined effect of both mechanisms.

Several international classification systems of travertine and tufa deposits are available. Some of them are based on the geomorphological position where the travertines form. Chafetz & Folk (1984) differentiate the following travertine types: waterfalls or cascades, lake fills, sloping mounds, fans or cones, terraced mounds and fissure ridges. Magnin *et al.* (1991) distinguish only two groups of travertines, namely source travertines and river or valley travertines. Other travertine types, such as spring and river bed travertines, in place and clastic travertines, laminated algal crusts in waterfall travertine deposits, perched springline, cascade, fluvialite, lacustrine and paludal travertine deposits, are described in Ramon (1983), Love & Chafetz (1988) and Pedley (1990). Other classifica-

tion systems are based on the dominant building components and the organisms present in the deposit. Pedley (1990) differentiates autochthonous and allochthonous tufas. Irion & Müller (1968) describe different types of tufas from the Schwäbische Alb (Germany), where they distinguish algal and moss tufa and calcareous sinter. Further subdivision is made according to the dominant algae or moss species. Also Riding (1991), Golubic *et al.* (1993) and Violante *et al.* (1994) use the organisms as criteria for classification. However, an international classification scheme classifying macroscopic morphotypes and microscopic textures is not yet available.

In our study, the building components of the present-day active and paleo-travertine deposit of Treignes will be described and their characteristic features discussed. The biological influence on carbonate precipitation will be addressed. Furthermore, we will focus on diagenetic alteration products and processes which affected the paleo-deposit. Consequently petrographical and major, trace and isotope geochemical data will be presented. The study of diagenetic alteration is important, since travertine deposits are recently also used for determination of variations in palaeoclimate, mainly

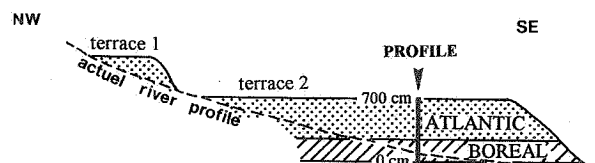


Figure 2. Longitudinal profile of the river «Fonds de Ry» at Treignes (modified after Mullenders *et al.*, 1963).

based on stable isotope analysis (Casanova, 1986; Pazdur *et al.*, 1988; Lecolle & Letolle, 1990; Andrews *et al.*, 1993). Diagenetic processes, however, are capable of changing the initial structures and geochemical signals, which, if not properly recognized, may lead to wrong paleo-environmental conclusions.

The studied travertine deposit is situated in a small river, named the «Fonds de Ry» at Treignes, a small village between Couvin and Givet in southern Belgium (Fig. 1). This travertine deposit was chosen since both present-day active travertine formation and paleo-deposits in a seven meter travertine terrace (Fig. 2) are easily accessible for research.

2. METHODOLOGY

Samples were taken during two sampling campaigns (August 1994 and March 1995). Recent deposits were sampled in the river bedding, while 33 samples within paleo-deposit (sample interval \cong 20 cm) were taken in a profile within the second terrace (Figs. 1 & 2). Ground-water was sampled from the source of the «Ancienne Fontaine du Bouc» and river water was taken from the river «Fonds de Ry» next to the location of active precipitation (Fig. 1). Water samples were collected in poly-ethylene bottles. The water samples for trace element analysis were slightly acidified by 5 ml HNO₃ (ultra-pure). Analysis was carried out within a month after sampling.

After drying under atmospherical conditions and binocular investigation of surface and cut samples, a more detailed petrographical study was carried out by conventional microscopy of thin sections. The samples were firstly impregnated by blue resin. Cathodoluminescence research of the cements in the samples was carried out with a Technosyn Cold Cathode Luminescence Model MKII. Operational conditions were 16-20 kV, 500 mA gun current, about 0.07 Torr vacuum and about 5 mm beam width. Since no visible luminescence occurred, microphotographs were taken with an exposure time of 6 minutes.

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 25 kV, 60 μ A and about 600 Å beam width. To reveal better some of the organic structures, representative samples were etched by immersing them in technical HCl (1 N) during 30 seconds.

Mineralogical identification was carried out by using an exL-LINK energy dispersive analytical system on SEM and by a Philips PW 1130 X-ray diffractometer. Scanning conditions were Cobalt K α -rays, 30 kV and 20 mA current, divergence slit of 1°, receiving slit of 0.1 mm and scatter slit of 1°. Scanning rate was 1° / min.

The geochemical study of the samples consisted of a trace element and a carbon and oxygen isotope analysis. After careful petrographical selection, a micro-drill assembly (drill-bit diameter 0.5 to 1 mm) was used to obtain powders of 1 to 10 mg. Isotopic analysis of carbon and oxygen was performed on a Finnegan Mat Delta E stable isotope ratio mass spectrometer at the stable isotope laboratory of the V.U.Brussel. Carbonate powders were dissolved in about 100 % orthophosphoric acid at 25°C. All data have been corrected following procedures modified by Craig (1957). Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported relative to the PDB international standard. Reproducibility, determined by replicate analysis of NBS 19 and NBS 20, is better than 0.1 ‰ for oxygen and 0.05 ‰ for carbon. Isotopic analysis of river and ground-water was carried out at the «Institut für Hydrologie» at Oberschleißheim in Germany. Reference to the SMOW international standards is made for the water analysis.

Trace element analysis of Mg, Na, Sr, Mn and Fe was carried out by using a AA1475 flame analyzer on carbonate powders of 1 g. These powders were firstly dissolved in 20 ml of a concentrated hydrochloric acid. After complete reaction, the dissolved sample was evaporated, the residue then was dissolved in 20 ml of 2.5 N HCl. After filtration, the fluid was diluted with demineralised water to 50 ml. The concentration in ppm was calculated by comparison with standard solutions with known concentrations. To avoid matrix interferences for Sr, the samples were compared with representative calcite calibration curves. Analytical precision was generally better than 10 % at the 95 % confidence level (Swennen *et al.*, 1986). The amount (%) of HCl insoluble residue (IR) was determined by weighing the filter-papers. Trace element analysis of the water samples was carried out at the «Vlaamse Maatschappij voor Watervoorziening» (Brussels) by ICP-MS. Results are given in ppm and ppb.

Dating of the organic-rich layers of the paleo-profile was executed with radiocarbon techniques at the «Koninklijk Instituut voor Kunstpatrimonium» (Brussel). Here, the organic material was transformed to benzene (C₆H₆) and the ¹⁴C activity was measured with a Wallac-Quantulus liquid scintillation counter. The conventional radiocarbon age is converted to calendar ages by using a computerised calibration program.

3. GEOLOGICAL SETTING AND AGE

The travertine deposit at Treignes (Fig. 1) has already been the subject of several investigations. Mullenders *et al.* (1963) provide a detailed description of the river Fonds de Ry and the travertine deposit. The river has a total length of 3,450 m and cuts through the Devonian limestones. The river profile has a mean slope of 2 %

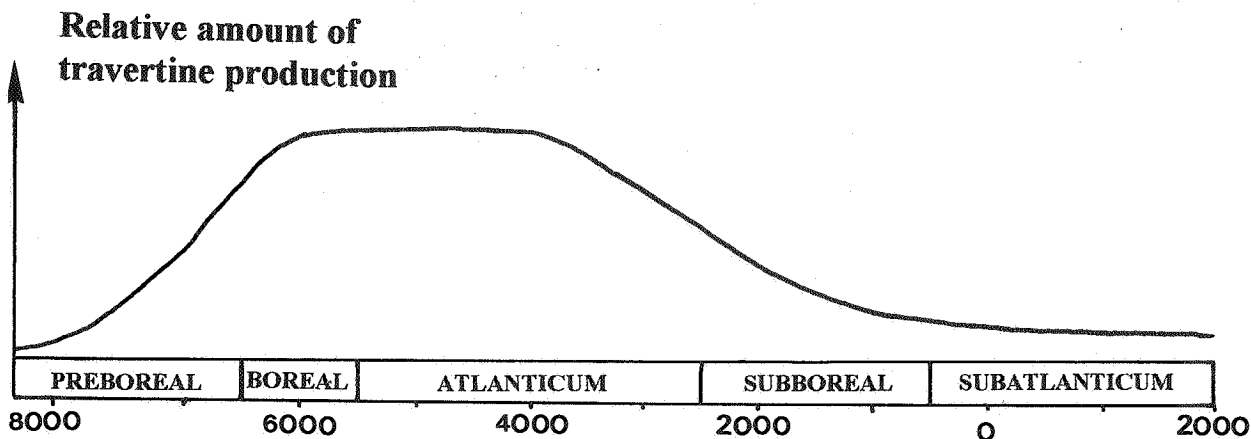


Figure 3. Evolution in travertine formation in the river «Fonds de Ry» at Treignes. This figure gives the relative amount of travertine production during the Holocene from the Preboreal till now. The travertine formation started in the Preboreal, a maximum in travertine production was reached during the Atlantic. Nowadays, active carbonate deposition is still visible (after Gullentops and Mullenders, 1972).

and three terraces, built by Holocene tufa deposits are present (Fig. 2). There is now still active travertine formation in the river, but nowadays erosion of the deposits laid down in the terraces is more important. In the second terrace a profile seven meter in thickness can be studied (Fig. 2). This profile has been described and studied by Gullentops & Mullenders (1972). The palynology was studied by Geurts (1976), while based on ostracods Van Frausum (1987) proposed a maximum age for the oldest deposits and deduced an evolution of the palaeoclimate. According to these authors, formation of the Treignes deposition started during the Preboreal due to the temperature raise at the beginning of the Holocene. During the Boreal, the travertine formation increased rapidly and a maximum in deposition generated during favourable climatic conditions was reached during the Atlantic. In the Subboreal and Subatlantic, travertine formation decreased again and is now inferior to erosion. This evolution in travertine formation is schematically given in Fig. 3.

To obtain more objective ages of the travertine, three organic-rich layers at the base of the paleo-deposit were dated by radiocarbon techniques (Fig. 4). The results are respectively 8,690-8,680 and 8,590 y.B.P. Those ages correspond well with the proposed palynological and paleontological ages.

This sequence in travertine deposits showing a maximum in the Atlantic and a facies variation from bottom to top of detritic deposits, travertine and again detritic deposits is also described in the Provence (France) (Magnin *et al.*, 1991; Vaudour, 1994).

4. PETROGRAPHY

Based on the binocular investigation of the recent and paleo-deposits, an own classification scheme of dominant morphotypes has been worked out and is shown in Table 1.

The recent precipitates can be divided in two major classes, namely: I. precipitates on inorganic substrates (mainly on limestone substrates) and II. precipitates on organic structures (mosses, leaves, branches, ...). In the second class precipitates on death and living assemblages form two recognized subdivisions. Both classes can be further subdivided into six subclasses (morphotypes) based on morphological criteria. Here the prickly precipitates are the dominant structure (Pl. 1: A).

The internal structure of these precipitates becomes visible in thin sections and under SEM. The recent precipitates are built up by three dominant components. In decreasing order of importance, we recognize precipitates on algal filaments, bacterial filaments and diatoms.

The algal filaments occur under SEM as long threads of several hundred μm in length and 5-40 μm in diameter. Those filaments construct porous open networks, which are continuously covered with small calcite crystals (Pl. 1: B). Several crystal forms can be differentiated, but irregular, euhedral and platy crystals are the dominant forms. In thin section often several hori-

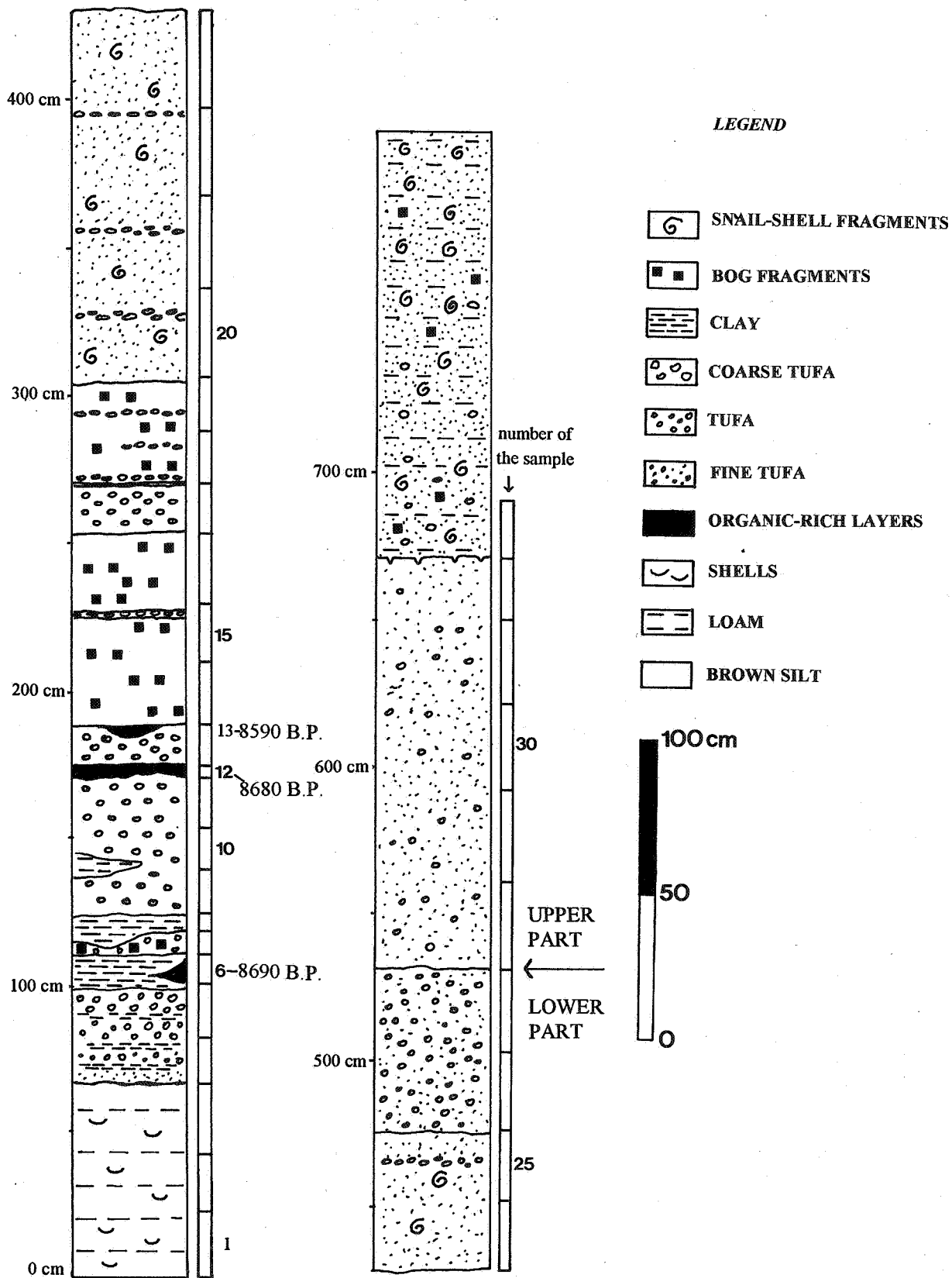


Figure 4. Paleo-profile in the second terrace of the river «Fonds de Ry» at Treignes. The organic-rich layers and their ^{14}C age are given here, as well as the distinction between the upper and lower part of the profile.

Recent deposits
<p>I. Precipitates on inorganic substrates</p> <p>II. Precipitates on organic structures</p> <p>1. <i>death assemblage</i> : on branches, leaves, pieces of wood, insects, snail-shells, acorns, fir-cones, ...</p> <p>2. <i>living assemblage</i> : roots, mosses, water plants, starlike tubes, ...</p> <hr style="border-top: 1px dashed black;"/> <p><i>Morphotypes</i> :</p> <p>A. ball precipitates : single ball shaped structures, 1-2 mm in diameter</p> <p>B. knotty precipitates : numerous small amalgamated ball structures</p> <p>C. branched precipitates : numerous little branched bushes of algae covered with CaCO₃</p> <p>D. cauliflower precipitates : single cauliflower-like CaCO₃ units</p> <p>E. granular precipitates : accumulation of many small grains, sand-like</p> <p>F. prickly precipitates : flat surface with small prickles (less than 1 mm)</p>
Paleo-deposits
<p><i>Morphotypes</i> :</p> <p>A. fine tufa</p> <p>B. aggregates with towerlike and knotty precipitates</p> <p>C. tubes with central opening</p>

Table 1. Classification of dominant morphotypes in the recent and paleo-travertine deposits in the river +Fonds de Ry+ at Treignes.

zonal laminations up to 500 µm thick can be recognized (Pl.1: C). Each lamination consists of two parts, namely upwards branching bushes of cemented algal filaments covered by brown micritic and transparent sparitic calcite crystals (Pl.1: D & E). The latter can form dense, non porous layers built up by parallel oriented crystals or upwards branching sparitic bushes (Pl.1: D). Similar horizontal laminations were described by Love & Chafetz (1988). They were interpreted as seasonal growth precipitates of the algae. The algae present in the deposit are the following: *Phormidium incrustatum* (Näg) Gom., *Phormidium faveolarum* (Mont.) Gom. and *Lyngbya nana* (Tilden) (Cyanophyta); *Chantrarsia incrustans* (Symoens, 1957) and *Batrachospermum sp.* (Rhodophyta) and

Cladophora glomerata (L.) Kütz (Chlorophyta). Of all those algae the Cyanophyta or Blue-green algae are the most important.

Smaller threads, with a length of 3 to 30 µm and a diameter of 1 to 2 µm are the second most common component (Pl.1: F). According to Pedley (1994), the dimensions are valid criteria to interpret these structures as bacterial in origin. The filaments connect the different aggregates and serve mainly as precipitation surfaces: they widen due to carbonate precipitation.

Between these threads, which are partly to entirely covered by minute calcite crystals, different organisms often can be differentiated. Diatoms (Bacillariophyta)

are very common (Pl.1: G). They may be present in large groups occurring on and between the filaments. Some of them have stalks by which they are attached to their substrate. Several species of the following genera were determined: *Achnanthes*, *Amphora*, *Cocconeis*, *Cymbella*, *Eunotia*, *Gomphonema*, *Gyrosigma*, *Navicula*, *Nitzschia*, *Rhoicosphenia* and *Surirella*. All these species are cosmopolitan and characteristic for oligotrophic waters. Furthermore, ostracods and unicellular bacteria also occur within these recent precipitates.

Active precipitation not only occurs on carbonate rocks (class I.), but also on organic substrates (branches, leaves, mosses, ..., class II.). The latter are sometimes covered with millimeter thick calcite crusts. On the one hand, small roots and stalks of plants are encrusted by a carbonate layer of two times the root diameter (up to 2 mm in thickness). This calcite precipitate exists of either algal filaments covered by stalky diatoms and irregular calcite crystals or a «pointed» calcite deposit. The latter is built up by thin parallel oriented calcite crystals, which often possess a triangular section in all cross-sections (Pl.2: A).

Mosses on the other hand, are often covered by thick knotty carbonate deposits. Precipitation mainly starts at the end of each moss leaf and continues towards the moss stalk. Here, also two types of building structures can be recognized. The mosses can be encrusted by very specific parallel oriented calcite crystals (Pl.2: B). In this case, no algal filaments are present. The moss leaves can also be covered by numerous diatoms of different species, which are attached to the moss surface, and by algal filaments, which are encrusted by irregular calcite crystals. Among others the mosses *Thamnum alopecurum* (Hedr.) B.J.G. and *Fissidens crassipes* Schimp. could be recognized in the river «Fonds de Ry».

It is obvious that a lot of organisms, such as bacterial filaments and diatoms, are present in the travertine deposit of Treignes. Most important, however, are the algae. They form porous open networks and determine the form of the whole travertine deposit. Those algae clearly provide an important crystallisation surface. Based on petrographical observations, however, it is not clear whether precipitation is organically or inorganically controlled. Algae may play an important role in precipitation by their photosynthesis (Geurts, 1976; Vervoort, 1984, ...). Furthermore, several species of algae are known to calcify during live, what also contributes to travertine formation (Adolphe & Rofes, 1973). However, further investigation of the relationship between filaments and crystals to determine the exact influence of the algae on carbonate precipitation is needed to define petrographical criteria,

which allow to infer whether photosynthetic activity exerts a major control on travertine formation. Plants in general seem to serve mainly as precipitation surfaces, but mosses in several cases clearly exert a major influence on crystal orientation which might relate to their photosynthetic activity.

Samples from the paleo-deposit were taken within a seven meter profile along the river as shown in Fig. 4. This profile starts 50 cm under the present groundwater (= river) level. Apart from reworked, i.e. allochthonous travertine material, clay, loam, bog and organic-rich layers can be differentiated. Three groups of travertine layers can be determined (Tab. 1), namely: a fine tufa (with components less than 1 mm; Pl.2: C), larger aggregates (several centimeters in diameter) with towerlike and knotty precipitates and finally millimeter to centimeter large encrusted tubes with central opening (Pl.2: D). Some of these tubes are up to 5 mm wide and 2-3 cm long.

The building components of these paleo-deposits clearly differ in their composition and texture from the recent precipitates. One of the major contrasting features is that only a few algal filaments have been recognized in the paleo-travertine. Within the latter deposits, three dominant crystal morphologies occur, namely:

- small fine crystal needles of less than 1 μm in diameter and up to 10 μm long, which fill up the pores. They form porous networks. Often they are arranged in two groups perpendicular to one another (Pl.2: E).
- brown micritic crystals deducible in thin sections and with a blocky outline under SEM (Pl.2: F). Diameters less than 10 μm are frequent. They usually have an irregular outline.
- large (10-40 μm in diameter) crystals with euhedral, well defined crystal outlines, occurring between the blocky crystals and within pores (Pl.2: G).

A comparison between the textural characteristics of recent and paleo-precipitates, allows to infer possible diagenetic products. The paleo-precipitates are characterized by the presence of euhedral crystals and crystal needles, which are absent in the recent precipitates. The large euhedral crystals can be interpreted as cements filling the pores. This interpretation is based on the crystal form and fabric and their pore filling nature. Under cathodoluminescence, the cements contain several faint luminescing zonations, which point to a variation in composition and precipitation conditions of the cements. Bright luminescing phases probably formed due to precipitation within the transition zone between oxic and suboxic, in contrast with the initial non-luminescing phases, which precipitated from the oxidizing meteoric water. These euhedral

element	Active precipitates n = 11		Paleo-precipitates n = 21			
	range (ppm)	mean (ppm)	upper part n = 5		lower part n = 16	
			range (ppm)	mean (ppm)	range (ppm)	mean (ppm)
Sr	137-302	165	168-182	173	69-204	170
Mg	900-1632	1203	1243-2022	1491	684-1376	1115
Na	75-141	106	87-137	107	63-118	140
Fe	3810-36036	8799	5758-20600	10003	733-3555	1992
Mn	268-5118	965	243-1026	650	28-300	118
stable isotope	range (‰ PDB) n = 11	mean (‰ PDB) n = 11	range (‰ PDB)	mean (‰ PDB)	range (‰ PDB)	mean (‰ PDB)
$\delta^{13}\text{C}$	-9.44 to -11.77	-10.78	-9.25 to -10.19	-9.88	-8.77 to -9.91	-9.75
$\delta^{18}\text{O}$	-5.77 to -6.78	-6.28	-5.76 to -5.87	-5.80	-5.48 to -6.21	-5.70

Table 2. Trace element concentrations and stable isotope values of the recent and paleo-precipitates of the travertine deposit at Treignes, n = number of samples.

crystals resemble the meteoric phreatic precipitates often described in shallow diagenesis of carbonate rocks (Longman, 1980).

Acicular calcite crystals similar to the needle crystals of the paleo-deposits are described by Jones & Kahle (1993) and Verrecchia & Verrecchia (1994). These authors bring forward a classification system for these crystals, as well as a proposed origin. In comparison, the needle crystals recognized in Treignes most likely formed during vadose diagenesis and they can be of both organic and inorganic origin. Notice also that in these paleo-deposits dissolution pores occur. They point to disappearance of organic material due to organic decay and to the presence of reactive fluids dissolving calcite. The lack of bacterial filaments, diatoms and the sparse number of algal filaments in the latter can be explained in a similar way. But noteworthy is also that the typical textures associated with these organic phases only locally have been recognized within the paleo-deposits. It could be that the precipitation mechanism in the past differed from the present-day dominant organic control on precipitation. But the presence of cements in the paleo-accumulations reflecting intense diagenetic overprinting rather points towards recrystallisation.

This recrystallisation most likely starts already during or immediately after precipitation. This is attested by the

fact that the older sparitic layers in the active precipitates visible in thin sections expand upwards, finally englobing the micrite crystals. This neomorphism of sparitic crystals is also mentioned by Love & Chafetz (1988).

Both recent and paleo-deposits were analysed for the mineralogical composition by XRD. Calcite is the only carbonate mineral detected. Quartz and feldspar occur as detrital components and Fe-oxy/hydroxides are present as coatings.

5. GEOCHEMISTRY

Representative samples of the different morphotypes of the recent precipitates as well as all carbonate layers of the paleo-deposit were analysed for trace element concentrations and carbon and oxygen isotopes.

In Table 2 the ranges as well as the mean values of the analysed trace element concentrations and stable isotope composition of the travertine deposit are given. Apart from data on the recent precipitates in Fig. 6, two intervals with different trace element contents can be differentiated in the paleo-deposits. Therefore also in Tab.2 the data of these intervals are given separately.

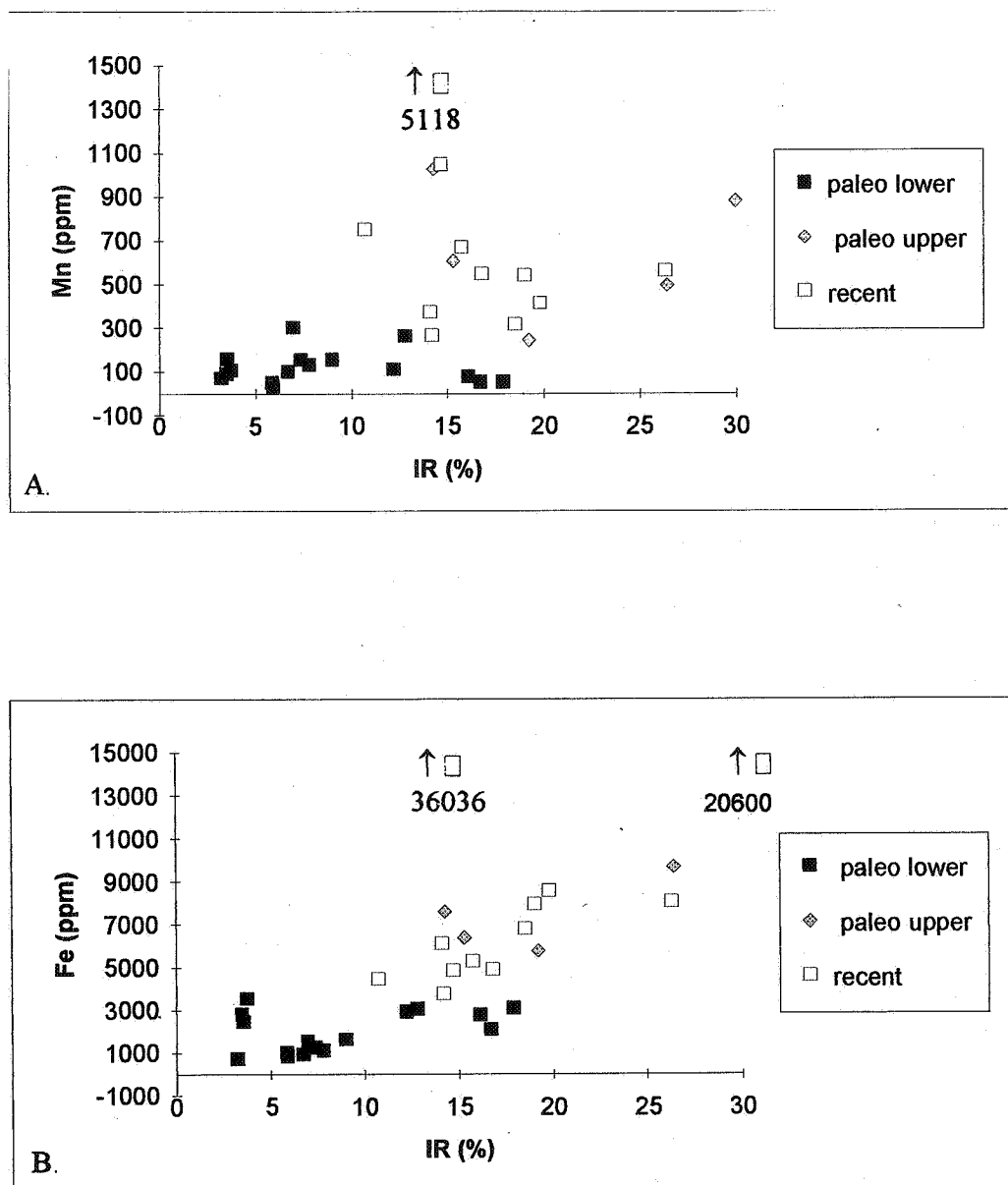


Figure 5. Trace element analysis of the travertine deposit at Treignes. Correlation diagram of insoluble of insoluble residue (IR) and Mn (A) and Fe (B). Correlation coefficients are 48% for Mn and 82% for Fe.

Clearly, the oldest paleo-deposit samples possess the lowest Fe and Mn concentrations, while the youngest deposits possess higher concentrations which are comparable to the concentrations encountered within the recent precipitates (Tab.2). This change in contents can either reflect another sediment source for the upper part of the profile in comparison to the lower accumulates or can be related to the position of a paleo-ground-water table. Since no apparent differences exist between the sediment phases occurring in the upper and lower interval, the first hypothesis seems not very likely. In the second case, however, below the mean paleo-ground-water level, oxides and hydroxides would have been dissolved under the prevailing suboxic to

reducing conditions. If leaching is complete, the measured Fe and Mn concentrations in the lower interval may relate to maximum contents incorporated within carbonate lattice, which would not be affected by these oxido-reduction reactions. However, contribution from other Fe-Mn-bearing non-carbonate constituents cannot be ruled out. Above the paleo-ground-water table, Fe and Mn will dominantly be incorporated in the oxides and hydroxides, which cause the very high and variable detected concentrations. The strong covariance between the Fe- and Mn-content and the amount of HCl-insoluble residue (IR) (Fig. 5, with correlation coefficients of 82 % for Fe and 48 % for Mn) is interpreted to relate to the increased presence of Fe- and

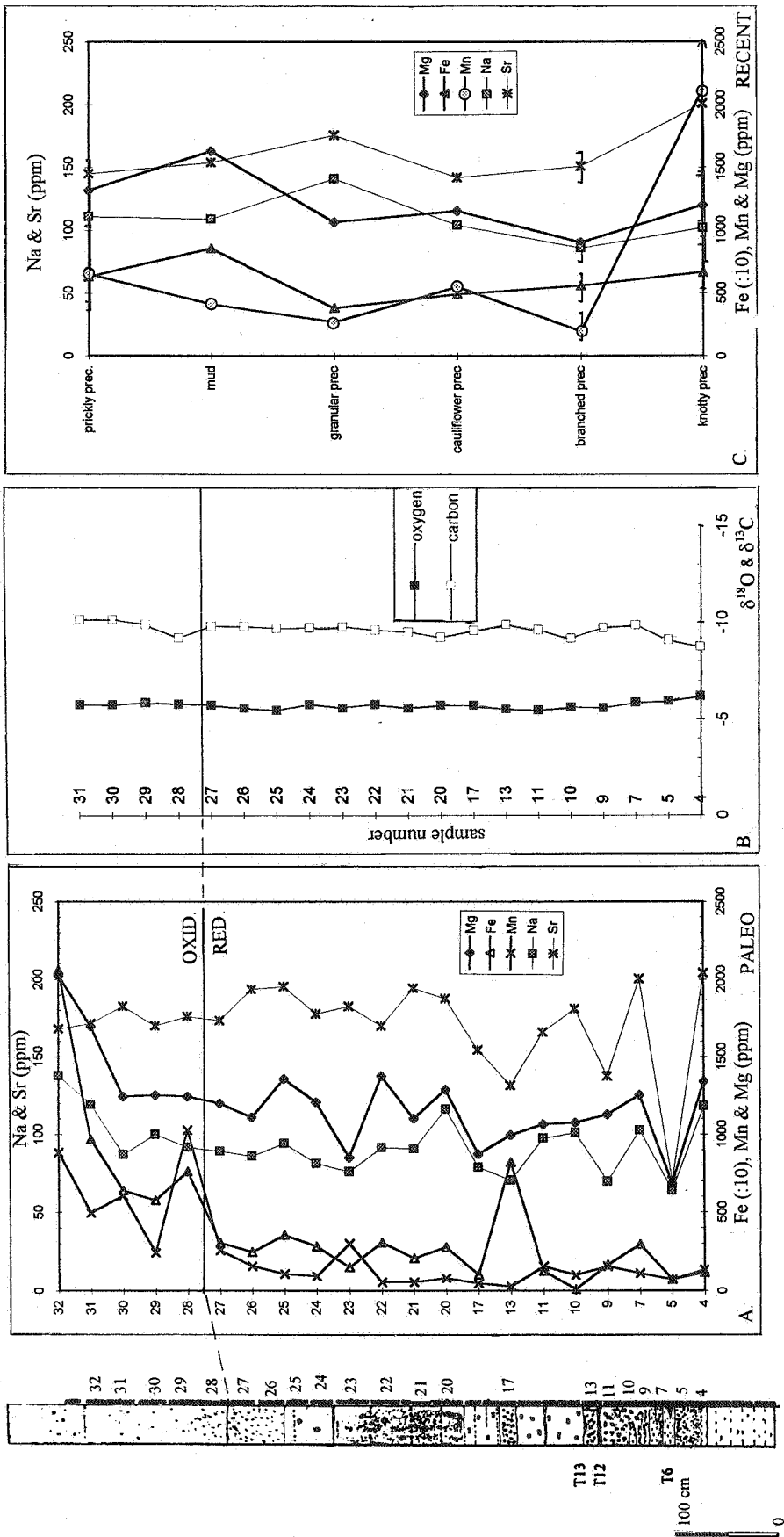


Figure 6. Trace element concentrations of the recent and paleo-deposits at Treignes. (A. Paleo-deposits and C. Recent precipitates). $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the paleo-profile are given in figure 6 B.

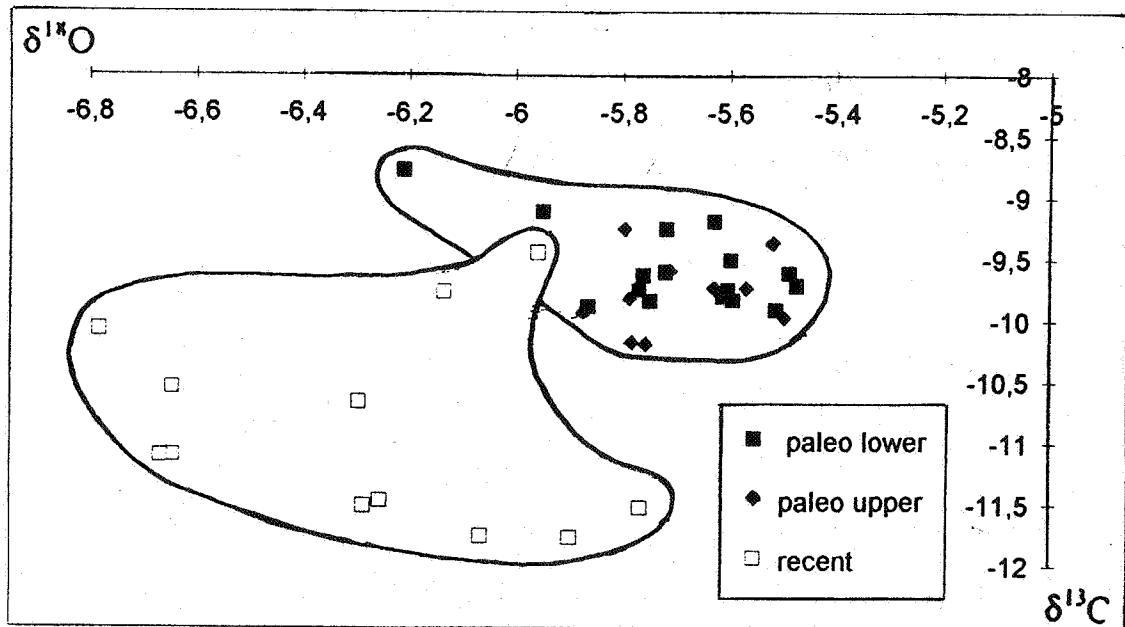


Figure 7. Stable isotope analysis of the recent and paleo-deposits at Treignes. The paleo-values are subdivided in the lower and upper part of the profile to illustrate the influence of the paleo-groundwater table.

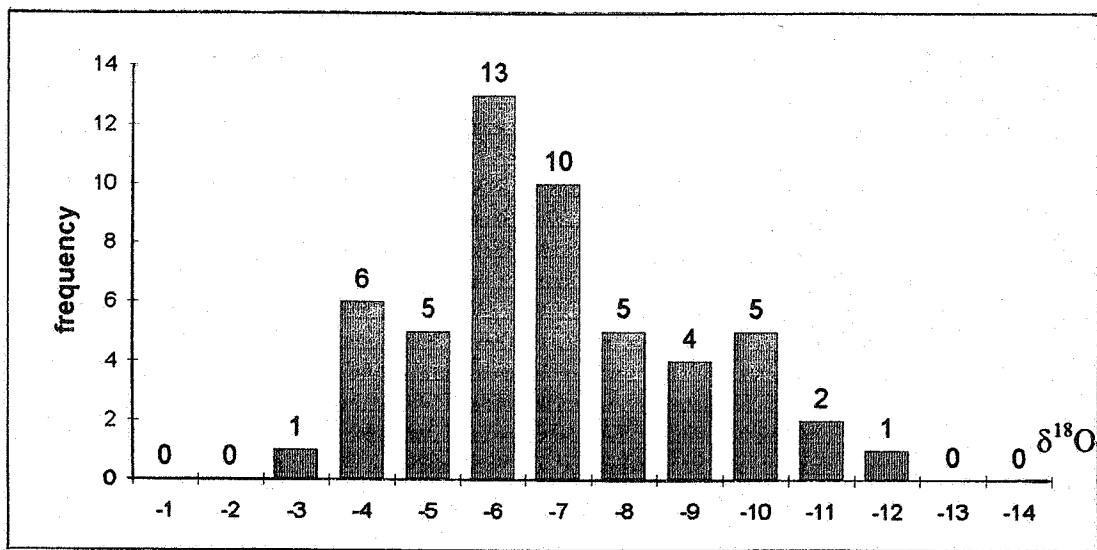


Figure 8. Frequency diagram of $\delta^{18}\text{O}$ rain water values at Liège from 1966 until 1970 (total number of samples is 52).

Mn-oxi/hydroxide coatings on detritals (clay, quartz, ...). Notice, however, that the present ground-water table is clearly much lower. Mg contents are highest in the youngest paleo-deposits (Fig. 6), but many of the samples in the upper interval have similar contents as detected in the lower interval. This is also the case for Sr. Na possesses slightly higher contents below the inferred paleo-ground-water table. If this interpretation of the existence of a paleo-ground-water table is correct, one comes to the conclusion that such a marked difference reflects a rather important time period over which this water table remained at a nearly

constant depth position. Furthermore, it reflects alteration of Fe- and Mn-oxi/hydroxides, which concurs with our interpretation of diagenetic alteration within the paleo-deposit.

Finally from the trace element concentrations of the recent precipitates, given in Fig. 6C, where the mean values and ranges for the different morphotypes are given separately, no systematic differences can be recognized. This points to similar mechanisms of trace element incorporation during travertine deposition in all recent precipitates.

Water	Sr (ppb)	Na (ppm)	Mg (ppm)	Fe (ppb)	Mn (ppb)	K (ppm)	Zn (ppb)	Cu (ppb)
river	331	9	9	230	22	9	8	dl
ground	312	8	12	33	11	3	1	dl
Water	Pb (ppb)	Cl ⁻ (ppm)	NO ₃ (ppm)	NO ₂ (ppm)	SO ₄ (ppm)	NH ₄ (ppm)	pH	DOC
river	6	33	25	0.05	7	0.05	7.63	1.6
ground	1	40	37	dl	6	0.01	6.73	0.6

Table 3. Trace element concentrations and other interesting data in the river and ground- water at Treignes (dl = detection limit).

The element composition of Sr, Na, Mg, Fe and other parameters of river and ground-water are given in Table 3. The pH value of the river water is increased in comparison to the ground-water. This increase points to the precipitation of CaCO₃ in the river. Compared with the ground-water taken at the source of the «Ancienne Fontaine du Bouc», Fe and Mn concentration is clearly higher in the river water, while the Mg content is slightly lower and Sr and Na contents are within the same order of magnitude. Important observation is the marked increase in trace element concentrations in the travertine carbonates compared with the water contents. Based on the distribution coefficients, this increase cannot be explained by the incorporation of trace elements in carbonates alone. It might also be influenced by the biological processes. However, it is very likely that the presence of non-carbonate impurities exert a major control on the trace element results in the travertine samples.

In Tab.2 and also in the crossplot in Fig. 7, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the recent and paleo-precipitates are given. Their spreading is in general low, especially within the paleo-deposits. For $\delta^{13}\text{C}$ and to a lesser extent for $\delta^{18}\text{O}$ the recent precipitates are clearly more depleted than the paleo-precipitates. To be able to interpret the $\delta^{18}\text{O}$ values correctly, also the river and ground-water were analysed. Their $\delta^{18}\text{O}_{\text{smow}}$ values are + 23.32 ‰ and + 23.18 ‰ respectively, which corresponds to -7.32 and -7.53 ‰ PDB.

$\delta^{13}\text{C}$ values in general provide information about the source of the CO₂ that is incorporated in carbonate phases. Different carbon sources such as CO₂ derived from an atmospheric origin or from organic matter degradation by bacteria (e.g. sulphate reduction, methanogenesis, ...) possess very characteristic signa-

tures (Hudson, 1977). Unfortunately, often the recorded signal in carbonates reflects mixture of different CO₂ sources (De Craen *et al.*, 1996).

The $\delta^{18}\text{C}$ values of the active and paleo-precipitates both are depleted. The mean value around -10 ‰ PDB points to the mixture of at least two CO₂ sources. Looking to the precipitation conditions, an atmospherical or recycled marine CO₂ source is one of the likely contributors. The latter is derived from the dissolution of the Devonian limestones, which possess a $\delta^{13}\text{C}$ signature varying around 0 ‰ PDB. Atmospherical CO₂ has also a similar value. On the other hand the presence of a biological (algal) CO₂ source (with values of -25 ‰ PDB) is also very probable. Consequently, these depleted $\delta^{13}\text{C}$ values show a rather important biological influence, most likely by photosynthesis, on carbonate precipitation.

The $\delta^{18}\text{O}$ values are in general also depleted. Here the $\delta^{18}\text{O}$ value of the carbonate depends of the $\delta^{18}\text{O}$ composition of the water from which the carbonates precipitated as well as of the precipitation temperature. Oxygen isotope values varying around -6 ‰ PDB, as is the case for our samples, are often regarded as typical for near-surface precipitation from meteoric water in the present-day latitudinal position of Belgium. If the $\delta^{18}\text{O}$ value of water and carbonate precipitated in equilibrium within this water are known, as is the case in our study, the precipitation temperature can be calculated, according to the fractionation equation of Shackleton & Kennett (1975) ($T(^{\circ}\text{C}) = 16.9 - 4.38 (\delta_{\text{c}} - \delta_{\text{w}}) + 0.1 (\delta_{\text{c}} - \delta_{\text{w}})^2$ with δ_{c} and δ_{w} the $\delta^{18}\text{O}$ values of the carbonate and the water respectively) (Müller *et al.*, 1986). For the $\delta^{18}\text{O}$ composition of carbonates, a mean $\delta^{18}\text{O}$ value for the recent precipitates of -6.28 ‰ PDB was used. As water composition, a value of -7.32 ‰ PDB allowed to calculate a precipitation tem-

perature of 12°C. The latter value corresponds well with the in situ measured temperature of the water during the summer sampling period. The $\delta^{18}\text{O}$ values of the recent precipitates have, however, a large spreading, which either reflects a range in precipitation temperatures or a range in $\delta^{18}\text{O}$ values of meteoric water. The latter case is very likely if one knows the variation in $\delta^{18}\text{O}$ values of rain water in our region. Data from Liège between 1966 and 1970 vary between -3‰ and -12‰ PDB around a mean value of -7‰ PDB (Fig. 8). Variation in precipitation temperature using a constant $\delta^{18}\text{O}_{\text{smow}}$ composition of +23.32‰, leads to a minimum and a maximum temperature of respectively 10.4°C and 14.6°C, which are reasonable values for temperature variations in our region.

Differences between the paleo- and the recent precipitates are also visible in the isotope values (Fig. 7). The recent deposits are more depleted with respect to the paleo-precipitates. This shift, in our opinion, relates to the diagenetic alteration of these paleo-precipitates. These processes can reset the primary signature and might also explain the decrease in spreading of the data. In fact, in the paleo-deposit the relative importance of primary precipitates will slightly decrease due to dissolution, while the effect of the meteoric and vadose cements will increase. Also recrystallisation will have its effects, especially on the $\delta^{18}\text{O}$ signature. Since it is likely that all these processes occurred in an open diagenetic system and that (with exception of vadose cementation) interaction with a homogenized meteoric fluid type took place, especially the signature for $\delta^{18}\text{O}$ will be homogenized and the $\delta^{13}\text{C}$ will proportionally shift towards the signature of inorganically precipitated meteoric cements. The influence of diagenesis on isotope composition is also visible in the evolution of the $\delta^{18}\text{O}$ signature in the paleo-profile (Fig. 6B). The $\delta^{18}\text{O}$ values of all carbonate layers point to an evolution towards more positive values in the younger deposits. This trend, however, is in contrast to the expected trend towards more depleted values, which are due to the evolution to the climatic optimum during the Atlantic. The climatic evolution of the Holocene is not directly visible in the measured $\delta^{18}\text{O}$ values of the travertine. It is obvious that under all these circumstances the diagenetic alteration of initial structures and geochemical signals makes it necessary to be very careful in interpreting isotope and trace element values of travertine deposits.

6. CONCLUSIONS

The sampled travertine deposit at Treignes formed during the last 8,600 years. Both paleo-deposits and recent precipitates can be recognized. The latter are mainly built by encrusted algal and bacterial filaments,

diatoms, mosses, ..., with algae being the most important constituent. Their morphology outlines exert a major control on the morphotypes that can be recognized, as well as the internal laminated nature of these deposits. Their role is probably not limited to provide passive precipitation surfaces. According to the depleted $\delta^{13}\text{C}$ signature (-10‰ PDB) of these precipitates, these algae also influence precipitation by their photosynthesis. This seems also to account for the encrusted bacterial filaments and mosses. Diatoms and plants, on the other hand, seem simply to provide precipitation surfaces. The paleo-deposits, however, consist mainly of three crystal morphologies. Here algal or bacterial textures are nearly absent most likely due to organic decay and diagenetic alteration. The latter is recognizable by the existence of recrystallisation textures, the creation of solution pores and the presence of needle-like and euhedral to blocky crystals, interpreted respectively as vadose and meteoric phreatic in origin. The latter possess different luminescing characteristics reflecting different precipitation conditions. It is therefore likely that the isotope and trace element compositions of the cements and recrystallisation products will influence the primary signature of the travertine. This diagenetic alteration, especially of the isotope distribution, makes it necessary to be very careful in determining palaeoclimatic signals from travertine deposits.

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PLATE 1

- A. Overview of prickly morphotype characterized by flat surfaces with small prickles.
Scale = 1 mm
- B. Secondary electron SEM photomicrograph of porous open networks constructed by calcite encrusted algal filaments. Scale = 100 μm .
- C. Secondary electron SEM photomicrograph illustrating horizontal laminations. Each layer consists of upwards branching bushes of algal filaments encrusted by calcite.
Scale = 100 μm .
- D. Photomicrograph of thin-section showing a detail of horizontal laminations. They become apparent due to the alternation of sparitic and micritic intervals.
Scale = 0.3 mm.
- E. Photomicrograph of thin-section showing a detail of algal bushes covered by micritic calcite, composing the micritic layers. Scale = 0.3 mm.
- F. Secondary electron SEM photomicrograph of bacterial filaments (arrows) which occur between the different aggregates. Scale = 5 μm .
- G. Secondary electron SEM photomicrograph of different types of diatoms occurring between partly encrusted algal filaments. Scale = 10 μm .

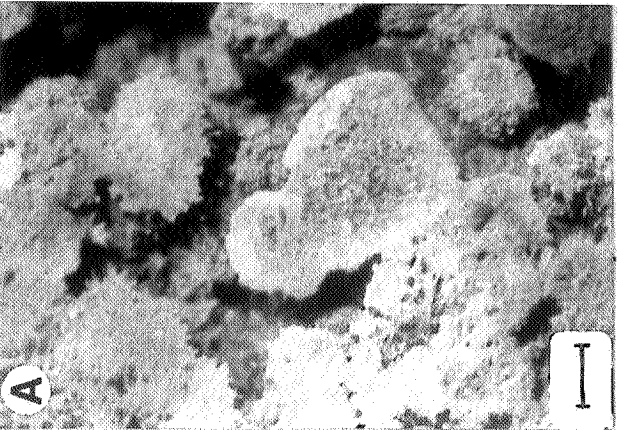
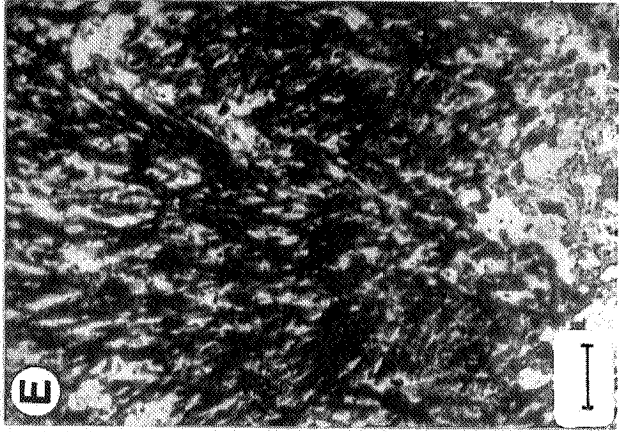
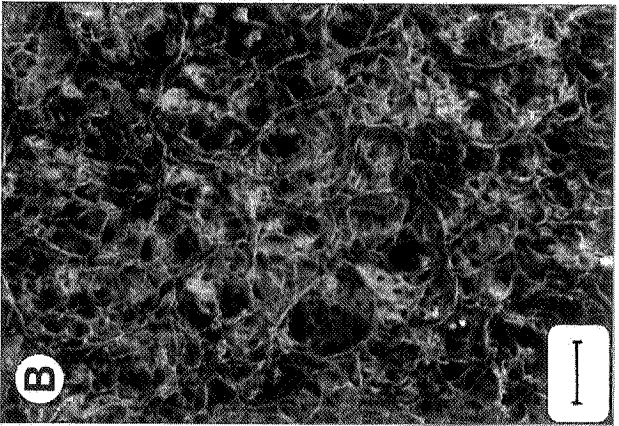
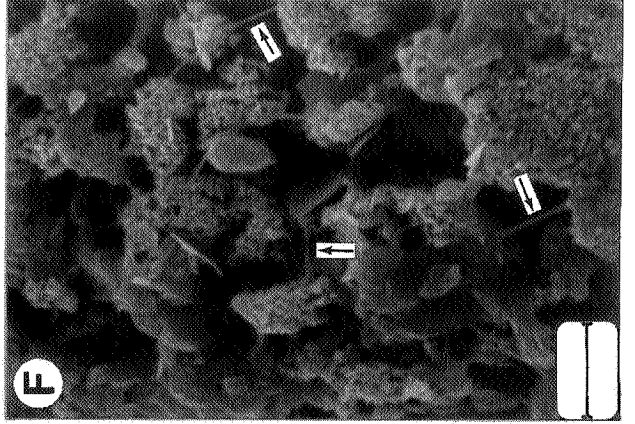
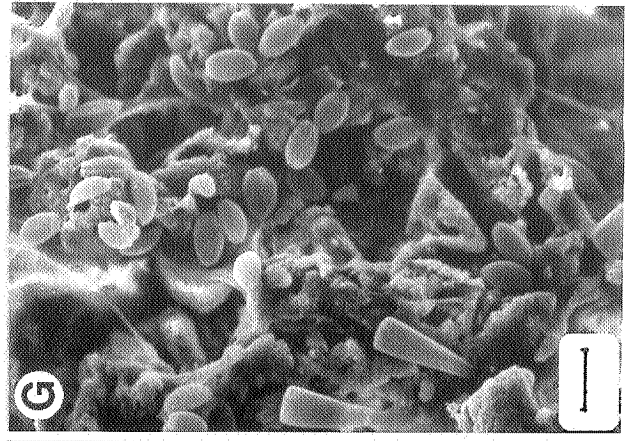
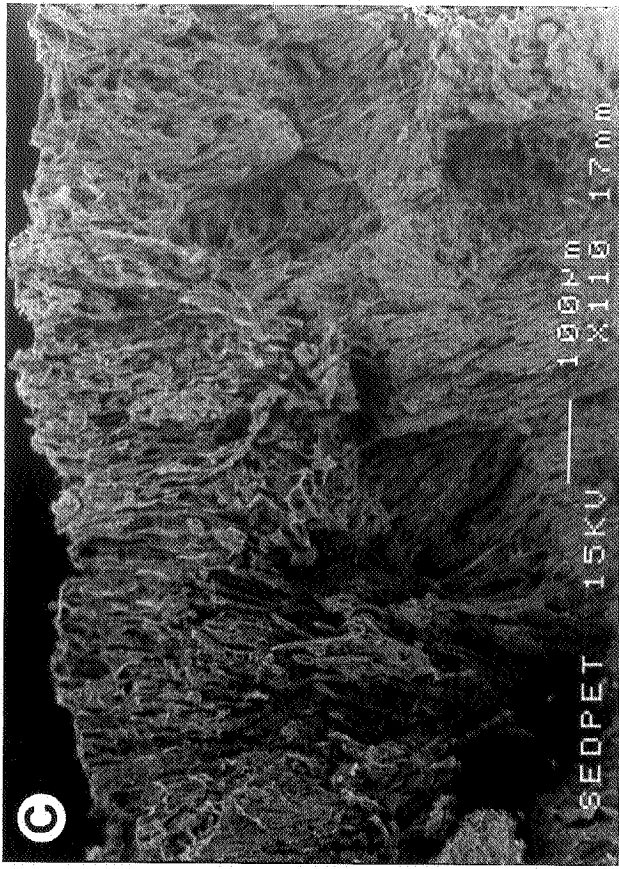


PLATE 2

- A. Secondary electron SEM photomicrograph of the «pointed» precipitates on roots, existing of parallel oriented calcite crystals with triangular section. Scale = 1 μm .
- B. Secondary electron SEM photomicrograph of the precipitates on mosses. The deposit exists of very specific parallel oriented calcite crystals which follow the moss leave outlines. Scale = 5 μm .
- C. Overview of fine tufa in the paleo-deposits, characterized by an accumulation of fine calcite crystals. Scale = 1 mm.
- D. Overview of tubes with central opening occurring in the paleo-deposits, covered with knotty precipitates. Scale = 1 mm.
- E. Secondary electron SEM photomicrograph illustrating fine needle crystals in the paleo-deposits. The needles are often arranged in two groups perpendicular to one another and they widen due to carbonate precipitation. Scale = 1 μm .
- F. Secondary electron SEM photomicrograph of the blocky crystals in the paleo-deposits. Scale = 10 μm .
- G. Secondary electron SEM photomicrograph illustrating the large, euhedral crystals (cements) occurring in the pores of the paleo-deposits at Treignes. Scale = 2 μm .

