[PS]Upper Pleistocene-Holocene? Terraced-Slope Hot-Spring Travertine System and Its Modern Analogue in the Albegna Valley, Southern Tuscany (Central Italy)*

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Abstract

In the Neogene Albegna Basin, southern Tuscany (central Italy), travertines are present in several deposits. They were deposited as fans and wedges with terraced slopes and are located at different topographic heights (from about 100 up to 700 m a.s.l). An interesting fossil travertine body (Upper Pleistocene-Holocene?) is well exposed along an active quarry situated on the Manciano sector of the Albegna Valley. The quarry faces exhibit a travertine terraced slope system (30-35 m thick) in which terrace walls (several cm to 2 m high), pools (1-10 m wide), pool rims (few cm to 1 m high) and waterfalls (2-3 m high) were identified. Thirteen carbonate fabrics at the cm-scale were distinguished in the field.

Petrographic analysis displays diversified microfabrics. Shrub structures usually consist of peloidal micrite. Crystal shrubs display a dentridic crystalline morphology; these also have undulated extinctions and sometimes build fun-shaped shrubs. Calcite crystals (generally micritized) show a range of morphology from feather to ray crystals and dominate the crystalline crusts. Feather crystals commonly show laminations while ray crystals appear to be vertically separated by elongated cavities. Thin or crude laminated micrite/microspar forms stromatolite-like structures. Honeycomb like-structures consist of thin micrite/microspar laminae aggregated into packages with large subspherical/lenticular discontinuous cavities bulged up by large gas bubbles or insect larvae. Actively forming travertines occur today at Baths of Saturnia. These could represent the modern analogue for the ancient travertine terraced slope system of Manciano (12Km far).

Present-day thermal activity is characterized by a 37°C thermal spring with a rate of about 800 l/s. Water is enriched in H_2S-CO_2-SO_{42}- and HCO_3- and divalent cations (Mg, Ca). Minerals dissolved in water amount to 2.94 g/l. The downstream surfaces of these modern travertines are colonized by a soft green biofilm. Elongated and rounded, several mms to cms in diameters, pisoids form in the pools (1-4 m wide; rims 0.2-1m high). Locally, reeds are present at the sides of the pools where there has been temporally no thermal water flow. The Baths of Saturnia ecosystem provides an important opportunity to study the biogeochemical and physical interactions that produce travertines similar to those of the past.

The study of Albegna travertines can improve the understanding of comparable carbonate reservoirs in the subsurface.

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PART I

1. Hot-spring travertine: general concepts

Travertines are all continental calcium carbonate deposits precipitated under open-air conditions by warm to hot water (> 20°) supersaturated with calcium bicarbonate degassing CO2 while out-flowing from a tectonically controlled hydrothermal vent (Fig 1).

Travertine deposition is linked to tectonic activity and form along the trace of major crustal-scale faults in primarily extensional tectonic regimes. Faulting and fracturing improve permeability and made it possible hydrothermal circulation.

The occurrence of thermal springs can produce different travertine body morphologies. According to the location and the typology of the orifices the issuing of the calcium carbonate rich-water builds ridge (Fig.2), mound (Fig. 3) and wedge-shaped (Fig.4) carbonate deposits. The flowing of the water from the spring to the lower morphology areas create different depositional systems ranging from terraced slope and smooth slope (Fig. 4 and 5) to flat pond.

Travertine precipitate in response to both inorganic and organic processes. Outgassing and vaporizing/cooling processes combined with turbulence and velocity of the flowing water appear to be the predominant mechanisms inducing calcium carbonate precipitation in fast flowing areas (Fig. 6 A) Microbial biofilm influence (Fig. 6 B-C)is dominant in slow-flowing settings such as hot-spring pools and ponds where precipitation seems to be associated with cyanobacteria biofilms and heat-tolerant bacteria. Photosynthetic CO2-uptake and other physiological activities of plants (e.g. HCO3 assimilation) enhance calcite precipitation. Bacterial colonies/algae incorporate carbonate particles in the mucilaginous biofilm (EPS) they produce. Plants provide sites for calcite nucleation and precipitation (Fig. 6 D), and for trapping calcite particles.

Fig. 1 - A) The Bollore Spring, Bagni San Filippo, Tuscany , Italy. B) Close-up of the active hydrothermal vent at Bagni San Filippo whit a temperature of the water of 52 °C and a discarge of about 20 l/s.

1.1 Travertine morphology

Fig. 2 - Fissure-ridge cropping out in the "Terme di S. Giovanni", Tuscany, Italy with Terraced slope and Smooth slope depositional systems . This structure 230 m long and 10-15 m thick is related to a normal fault.

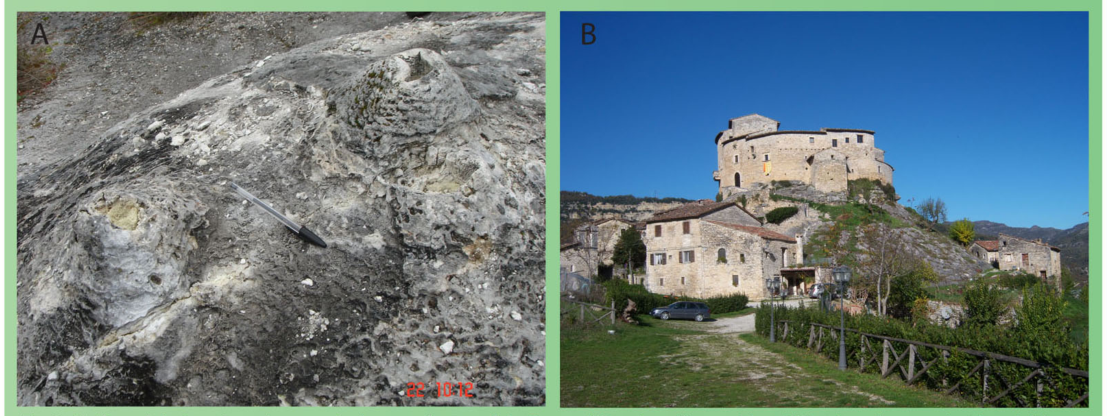

Fig. 3- A) Aligned decimetric-scale mounds along at the top of the Terme di Rapolano Fissure ridge. B) Metric scale mound at Castel di Luco, Marche, Italy. Image of De Bernardo.

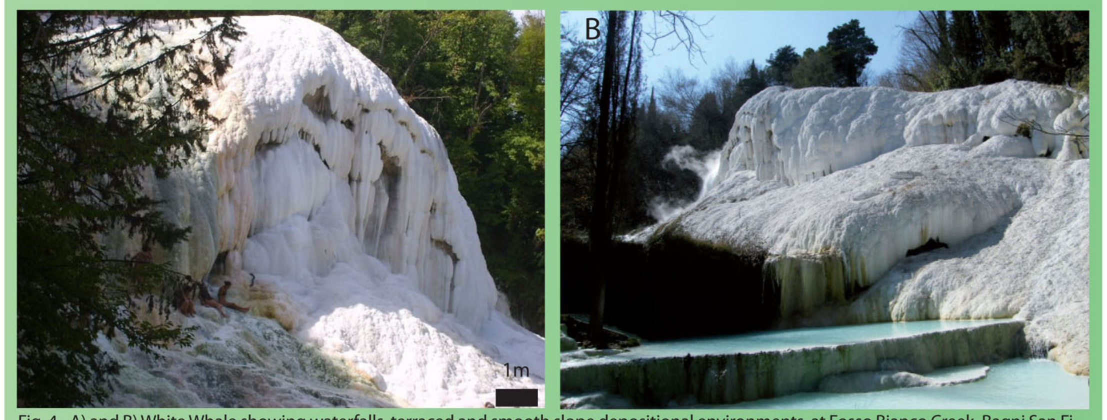

Fig. 4 - A) and B) White Whale showing waterfalls, terraced and smooth slope depositional environments at Fosso Bianco Creek, Bagni San Filippo, Tuscany, Italy.

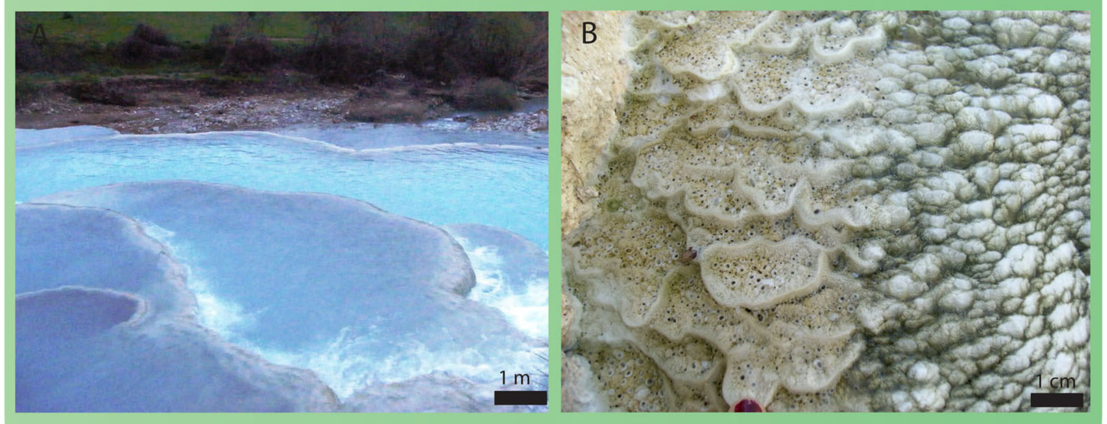

Fig. 5- A) Meter-scale terraced slopes at Bagni di Saturnia, Tuscany, Italy B) Microterraces at Bagni San Filippo, Tuscany, Italy.

1.2 Travertine precipitation: interplay between abiotic and biotic processes

Fig. 6- A) Outgassing and vaporizing/cooling processes combined with turbulence and velocity of the flowing water at Baths of Saturnia, Tuscany, Italy. B) and C) Travertine precipitation related to microbial activity at Bagni San Filippo, Tuscany, Italy. D) Travertine precipitation around reeds at Bagni San Filippo, Tuscany, Italy.

2 . Introduction

Travertine are developed are wideaspead in different geographic areas (Fig /). The deposition of hot-spring travertines in Central Italy is related to the magmatic and hydrothermal activity linked to the Plio-Pleistocene extensional tectonics developed during the opening of the Tyrrhenyan Sea, following the formation of the Apennine thrust belts during the Miocene (Tortonian). Central Italy has extensive travertine accumulations all younger than 400 kyrs that include present-day deposits (Fig. 8)

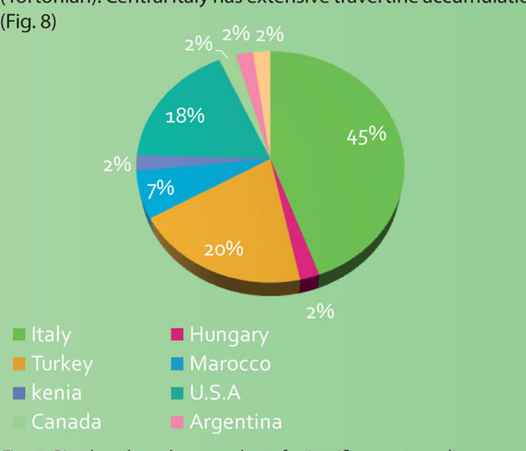

Fig. 7 Pie chart based on number of scientific papers on literature rewiev data shows the geographic distribution of thermal travertines.

Fig. 8 Map of central– southern Italy showing location of active-precipitating and fossil travertine deposits. From Minissale, 2004.

In the Neogene Albegna Basin (Fig. 9), southern Tuscany (central Italy), travertines are present in several deposits and are located at different topographic heights (from about 100 up to 700 m a.s.l.). Of these a Pleistocene-Holocene? travertine body and a present-day terraced slope system analog were studied. The interesting fossil wedge-shape travertine body is well exposed along an active quarry (Fig. 10) situated on the Manciano sector of the Albegna Valley. The quarry faces exhibit slope depositional systems and flat ponds. Different carbonate fabrics at the cm-scale were distinguished in the field. Petrographic analysis displays diversified microfabrics and associated pore structures. This variety reflects their origin that is the product of an interplay of biotic and abiotic processes (See Part III) and subsequent diagenesis (See Part III).

Actively forming travertines occur today at Baths of Saturnia (Fig. 11) 14 Km far from the fossil body. This moder analog provides an important opportunity to study the biogeochemical and physical interactions that produce travertines similar to those of the past.

3. Geological setting of Albegna Valley

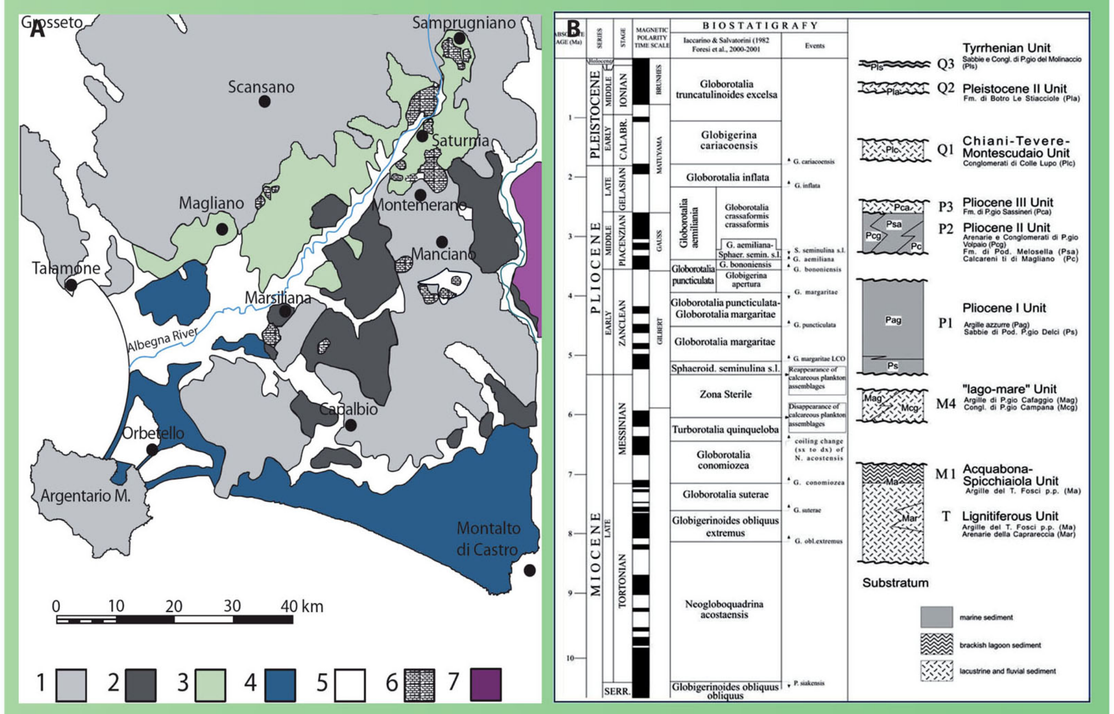

Fig. 9 - A) Simplifed geological map of Albegna Valley. Legend: 1) Tuscan series and allochtonous units; 2) Messinian continental, brackish and marine sediments; 3) Pliocene marine sediments; 4) Pleistocene marine and coastal sediments; 5) alluvial-colluvial deposits; 6) From Miocene to Holocene Travertines; 7) volcanic deposits of Vulsini Mounts. (Modified after Bosi et al. 1996).
B) Depositional units and hiatus of the Neoautoctonous Succession of the Albegna River Basin. Bossio et al., 2004.

4. Plestocene/Holocene travertine body: Saturnia Travertine Quarry

Fig. 10- A) Aerial view of Saturnia Travertine Quarry. From Google Earth. B , C and D) Panoramic views of Saturnia Travertine Quarry. E) Possible fossil thermal spring into Saturnia Travertine Quarry and karstic dissolution.

5. Modern analog: Baths of Saturnia

Fig. 11 - A) Aerial view shows the distance between Saturnia Travertine Quarry and the actively forming travertines at Baths of Saturnia. From Google Earth. B) Travertine terraced slope systems at Bath of Saturnia. Present-day thermal activity is characterized by a 37°C thermal spring with a rate of about 800 l/s. Water is enriched in H2S-CO2-SO42- and HCO3- and divalent cations (Mg, Ca). Minerals dissolved in water amount to 2.94 g/l. People for scale. C) Close-up of pools, rims and walls at Baths of Saturnia.

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Part II

6. Pleistocene/ Holocene Saturnia Travertine Quarry: Geometries

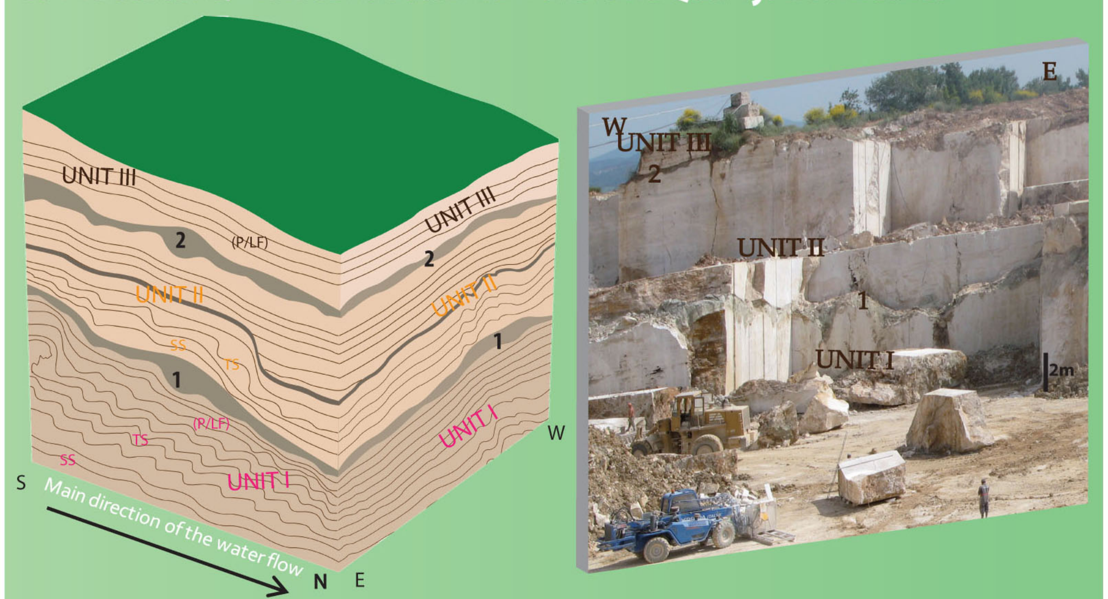


Fig. 12 - A) Interpretative sketch of travertine geometry in Saturnia Travertine quarry. Travertine Unit are numbered I, II and III. Unit boundaries are marked by the two clay layers (1-2) present at 11 and 20 respectively suggesting an intermittent accrection of the travertine bodies. Lateral and vertical transitions between Smooth slopes (SS), Terraced slopes (TS) and Ponds/Lateral flat (P/LF) depositional environments characterize each unit. B) Different stage of non deposition/ erosion (clay layers 1 and 2) within the travertine deposits.

7. Saturnia Travertine Quarry: Depositional enviroments

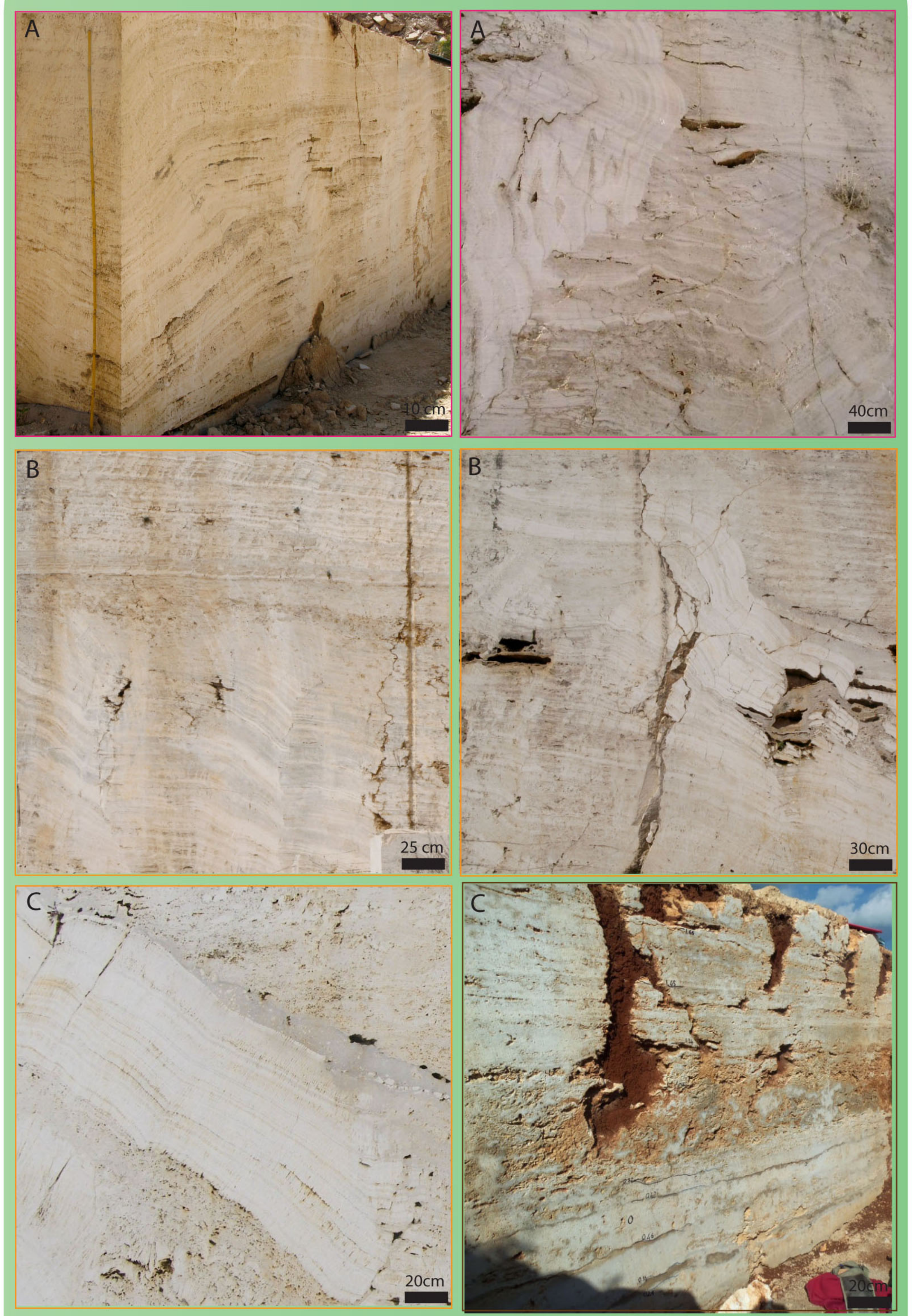
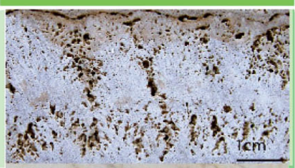
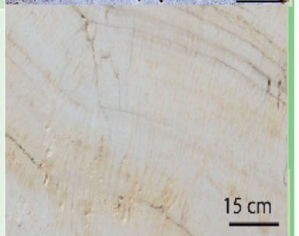
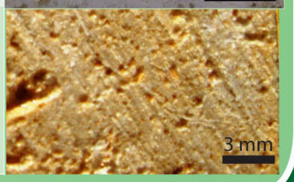


Fig. 13 - Smooth slope (SS) consist of non -terraced system. A) Low-angle smooth slope at Unit I. B) Medium -angle smooth slope of Unut II. Sub-horizontal travertines of Pond/Lateral Flat depositional (P/LF) system rest on SS. C) P/LF travertines unconformably (gray level) rest on high-angle SS travertines.

Fig. 14 - Terraced slope consist of vertical terrace wall, pools and rims confining the margin of the pools; waterfalls can be also present. A) 2 m high waterfall with pools and rims at Unit II. B) TS system vertically and lateraly transitional to a P/LF travertinesat Unit II. C) Sub-horizontal P/LF travertine of Unit III.

8. Saturnia Travertine Quarry: facies type

Fabric Type	Porosity	Depositional Environment	Field appearance
Clotted peloidal Dendritic boundstone	Inter dendritic branch porosity	Pool of TS, flat area of SS	
Non-crystallographic/Crystallographic dendritic boundstone	Inter dendritic branch often horizontally layered, channelized	Rim of TS, SS systems	
Wavy Laminated boundstone	Inter laminae porosity, bubble porosity, fenestrae.	Pool of TS, from flat to low angle area of SS and in Pond/Lateral flat.	
Coated gas bubble boundstone	Non connected intra-bubble porosity	Pool of TS, SS and P/LF	
Raft boundstone	Vug porosity, inter-raft porosity	Pool of TS, horizontal area of SS and P/LF	
Reed boundstone	Biomoldic porosity	P/LF	
Carbonate grains (from rudstone to grainstone)	Inter-grain porosity	In between rim and pool transition and in distal part inclined area of TS	

9. Present-day travertine: Baths of Saturnia Geometry

Fig. 15 -. Actively forming travertines occur today at Baths of Saturnia. These could represent the modern analogue for the ancient travertine terraced slope system of Manciano (12Km far). Present-day thermal activity is characterized by a 37°C thermal spring with a rate of about 800 l/s. The water flowing from the vent along the channel. Water is enriched in H2S-CO2-SO42- and HCO3- and divalent cations (Mg, Ca). Minerals dissolved in water amount to 2.94 g/l. The Baths of Saturnia ecosystem provides an important opportunity to study the biogeochemical and physical interactions that produce travertines similar to those of the past.
A) Channel depositional enviroment; B) Holocene precipitates; C) Terraced slope.

GPS Position	PH/T
N 42° 39' 25,2" E 11° 30' 52,3"	PH 6,79 T° 35,5 °C
N 42° 39' 24,3" E 11° 30' 51,1"	PH 6,84 T 35,1°C
N 42° 39' 23,8" E 11° 30' 50,3"	PH 6,84 T 35,2°C
N 42° 39' 23,5" E 11° 30' 50,0"	PH 6,84 T 35,2°C
N 42° 39' 22,6" E 11° 30' 48,8"	PH 6,86 T 35,1°C
N 42° 39' 22,3" E 11° 30' 48,6"	PH 6,86 T 35,2
N 42° 39' 21,9" E 11° 30' 47,9"	PH 6,87 T 35,3
N 42° 39' 21,2" E 11° 30' 47,1"	PH 6,88 T 35,4
N 42° 39' 20,5" E 11° 30' 46,3"	PH 6,89 T 34,9°C
N 42° 39' 19,4" E 11° 30' 45,2"	PH 6,90 T 35,3°C
N 42° 39' 19,0" E 11° 30' 44,7"	PH 6,90 T 35,1°C
N 42° 39' 18,6" E 11° 30' 44,2"	PH 6,91 T 35,3
N 42° 39' 17,9" E 11° 30' 43,5"	PH 6,91 T 35,2°C
N 42° 39' 16,3" E 11° 30' 41,7"	PH 6,92 T 35,3°C
N 42° 39' 16,2" E 11° 30' 41,7"	PH 6,93 T 34,9 °C
N 42° 39' 15,8" E 11° 30' 41,8"	PH 6,93 T 34,9°C
N 42° 39' 06,6" E 11° 30' 42,8"	PH 6,99 T 34,7°C
N 42° 38' 53,7" E 11° 30' 46,0"	PH 7,72 T 33,9°C
N 42° 38' 53,6" E 11° 30' 45,6"	PH 7,72 T 33,9°C
N 42° 38' 53,6" E 11° 30' 45,6"	PH 7,76 T 33,8°C
N 42° 38' 53,4" E 11° 30' 44,9"	PH 7,81 T 33,8°C

Fig. 16- Chemical parameters measured along the channel and the TS (green values).

10. Baths of Saturnia: Depositional enviroment

Fig. 17- Depositional environments at Baths of Saturnia. A) Channel depositional system characterized by fast flowing water; A2) Ponds (low-flowing area) of channel depositional environment; A2) Cross-section through pond microbial mat showing stratified white layers of carbonate precipitates alternating with organic layers; A3) Downstream surface soft green-biofilm into ponds. B) Waterfall depositional environments; B1-B2) Waterfall travertines exhibit bright orange and green pigments; B3) Waterfall travertines colonized by dark green microbial mat. Reeds are present where there has been temporally no thermal water flow; reeds could be subsequently encrusted by carbonate precipitation. C) Terraced Slope depositional environment consists of vertical terrace walls, pools and rims confining the margin of the pools. C1) Pools varying from 1 to 4 m in wide; rims from 0.2 to 1m in high; C2) Elongated and rounded, several mms to cms in diameters, from pisoids to oncoids form in the pools; C3) Pool floor showing anoxic conditions.

12. Baths of Saturnia travertines: Petrographic observations

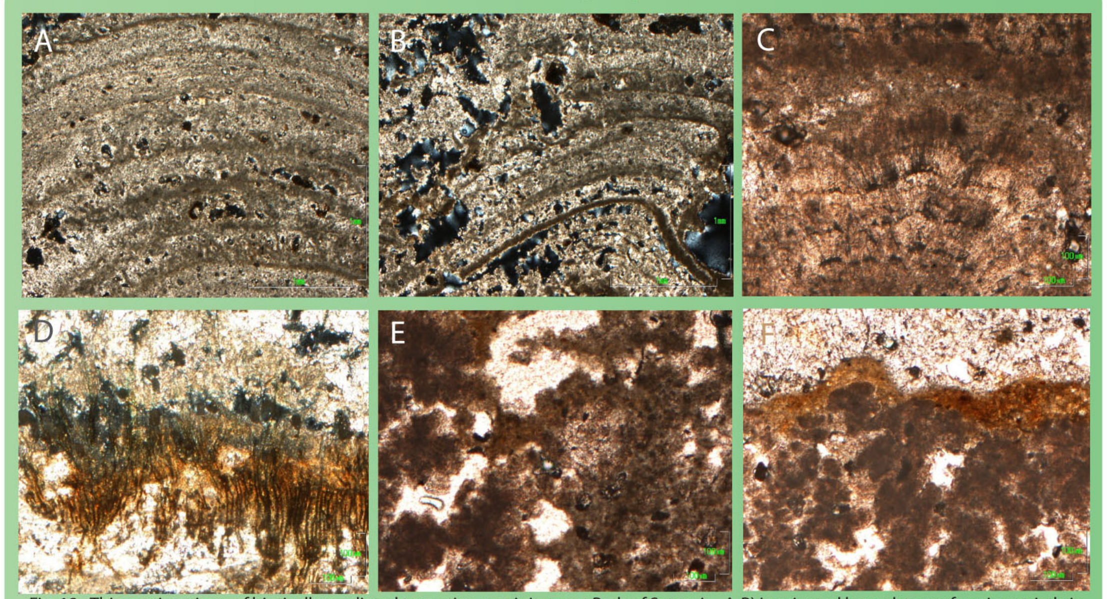


Fig. 18 - Thin section views of biotically mediated travertine precipitates at Bath of Saturnia. A-B) Laminated boundstones forming strictly in association with a biofilm; C-D) Dendritic fabrics contain upward-branching filaments a few micron in diameter, forming bush-likes fans. E-F) Clotted peloidal micrite (related to bacteria) and organic matter.

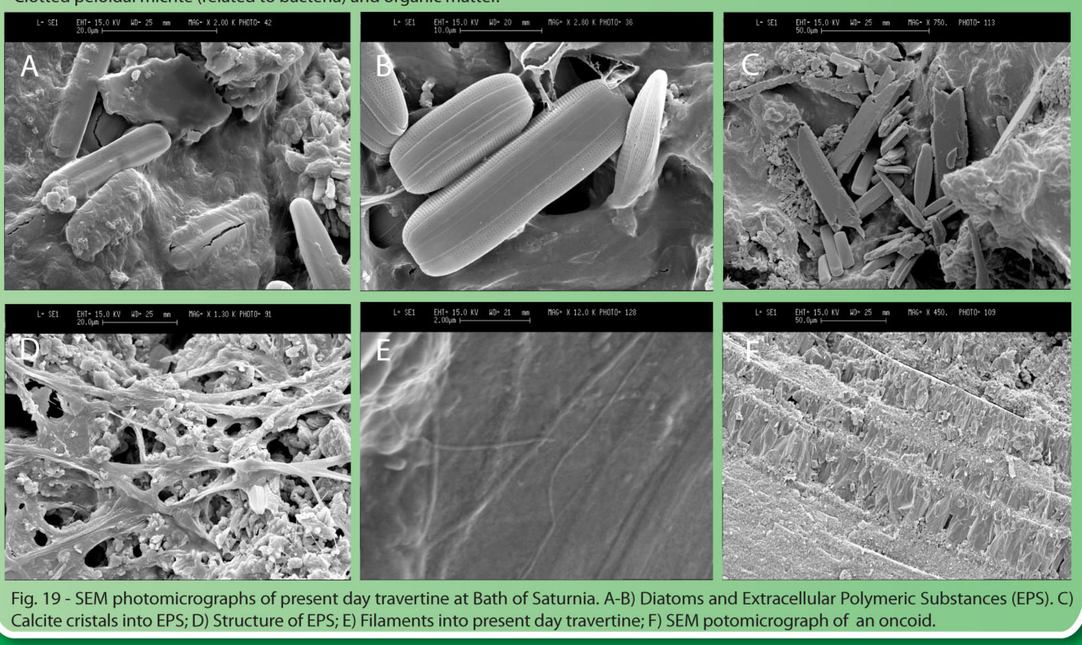


Fig. 19 - SEM photomicrographs of present day travertine at Bath of Saturnia. A-B) Diatoms and Extracellular Polymeric Substances (EPS). C) Calcite cristals into EPS; D) Structure of EPS; E) Filaments into present day travertine; F) SEM potomicrograph of an oncoid.

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Part III

13 Discussion : Abiotic versus biotic fabric types, porosity and diagenesis

Biogenic or abiogenic processes, alone or in combination, and subsequently subsequent diagenesis, can produce the large variety of growth fabrics and and associated pore structures characteristic of travertine deposits. However, it is not completely understood exactly the clear boundary between the biotic and totally abiogenic processes and how diagenesis affects the corrispondent fabrics.
The wide range of travertine fabrics can be essentially distinguished into three categories:
1) Travertine Boundstone s.l. in wich the original components are directly precipitated from hot thermal water independently from abiotic or microbially mediated processes (biologically induced by microbial metabolic process or simply influenced by nucleation on microbial biofilm substrate);
2) Travertine Boundstone s.l. in which original component (act as substrate) are directly encrusted by thermal water independently from abiotic or microbially mediated processes;
3) Carbonate grains formed by fragment of already lithified travertine precipitates.
Travertine fabrics show wide range of depositional porosity (inter-dendritic form, bubble, inter-stromatolitic laminae, shelter, intraskeletal) and secondary porosity (biomoldic, vuggy meteoric dissolution, fractures). This porosity can be partially o totally occluded by cement (meteoric or related to a subsequent circulation of hydrothermal water). Diagenetic processes (Fig 29) potentially can alter the fabric appearance and thereby possibly influencing the interpretation of their origin.

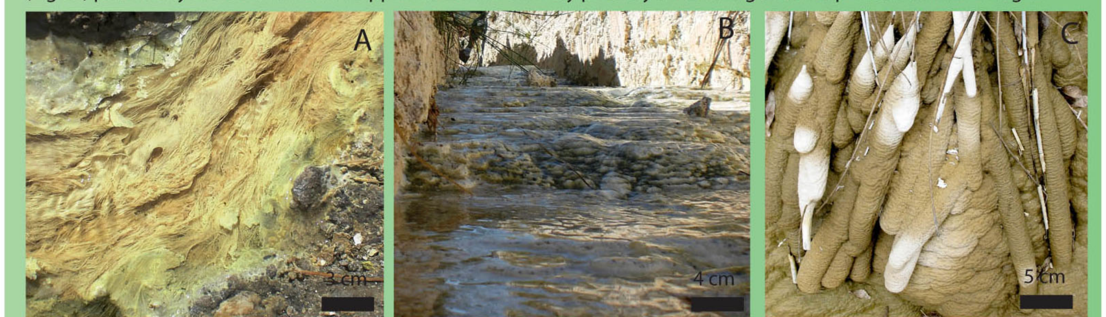

Fig. 20 - A)and B) Interplay of abiotic and biotic processes involving the precipitation of travertines at The Bollore Spring, Bagni San Filippo, Tuscany , Italy. B) Encrusted reed at Borro Canatoppa, Rapolano Terme, Tuscany, Italy.

13.1 Directly precipitated boundstone s.l

Pleistocene/Holocene travertines | Present-day travertines

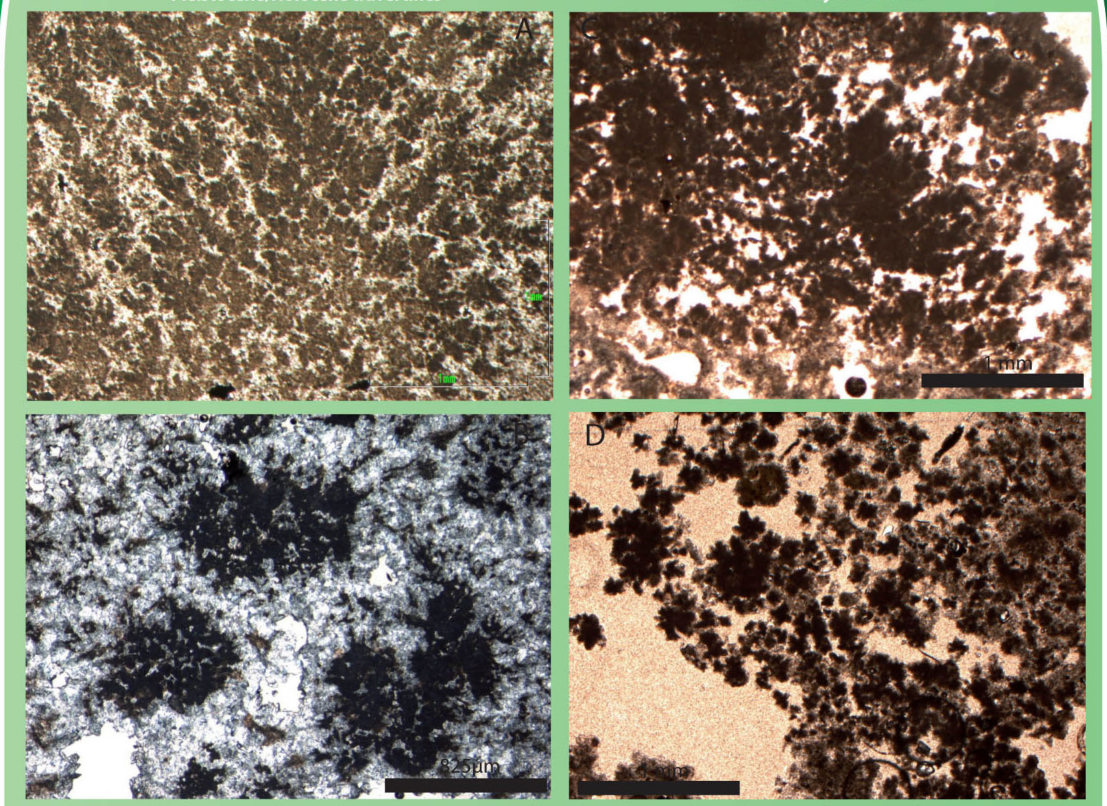

Fig. 21- Biotic dendritic boundstones directly precipitated from hot thermal water through microbially mediated processes. A) and B) Holocene/Pleistocene dendritic boundstone. STQ. C) and D) Present-day dendritic boundstone at Fonte Cannella and Baths of Saturnia, respectevely. Initially these are very delicate and porous and become more robust as cements fill pore spaces.

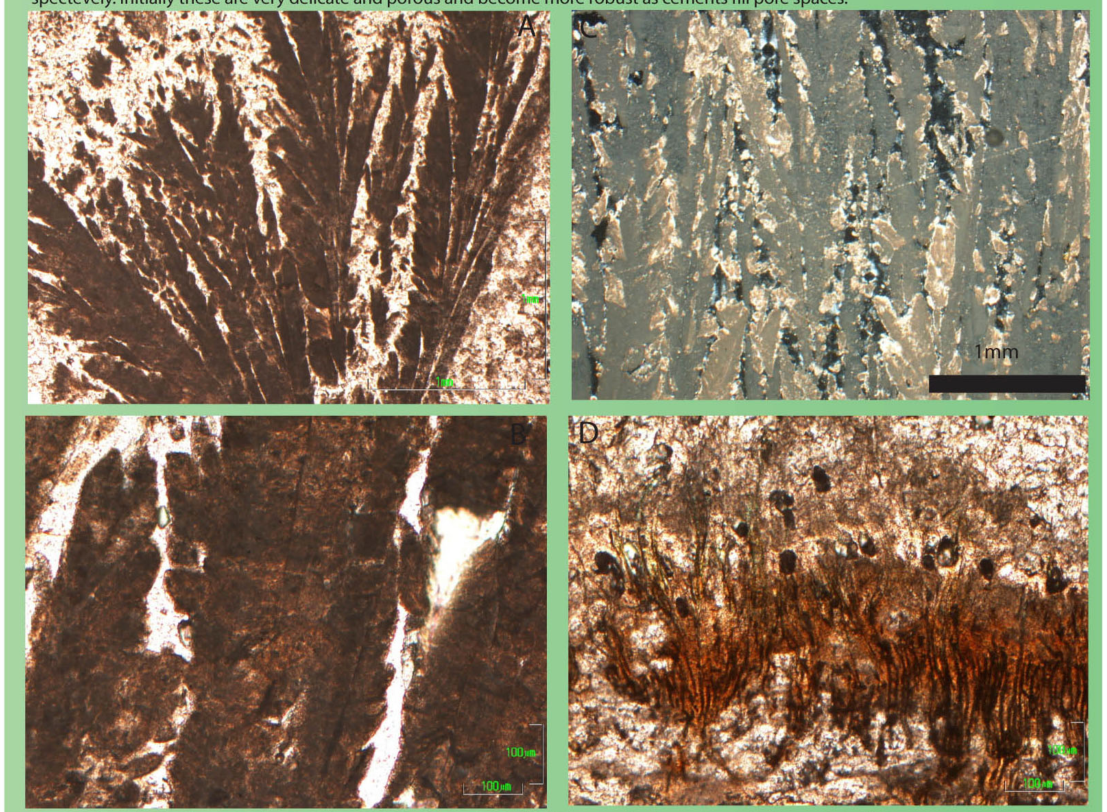

Fig. 22- Dominatly abiogenic dendritic bounstones. A) and B) STQ. C) Present day. Fonte Cannella, Saturnia, Italy D) Baths of Saturnia. Abiogenic dendritic bounstones possess thin central stalks with thin regular reapiting of branches and straight leaves; branches and stalks can encased in single crystals of calcite. (C). Although microbes may have initiated the precipitation of calcium carbonate (B and D) , abiogenic precipitation is the dominant influence on the shape of abiogenic dendritic bd. These are tipical of fast flowing areas.

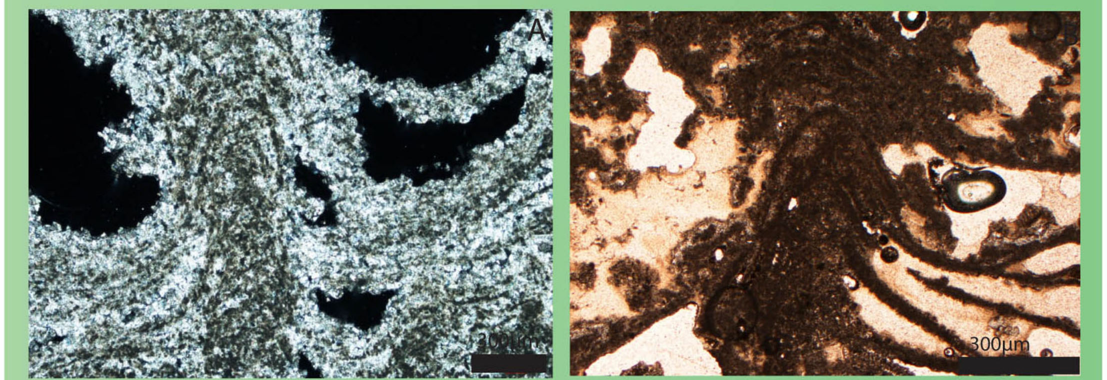

Fig. 23-Biotic wavy laminated boundstones directly precipitated from hot thermal water through microbially mediated processes. A) Holocene/Pleistocene laminated boundstone. STQ. B) Present-day laminated boundstone at Baths of Saturnia.

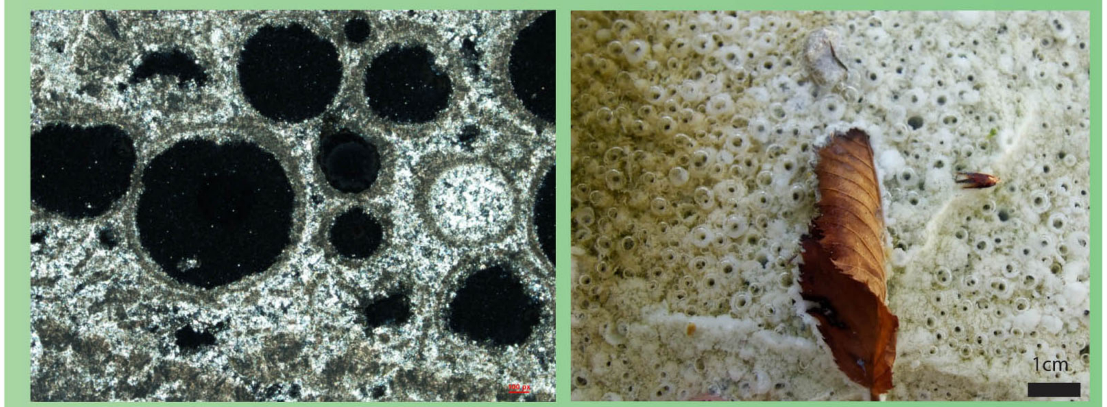

Fig. 24 A) Holocene/Pleistocene bubble boundstone. STQ. and B) Present-day biotically mediated bubble boundstone at Bagni San Filippo.

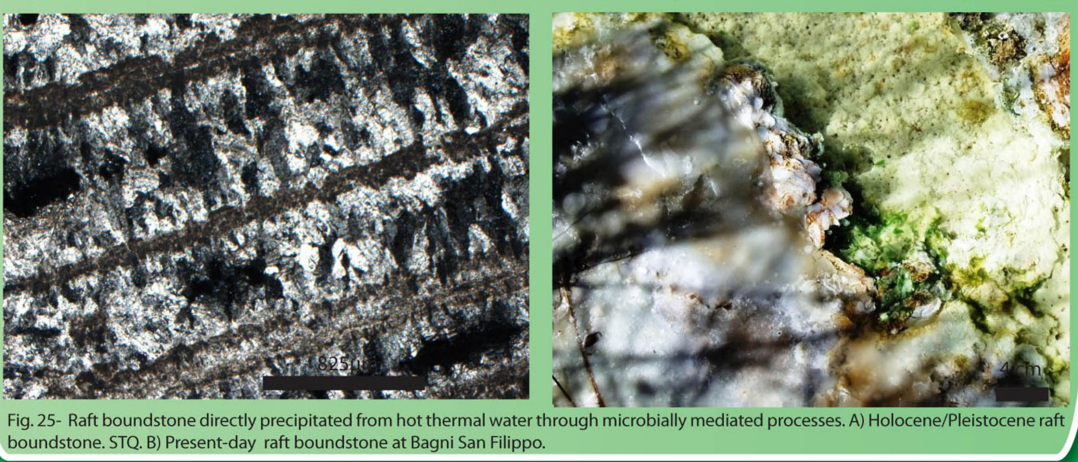

Fig. 25- Raft boundstone directly precipitated from hot thermal water through microbially mediated processes. A) Holocene/Pleistocene raft boundstone. STQ. B) Present-day raft boundstone at Bagni San Filippo.

13.1 Directly encrustated boundstone s.l

Present-day travertines | Pleistocene/Holocene travertines

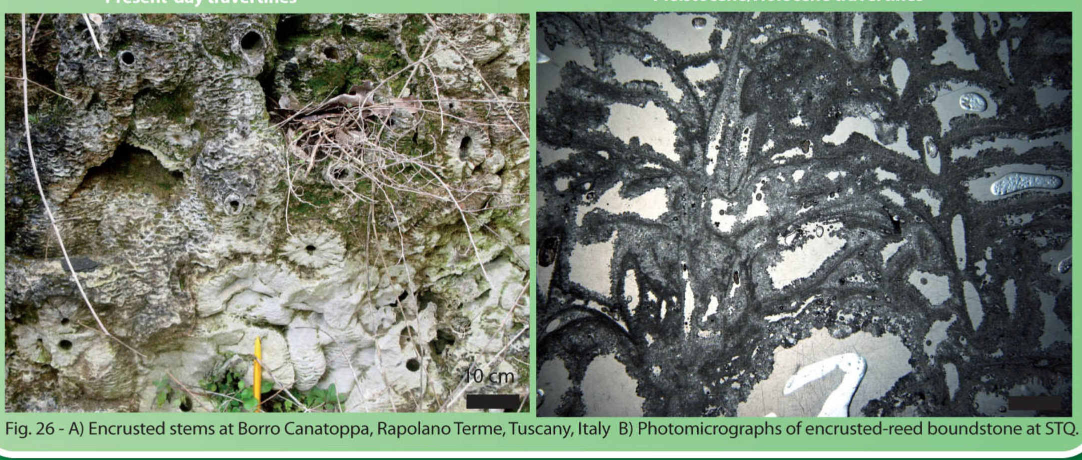

Fig. 26 - A) Encrusted stems at Borro Canatoppa, Rapolano Terme, Tuscany, Italy B) Photomicrographs of encrusted-reed boundstone at STQ.

13.4 Carbonate grains

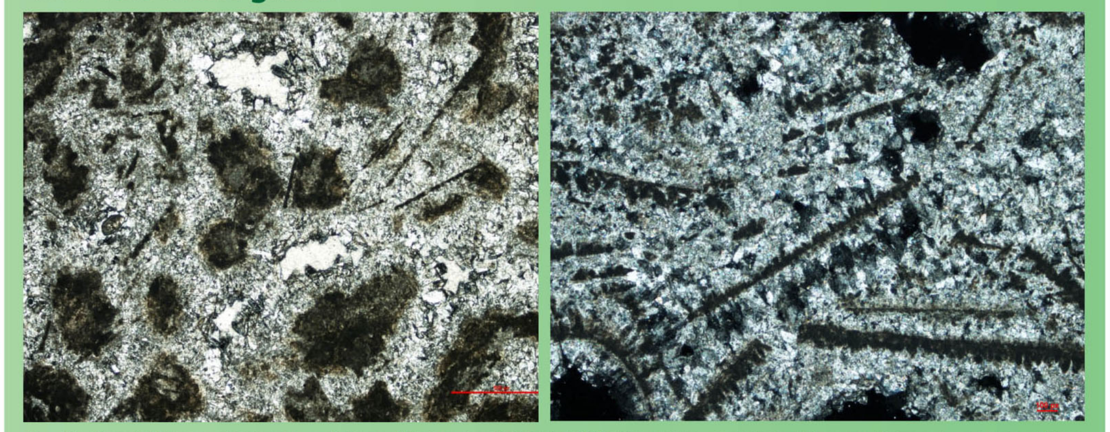

Fig. -27- A) and B) From grainstone to rudstone of fragments of already lithified travertine precipitates. They result as a conseguence of transport and relative alteration. Carbonate grain fabric occurs in between rim and pool transition and in distal part inclined area of TS.

13.5 Porosity

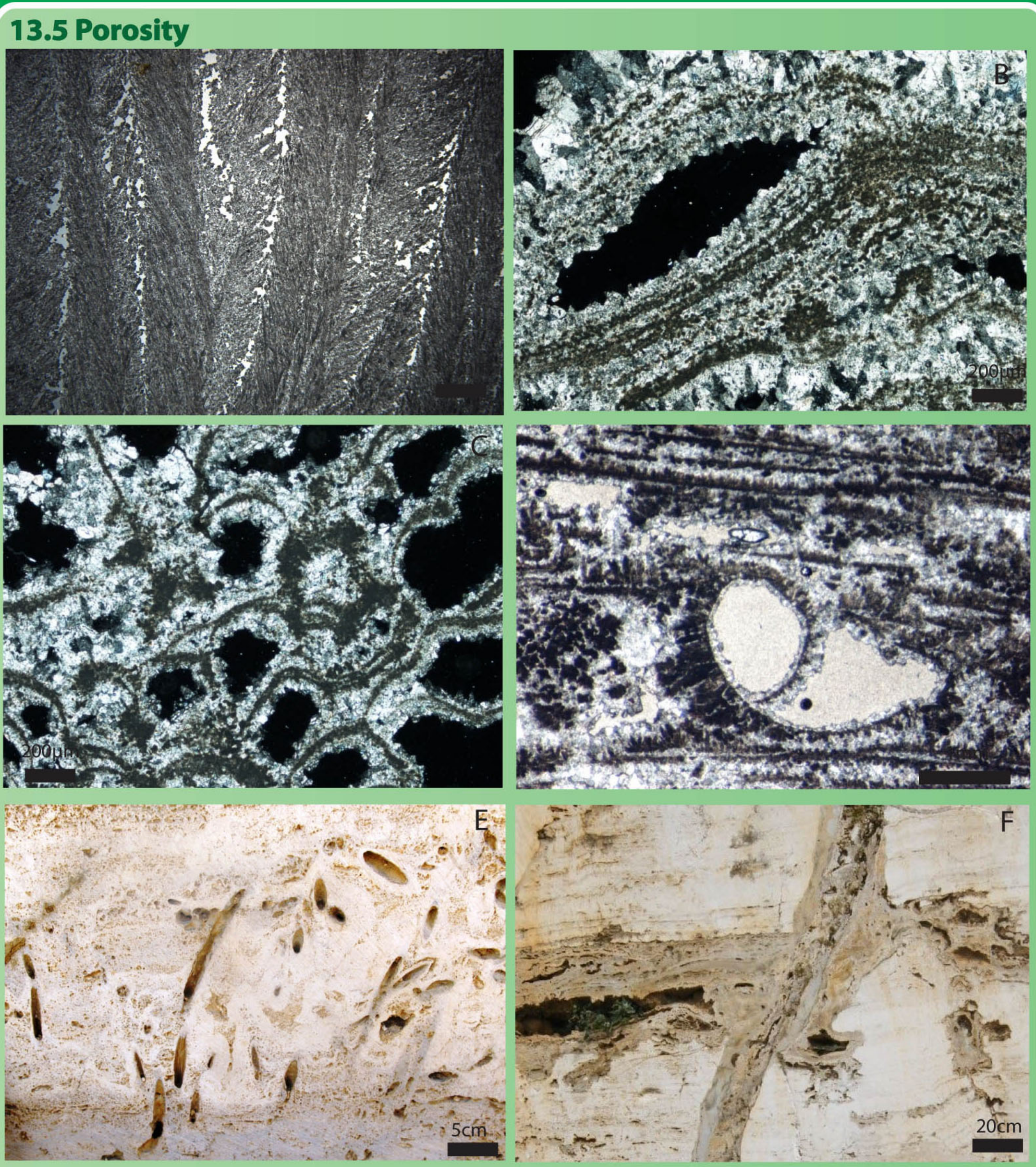

Fig.28 - Primary (A-C) and secondary (D-F) pore system. A) Inter-dendritic and chanalized porosity. Saturnia Travertine Quarry (STQ). B) Interlaminae porosity.STQ. C) Inter-bubbles porosity .STQE) and D) Biomoldic porosity . STQ. E) Secondary porosity related to the decay of encrusted vegetation. F) Secondary porosity related to karstic dissolution and fractures at STQ

13.6 Diagenesis

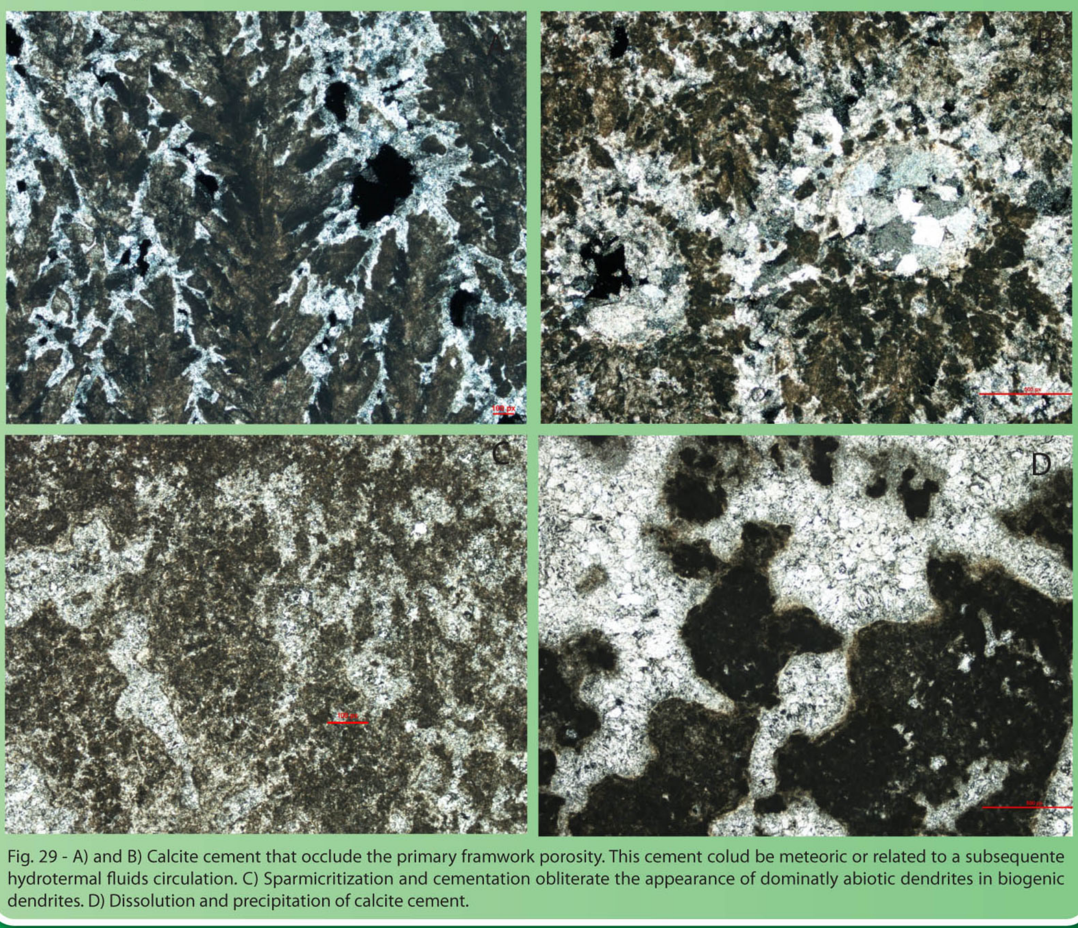

Fig. 29 - A) and B) Calcite cement that occlude the primary framwork porosity. This cement colud be meteoric or related to a subsequente hydrotermal fluids circulation. C) Sparmicritization and cementation obliterate the appearance of dominatly abiotic dendrites in biogenic dendrites. D) Dissolution and precipitation of calcite cement.

14 Conclusion

1) Different depositional environments: terraced slopes, smooth slopes, ponds and channel depositional enviroments
2)A large variety of growth fabrics that can be divided into three categories: a) directly precipitated boundstones sl.; b) directly encrusted boundstones sl.; c) carbonate grains.
3) The variety reflects their origin (by interplay of biotic and abiotic processes) and subsequent diagenesis.
4) Petrographic observation can help to distinguish between biogenic (typical in low flowing areas) to predominatly abiotic fabrics (predominant in fast flowing areas). However, a clear boundary between the biotic and totally abiogenic fabric could not be completly defined.
5) Wide range of depositional porosity (inter-dendritic form, bubble, inter-stromatolitic laminae, shelter, intraskeletal) and secondary porosity (biomoldic, vuggy meteoric dissolution, fractures).
6) Meteoric blocky calcite cementation occludes partially or completely the depositional porosity. Calcite cementation is also related to secondary circulation of thermal fluids.
7) In the STQ cementation is inverse proportional to the age of these travertines.
8) Clotted peloidal micrite is a primary component of travertines however, dissolution and precipitation, resulting in sparmicritization could potentially obliterate the appearance of dominatly abiotic dendrites in biogenic dendrites.
9) Recrystallization of micrite to microspar or spar might take place.

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