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THE MAIN LITHOID MATERIAL ORIGIN OF THE TEMPLE OF HERCULES IN SAN MARCO D'ALUNZIO (SICILY, ITALY)

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(Nota presentata dal Socio Aggregato Carmelo Saccà)

ABSTRACT. This study compares four samples of travertine collected in the lithoid material of the Temple of Hercules (III-IV century B.C.) in San Marco d'Alunzio (Messina) and other four samples of the same lithotype collected in an outcrop found in the surroundings of Alcara Li Fusi (Messina). Analyses on sedimentary petrology, paleontology, X-Ray diffraction and infrared spectroscopy have been carried out on both series of samples. Chemical analyses, for the determination of the major and trace elements, were carried out too. Sedimentary petrology and paleontological studies have indicated that all samples consist of Quaternary soft and porous organic limestones with plant remains, formed in wet and warm zones. X-ray diffraction analyses have shown that studied travertines are prevalently made up of calcite. Infrared spectroscopy studies also showed small quantities of kaolinite and dolomite. Chemical analyses have confirmed the compositional homogeneity among the different samples. Data, as a whole, allow us to hypothesize that the travertines used to build the Temple of Hercules were extracted in the surroundings areas of Alcara Li Fusi, in ancient open quarries set up in Quaternary travertines.

1. Introduction

In this article, data about comparison between travertines forming the main lithoid material of the Hercules Temple in San Marco d'Alunzio, and travertines, sampled in an outcrop far away about 6 kms from the Temple, in the surrounding areas of Alcara Li Fusi (Calamona locality; Figs. 1a and 1b), are here reported.

The aim of this paper is to verify the hypothesis that travertines used to build the monument came from the Alcara Li Fusi outcrop where the examined samples were collected.

In the past, the same lithoid material has also been used for the building of almost all the historical monuments of Alcara Li Fusi. This is due to the physical characteristics that confer lightness but, at the same time, the ability to carry a relatively high load. The cantonals of Churches of the sixteenth and seventeenth centuries (Mother Church, San Pantaleone Church, Rosary Church) are made up of well-squared travertine ashlar [1].

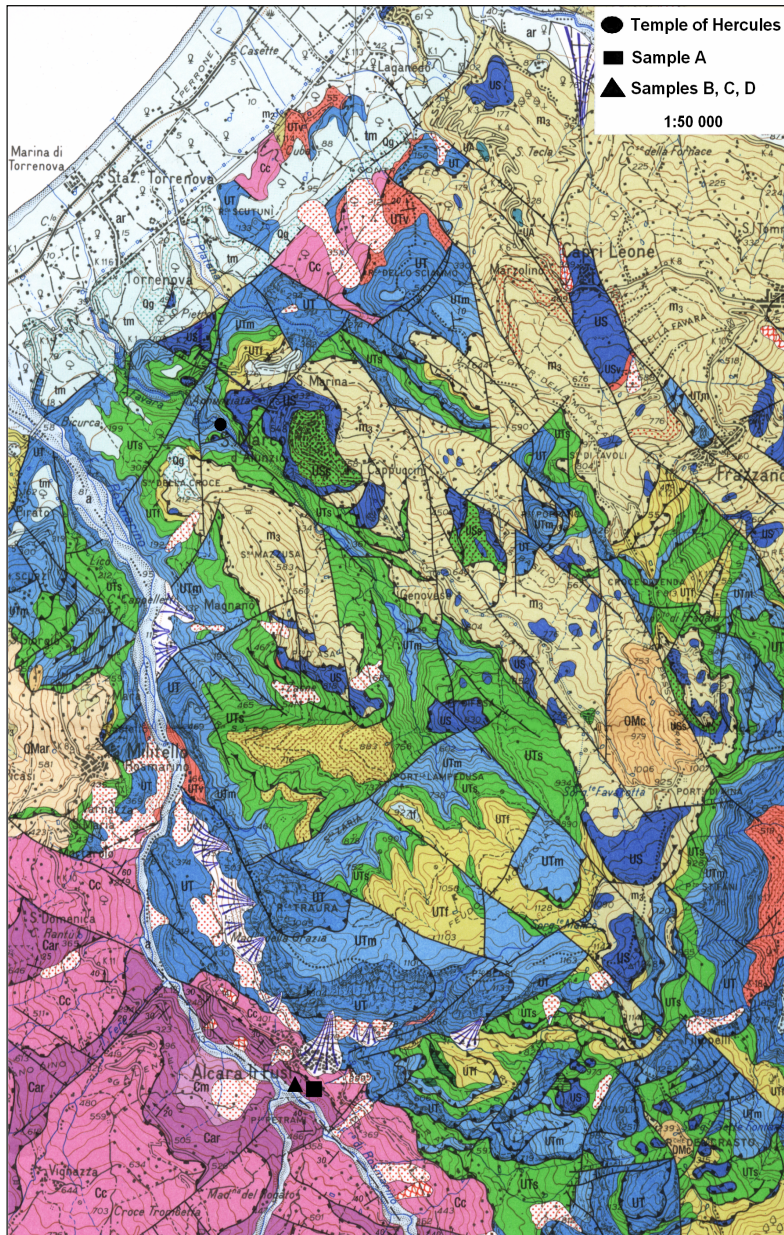


Fig. 1a - Geological sketch map (from Lentini et al., 2000).



Fig. 1b - Legend of the geological sketch map (from Lentini et al., 2000).

The houses of the nineteenth century in the historical centre also show elegant archivolts of the same material. It has also been used as a decorative element thanks to its easy extraction and workmanship.

Four samples have been examined both in the Temple (1, 2, 3, 4) and in the Alcara Li Fusi outcrop (A, B, C, D). Besides sedimentological, paleontological and petrographical observations, X-Ray investigations (XRD), infrared spectroscopy (FTIR) and chemical analyses have been carried out on both series. The results have been compared.

2. Geological setting and location of the travertine outcrop

In the Peloritani and Nebrodi Mts., travertine deposits are very rare and discontinuous in space.

The examined outcrop of travertines is sited in the Calamona locality (Figs. 1a and 1b), to the south-east of the inhabited centre of Alcara Li Fusi.

This site is localised to the south of the tectonic “lineament” known in literature as Taormina Line [3].

This Line represents the thrust front [4] of the Kabilo-Calabride Chain [5, 6] on to the Apenninic Maghrebic Chain (AMC) [5, 6, 7].

The former is prevalently made up of tectonic units formed by low to high-grade metamorphic crystalline rocks and subordinately by Meso-Cenozoic sedimentary covers [8, 9].

The second one is represented by the Sicilide Complex [10]. It is formed by the tectonic unit of the *Flysch del Monte Soro* and by the overlying unit of the *Argille Scagliose Superiori*, both Early Cretaceous in age [2, 11, 12].

Particularly, in the studied area, the thick Liassic limestones (Sinemurian-Pliensbachian) of the Longi-Taormina Unit constitute the steep cliff of the karstic carbonate massif of Rocca Traora-Pizzo Blasi which overthrusts the *Flysch del Monte Soro* (Fig. 1a).

The travertine outcrop of Alcara Li Fusi, in the past exploited by means of open quarries (Fig. 2), extends for a limited area (1 km²), comprised from the south ring-road of the village up to the right border of the Fiumara Rosmarino.

The analysed travertines, exposed as 3 to 4 m high terraces (Fig. 2), are mainly represented by carbonate deposits and concretions encrusting and sealing the Quaternary detritus. This observation allows us to ascribe the studied travertines to the Quaternary.

The encrusted detritic deposit, mainly formed by blocks of Liassic carbonates, has a mid-high inclination and an apron slope morphology.

Karstic springs with a mean flow higher than 20 l sec⁻¹ are localised at the detritus wedge apex and along the overthrust of the karstic massif. The recharge of these springs depends on rainfall while discharge occurs exclusively through the springs located along the massif border.

The travertine deposition, inactive today, could depend on the ancestral origins of the Alcara Li Fusi modern springs.

3. Location of the Temple

The Temple of Hercules (Figs. 3 and 4) of the Greek period (III-IV century B.C. [13]), whose intact cell is preserved, represents the only remaining construction of the kind in the

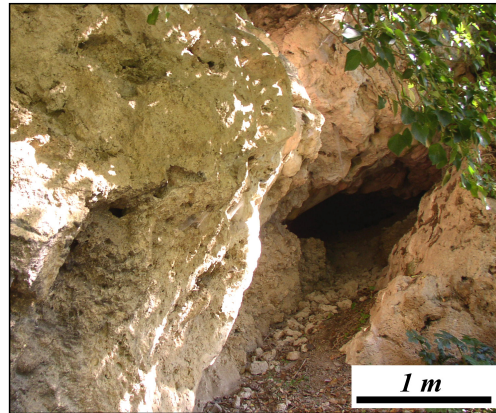


Fig. 2 - Detail of a travertine open quarry in Alcara Li Fusi (Calamona locality).

Messina province. It was in Doric order, with a rectangular plant, and probably used for sporting activity related to the cult of Hercules.

The building was then transformed into a church and devoted to Mark the Evangelist.

The Baroque façade with its precious portal and the two windows date back to the 17th century. It rises to the left of the road that leads to San Marco d'Alunzio, before entering the residential centre.

The main lithoid materials forming the walls of the Temple are represented by travertines.

Part of the construction is made up also of some blocks of the Liassic red limestones (Rosso San Marco) of the Longi-Taormina Unit. These last limestones form the substratum on which the building is founded.



Fig. 3 - The Temple of Hercules (San Marco d' Alunzio).



Fig. 4 - Detail of the front of the Temple of Hercules.

4. Sample descriptions of travertines

Analyses considered useful for an accurate evaluation have been carried out on small portions of material sampled on the Temple of Hercules lithoid material (1, 2, 3, 4) and on hand specimens collected in the Alcara Li Fusi outcrop (A, B, C, D).

The travertines commonly originate from physico-chemical and microbiological carbonate deposition from groundwater and/or water springs containing elevated carbon dioxide concentrations. These rocks, representing the major freshwater carbonate rocks over most of the world, are generally of great economic value as they are used as monument lithoid materials.

The travertines analysed in the Alcara Li Fusi outcrop (Fig. 5a) are fresh looking and are mainly represented by soft and highly porous organic limestones, whose rich organic content is formed by plant remains. These latter consist of broken stems of rushes and canes, preserved in tubular forms.

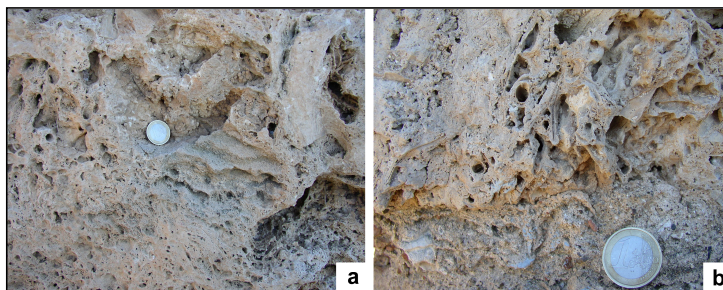


Fig. 5 - Mesoscale photographs of travertine deposits. a) Alcara Li Fusi travertines; b) Travertine of the Temple of Hercules building stone.

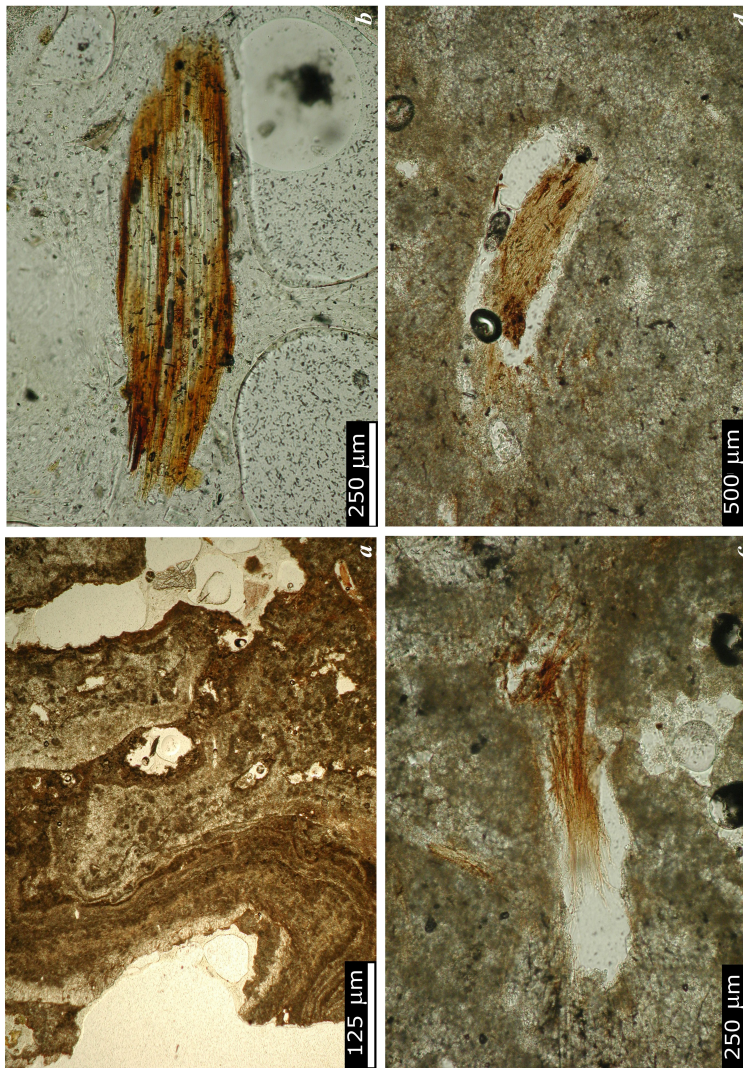


Fig. 6 - Photomicrographs (P.P.L.) of travertine. a) Peloidal packstone-wackestone; b-c) Plant remains (Alcara Li Fusi outcrop); d) Plant remains (Temple of Hercules).

These carbonates generally present an intense beige-colour and are locally associated with decimetre-thick layers of pisolite and oncolite limestones. Both carbonates are characterised by voids partially filled by planar and mammillary, laminated and speleothem-like encrustations, whose thickness can reach 0,5 metre. Stalagmites in larger cracks give evidence of weathering.

The travertines forming the Temple of Hercules lithoid material (Fig. 5b) present facies very similar to those observed in the Alcara Li Fusi outcrop. Lithoid material mainly consists of very porous beige organic limestones containing plant remains, and rare gasteropods observable with a magnifying lens. Pisolitic and oncolitic limestones, and carbonate laminae exclusively form restricted portions of the construction stone.

Sedimentological analyses indicate that all studied travertines mainly consist of two interfingering microfacies. The former is constituted by bafflestone [14], the latter is made up of peloidal packstone-wackestone [15], both fine-grained recrystallised (Fig. 6a). Particularly, the travertines of the Temple contain some specimens of continental gasteropods smaller than a millimetre.

Both microfacies, formed by a mixture of micritic and sparitic calcite, are characterised by the presence of porous portions encrusted by planar and micritic laminae. In all analysed samples, these voids contain very weathered and/or dissolved remains of plants (Fig. 6b,c,d), similar to those living today around the springs. Longitudinal sections of this plant show fibrous cells and grains of amorphous silica with carbonised or calcitized cellulose.

5. Experimental methods

The instrumental analysis was preceded by an observation of the samples by optical microscopy in order to verify details not easily visible to the naked eye.

Chemical analyses of trace elements were carried out by ACME Analytical Laboratories Ltd in Vancouver, Canada. Powdered and separated samples of minerals were digested by HCL:HNO₃ (3:1) mixed reagent followed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis. Results give total concentrations (or almost) for noble metals and partial concentrations for minerals making up the rocks. Where materials were pure, tests were complemented by Atomic Absorption (A.A.) according to the following procedures: 300mg of powdered mineral bonded by heat to an HNO₃:H₂SO₄ mixture (1:1) concentration, refluxed reaction for 2-3 hours until completely dissolved. The solution was analysed by Atomic Absorption Varian AA-1475 spectrophotometer, equipped with a Varian GTA-95 graphite oven. The adding method was used together with an absorption correction system by deuterium lamp. As and Se were determined by the same method and an accessory can be used to determine iodides or volatile elements. The efficiency of the analytical method verified by known standards (Recovery tests) is ± 2.5 . Laboratory reproducibility shows maximum oscillations lower than 2% for analytical determinations.

The above-mentioned analytical methods (ICP-MS and A.A.) have been selected to have data reliable on trace elements.

The X-ray diffraction analyses (XRD) of the powder samples were performed with an Ital Structures diffractometer (Model APD 2000) equipped with a monochromator, a scintillation counter NaI detector and a x-ray tube with Cu anode operating at 40 kV and 30 mA; scans were carried out in step scan mode (2 theta step scan= 0,04, acquisition time= 1 sec), with soller slit on primary and diffracted beam, with a monochromator, with divergence slits= 1°, anti-divergence slits= 1°, receiving slits= 0.1 mm. Diffraction peaks were compared with those reported in the JCPDS data files.

The samples have also been analyzed in Fourier transformed infrared spectroscopy (FTIR) by the Environment Research & Service ERS srl. FTIR Jasco 430 was used to

investigate a reduced quantity of samples ($\sim 2\text{mg}$) for a characterization of inorganic and organic substances. Work was carried out by diffused reflectance on powdered samples and dispersed in $\sim 200\text{mg}$ of powdered KBr, that is transparent in the considered spectral range, which varied from 400 to 4000 cm^{-1} .

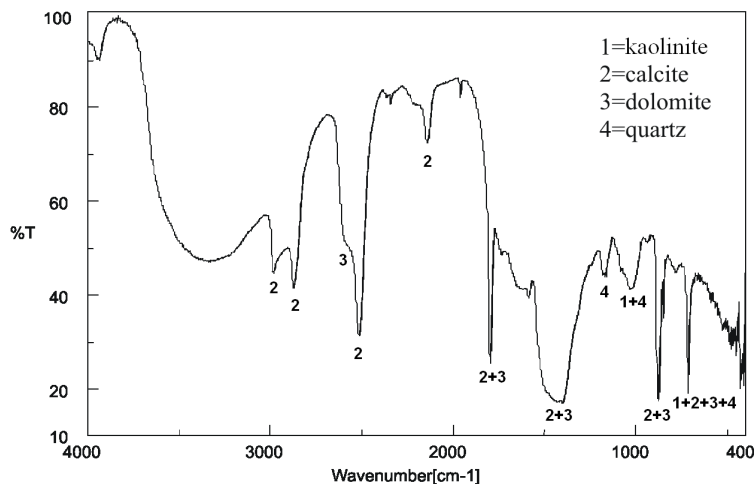


Fig. 7 - FTIR spectrum of the outcrop samples.

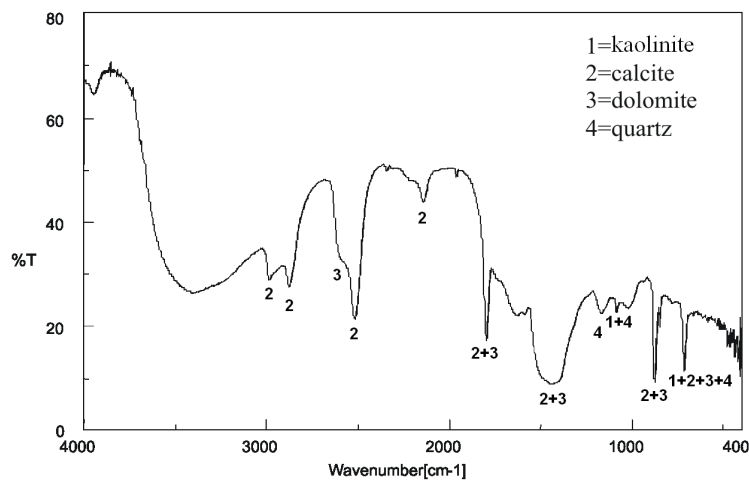


Fig. 8 - FTIR spectrum of the Temple samples.

6. XRD and FTIR data

The X-ray diffraction analyses indicate that the studied lithotypes are prevalently made up of calcite and small quartz quantities. Kaolinite is pointed out by low intensity peaks but its presence has been confirmed by FTIR analyses. From a diffractometric point of view, the samples of the Alcara Li Fusi outcrop (A, B, C, D) show diffractograms whose peaks are perfectly comparable with the analogous ones related to the Temple samples (1, 2, 3, 4).

For an accurate investigation, FTIR spectra related to both series of samples have also been compared. From their superimposition and from the comparison with some standard spectra, it is deduced that the peaks are similar to each other (Figs. 7 and 8) and compatible with the presence of kaolinite, calcite, small dolomite and quartz quantities, that however is more marked in the samples of outcrop than in the material of the Temple.

The presence of the Ca and Mg carbonates agrees well with the values shown by the chemical analyses (see later).

7. Chemical data

The chemical data (Table 1) showed that samples are mostly made up of CaO, whose values vary from 43.29 to 53.76%, with an average of 50.06% for the travertine outcrop and 47.84% for the travertine lithoid material of the Temple. Standard deviation is 3.69 in the first case and 4.35 in the second case.

In all samples MgO and SiO₂ are also present. MgO content, unlike SiO₂, shows in the Temple samples values slightly higher than in outcrop samples. Its presence allows us to hypothesize the presence of a small dolomite amount which is not appreciable in diffractometric analyses but its peaks are observable in FTIR.

The values of trace elements (Table 2) are not always similar and mostly Sr and Ba contents, in samples 1, 2, 3 and 4, and Pb contents in samples 1, 2 and 3, are higher than in other samples.

Table 1
Chemical analyses of oxides (%)

Elements	CaO	SiO ₂	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	Al ₂ O ₃	P ₂ O ₅	SO ₂
	%	%	%	%	%	%	%	%	%
Samples									
1	46.99	1.00	1.03	0.15	0.04	0.05	0.24	0.09	0.08
2	43.29	1.28	1.60	0.55	0.04	0.13	0.71	0.31	0.28
3	47.33	0.74	1.14	0.18	0.17	0.11	0.28	0.12	0.68
4	53.76	0.64	1.68	0.06	0.05	0.05	0.13	0.03	0.02
A	48.49	3.34	0.92	0.04	0.16	0.13	0.13	0.04	0.18
B	52.65	3.00	0.48	0.21	0.01	0.06	0.32	0.06	0.16
C	45.60	3.69	0.43	0.13	0.01	0.05	0.19	0.04	0.24
D	53.51	2.30	0.49	0.11	0.01	0.05	0.22	0.06	<.02

Table 2
Chemical analyses of trace elements (ppm, ppb)

Elements	Sr ppm	Ba ppm	Pb ppm	Mn ppm	Ti ppm	As ppm	Zn ppm	Cu ppm	B ppm	Ni ppm	Co ppm	La ppm	Cr ppm
Samples													
1	676.5	160.2	104.1	34.0	30.0	4.0	20.9	3.9	8.0	1.8	0.7	1.2	1.9
2	559.4	121.0	43.7	146.0	70.0	3.3	21.5	9.8	7.0	6.3	2.3	4.2	5.2
3	497.4	134.4	35.6	83.0	40.0	2.2	23.2	4.8	11.0	3.2	1.0	1.6	3.3
4	740.2	141.8	6.1	28.0	10.0	110.6	11.6	5.5	6.0	<.1	0.4	<.5	1.1
A	168.3	90.0	5.9	37.0	10.0	0.4	8.4	2.7	8.0	0.7	0.3	<.5	1.6
B	149.9	75.2	12.8	78.0	10.0	0.2	26.8	3.8	4.0	2.8	1.0	0.5	3.3
C	126.7	63.5	5.7	75.0	10.0	2.7	23.3	3.4	3.0	2.0	0.8	0.5	3.0
D	104.7	50.3	10.2	103.0	10.0	92.6	43.5	6.3	2.0	1.8	0.6	0.5	2.5
Elements	Se ppm	Sb ppm	Sc ppm	Cd ppm	Mo ppm	U ppm	Ga ppm	Tl ppm	Te ppm	Bi ppm	Ag ppb	Hg ppb	Au ppb
Samples													
1	0.4	0.3	0.4	0.1	0.1	0.1	0.3	0.1	0.1	0.0	136	8	2
2	0.4	0.3	1.0	0.1	0.3	0.1	0.9	0.1	0.1	0.1	68	38	48
3	0.4	0.6	0.6	0.1	0.2	0.1	0.3	0.0	0.0	0.0	59	6	4
4	0.5	0.1	0.1	0.1	0.2	0.1	0.2	0.0	0.0	0.0	46	6	22
A	0.5	0.1	0.3	0.0	0.1	0.1	0.2	0.1	<.02	<.02	17	9	1
B	0.4	0.2	0.6	0.1	0.0	0.1	0.4	0.1	0.0	0.0	26	5	1
C	0.4	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.0	0.0	18	12	1
D	0.3	0.1	0.4	0.2	0.0	0.1	0.3	0.1	<.02	0.0	91	13	8

Cu shows varying values from 2.7 to 6.3 ppm reaching the value of 9.8 ppm only in the sample 2.

Zn has almost similar values in all samples except in A, where it reaches the minimum value of 8.4 ppm, and in D where it reaches the maximum value of 43.5 ppm.

Amongst the noble metals, the Ag values oscillate from a minimum of 17 ppb in sample A to a maximum of 136 ppb in sample 1, while the Au reaches 48.4 ppb only in the sample 2. Sample 2 is different from the rest also for La and Cr.

Mn has a content higher than 100 ppm only in samples 2 and D. The samples 4 and D show an As content much higher than those of the other samples. Hg reaches values of 38 ppb only in sample 2.

8. Conclusions

The features of the sedimentary fabric and of the fossil content (plant remains and gasteropods) analysed in all studied travertines and the fact that the Alcara Li Fusi carbonate deposits encrust and seal the Quaternary detritus, have indicated that all selected samples are Quaternary in age.

These travertines consist of very soft and porous organic limestones with plant remains represented by broken rushes and canes.

As in other sectors of the Mediterranean, travertines have episodically formed in the Quaternary, during warm and wet periods, generally related to interglaciations, characterised by large spring flows, underground dissolution and carbonate precipitation. Quaternary travertines represent an important paleoclimatic marker, because their growth generally ceases during glaciations because of reduced recharge and permafrost [16].

The sedimentological analyses, corroborated by chemical, diffractometric and spectroscopic data, have shown a compositional homogeneity among the analysed samples of travertine. The only difference is that the Temple samples show higher Sr, Ba and Pb contents than outcrop samples, probably due to the sampling of the material from different layers. They mainly consist of freshwater carbonates (calcite and small quantities of dolomite), with a silica content (shown by chemical analyses) probably due to amorphous silica grains contained in the plant remains.

So we can hypothesize that the lithotypes used to build the Temple of Hercules were those mined from the Alcara Li Fusi open quarries, exploited in the past. It is therefore believed that there is a close correlation between outcrop and place of use. This is probably a consequence of practical needs and the greater ease of working with such materials rather than with the “Rosso San Marco” limestones of San Marco d’Alunzio.

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