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Geological Insights on the Calcareous Tufas (*Pietra Spugna*) Used as Building and Ornamental Stones in the UNESCO Historical Centre of Urbino (Marche Region, Italy)

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Abstract: This study is addressed at the cultural heritage of the UNESCO historical centre of Urbino (Italy) through the focus on a very peculiar building and ornamental carbonate porous (spongy) stone also found in the opus quadratum Roman dry walls. For these rocks, the mathematician and historian Bernardino Baldi (16th century AD) and the mineralogist Francesco Rodolico (middle of the 20th century AD) introduced, respectively, the popular terms of *Tufo spugnoso* or *Pietra Spugna.* Physical observations and stable isotope data ($\delta^{13}C$ and $\delta^{18}O$) of these rocks allowed, for the first time, their classification as calcareous tufas, thus contributing to the valorization of the stone heritage of the city. This carbonate lithotype was formed by the chemical precipitation of $CaCO_3$, driven by the CO_2 degassing of supersaturated calcium-bicarbonate-rich waters, coupled with the passive encrustations of organic material in continental environments. Radiocarbon analyses dated these stones mostly between 9100 and 4700 yr. BP when a maximum growth of these carbonate continental deposits occurred in Mediterranean regions and northern Europe, i.e., during the Holocene Atlantic climatic optimum. Work is still in progress on a perched springline of calcareous tufas found along the Metauro Valley (a few km from Urbino), being good candidates for provenance, at least for those blocks exploited by the Romans and successively reused in the architectural framework of Urbino.

Keywords: cultural heritage; calcareous tufa; travertine; ^{14}C dating; C and O stable isotopes; building and ornamental stone; Urbino; UNESCO

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1. Introduction

The historical centre of Urbino (Marche Region, Italy) is listed as a UNESCO World Heritage Site since 1998. The first important architectural remains of Urbino, dating back to the 3rd–2nd century BCE (*Urvinum Mataurense;* [1]), are located on the southernmost part of the town, in one of the two hilltops of the present historical centre (Figure 1). The historical centre of Urbino was mainly built using bricks, and, subordinately, local sedimentary rocks. Since Roman times, carbonate formations of the Umbria–Marche Succession were exploited in different quarries located in the adjacent Apennine Chain. Big ashlars for defensive walls, slabs and squared blocks in some portals, stone cladding, and flooring were made using limestones to marly limestone lithotypes, all characterized by light colours: *Calcare Massiccio*, *Bugarone*, *Maiolica*, *Scaglia Bianca/Rossa*, and *Bisciaro* Formations [2]. This work deals with a less widespread, but very peculiar, carbonate lithotype used in some contexts of the historical centre of the city, known by the popular term of *Pietra Spugna* (i.e., spongy stone) because of its spongy/porous appearance. Bernardino Baldi, mathematician, poet, and historian of the 16th century, first realized that the old city walls were partly built, among other stones and bricks, by squared blocks of a so-called *Tufo spugnoso* (spongy tufa) resembling, in a rough manner, the travertine from Tivoli [3]. The mineralogist and historian Francesco Rodolico, in his famous book (middle of the 20th century) on the stones of the Italian towns, among the stones of the historical centre of Urbino, also reports a peculiar carbonate rock kneaded by a huge quantity of leaves, already known as *Pietra Spugna* [4]. This spongy stone was used in Urbino during ancient times, as big ashlars (ca. 59 × 59 or 59 × 74 cm) nowadays visible in some remnants of the most ancient Roman walls in *opus quadratum*, or as reused building blocks throughout the historical architectural framework. More recently, it was also employed as outdoor ornamental stones in portals (17th century AD) or indoor, to create cave-like spaces in some monuments and churches (e.g., Oratorio delle Grotte, Oratorio della Morte, and all around the Federico Brandani's putty sculpture of Nativity in the Oratorio di San Giuseppe). The *Pietra Spugna*, made of carbonate encrustations of vegetation such as reeds, frustules, and leaves, is often and erroneously considered as a hydrothermal travertine rock type. By contrast, it seems to be a calcareous tufa stricto sensu [5,6] representing freshwater rocks deposited by chemical precipitation from low-temperature calcium-bicarbonate-rich waters under subaerial conditions in a large variety of continental depositional and diagenetic environments [7]. Ornamental and building stones made of these calcareous tufas were considered in the open-air stone itinerary across the historical centre of Urbino [8] addressed to geotourism and the best fruition of the geological and cultural heritage of the UNESCO World Heritage Site itself. In the present paper, we are going to focus, for the first time, on the geological origin of these calcareous tufas used in the historical centre of Urbino, also contributing to the stone heritage of the UNESCO site. Physical parameters may be different among carbonate stones, due to the different original depositional environment (e.g., marine vs. continental origin and relative degree of diagenesis and cement vs. matrix content), all factors influencing stone behavior during exposure to weather conditions. As recently pointed out by [9] comparing calcarenites and calcareos tufas, «the conservation and restoration of cultural heritage must be based not only on the monument and territory history but also on the deep knowledge of the materials». In this way, the conservation of the calcareous tufas of the Urbino historical center cannot be considered, in toto, in the same way as the degradation processes of other carbonate stones (limestones with vacuolar structures, calcarenites, and hydrothermal travertines *stricto sensu*) used as building stones in the UNESCO site [8].

The investigation of an active deposition of calcareous tufas near Urbino, along the Metauro Valley [10] where some ancient houses and churches from the end of the 12th to 19–20th century are even entirely built with this kind of lithotype, is in progress. Because of obvious conservation reasons, only a few grams of samples were collected from ashlars and blocks of calcareous tufas of the historical centre of Urbino, and these aliquots were almost totally addressed through radiocarbon (^{14}C) dating and stable isotopes ($\delta^{13}C$ and $\delta^{18}O$) analyses. Only a few larger-sized samples allowed a thin section preparation. A comparison with the main calcareous tufa deposits formed in Italy and Europe during the Holocene Atlantic climatic optimum, based on carbon and oxygen stable isotopes, was also performed.

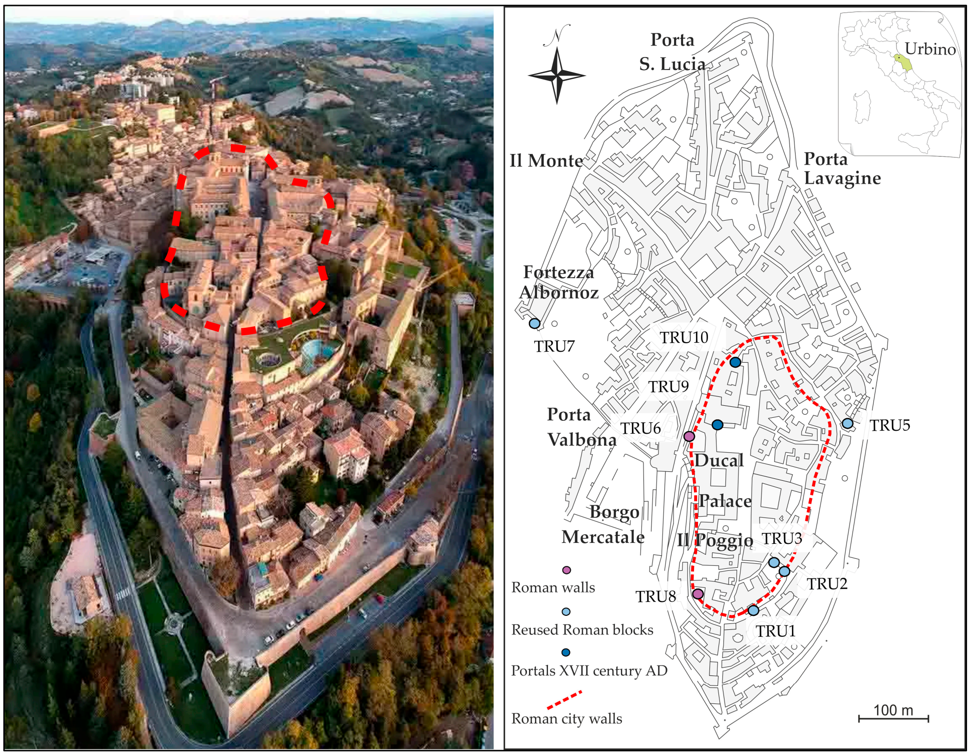

Figure 1. Left: panoramic view (from south) of the Urbino historical centre (photo courtesy of Paolo Mini). Right: map of the location of the studied samples; the outline of the defensive Roman walls (dashed red line) is defined (also reported in the panoramic view on the left).

Travertines vs. Calcareous Tufas

For a long time, and even nowadays, there has been a controversial nomenclature concerning the two terms "travertine" and "calcareous tufa" often used indiscriminately as alternative names to describe continental carbonate deposits precipitated from thermal springs or fresh waters. In any case, the term travertine should only be used for continental carbonates mainly consisting of $CaCO_3$ deposits produced from supersaturated calcium-bicarbonate-rich waters, typically hydrothermal in origin [6,7,11–13]. Travertine is characterized by a high depositional rate, with regular bedding and fine lamination, medium to low porosity, and an inorganic crystalline fabric. Areas of typical travertine deposition are tectonically active [14], with relatively high geothermal heat flux, such as the area of Tivoli, near Rome, where the famous *Lapis Tiburtinus* was extensively exploited by the Romans in ancient times [7,15–20]. Instead, the term calcareous tufa [6,21] should be used to refer to continental freshwater carbonates mainly consisting of calcite precipitated from ambient (cool) temperature calcium-bicarbonate-rich waters, and characterized by relatively low depositional rates, highly porous bodies with poor bedding and lenticular profiles, and abundant remains of microphytes, macrophytes, invertebrates, and bacteria. Remnants of vegetal organisms such as mosses or algae (blue-green algae and bryophytes) contribute to calcite precipitation through respiration and photosynthetic processes, giving rise to massive phytohermal or layered phytoclastic (sandy-silty to gravel-rich) facies [5]. Calcareous tufas are typically located around, or not far from, springs, in correspondence to waterfalls and river knickpoints where they build up dams, or in swamps or lakes [22]. Pedley [6] proposed a classification of calcareous tufas into five depositional models: (a) perched springline, (b) fluvial, (c) lacustrine, (d) paludal, and (e) cascade. The precipitation of $CaCO_3$ mostly derives from the degassing of CO_2 from the supersaturated waters, coupled with passive encrustations of any organic (vegetal or animal) materials, whereas the biologic and photosynthetic activity of the vegetation may give a minor contribution. Calcareous tufa deposition and aggradation of dams are generally controlled by climatic conditions, with warm and wet periods enhancing deposition due to the rise of biogenic CO_2 levels in the topsoil [23,24], which in turn increases the rate of bedrock limestone dissolution. Groundwater percolating through progressively colder layers of deep limestone aquifer would become enriched in dissolved $CaCO_3$ and, at the emergence of spring waters, higher air temperatures would induce carbonate oversaturation and enhance calcareous tufa precipitation. These reverse thermal gradients between the ground surface and the deep limestone aquifer are boosted at major climatic changes to warmer conditions, therefore favouring calcareous tufa formation. On the contrary, with changes towards colder conditions, the $CaCO_3$ deposition involves the upper bedrock layers leading to the emergence of bicarbonate-undersaturated spring waters. Finally, calcareous tufas represent a powerful geological archive in the continental environment providing, mainly through stable isotopes ($\delta^{13}C$ and $\delta^{18}O$), independent records of regional climatic changes that can be dated precisely by ^{14}C or U-Th methods [7,25].

2. Materials and Methods

Due to the requirements of minimum intervention during the sampling of the architectural structures, it was not possible to obtain enough material for all the originally planned analyses. As the overall size of each sample was less than 1 cm^3, a hierarchical strategy in planning types of analyses was established, giving priority to radiocarbon ^{14}C dating and isotopic investigations ($\delta^{13}C$ and $\delta^{18}O$). Radiocarbon analyses were performed using the Accelerator Mass Spectrometry (AMS) with a 3 MV Tandetron-type accelerator (Mod. 4130HC by High Voltage Engineering Europa BV) whereas stable isotope values were acquired through DELTA V Plus by Thermo Scientific [26]. Both facilities are at the Centre for Applied Physics, Dating, and Diagnostics (CEDAD), University of Salento (Italy).

It is important to underline that the interpretation of radiocarbon data obtained on calcareous tufa is not straightforward due to the possible contribution of ^{14}C-depleted carbonate in the tufa formation. In other words, the ^{14}C concentration in the samples can be lower than the corresponding atmospheric level, resulting in ^{14}C ages older than the real ones. To correct this effect, the Dead Carbon Proportion (DCP), i.e., the proportion of ^{14}C-depleted carbon incorporated in the rock, must be measured. To do this, the ^{14}C concentration in a freshly deposited tufa layer and an organic sample embedded in it was measured. The difference between the two ages was then used to calculate DCP [27,28].

Only a few representative thin sections were made on larger-sized samples.

Nine samples of calcareous tufas analysed in this work come from Roman walls and more recent buildings of the historical centre of Urbino (with TRU labels; Table 1). TRU6 and TRU8 represent the original ashlars of the Roman fortification. In particular, TRU6 stands just over the outcrop of the *Marnoso Arenacea* Formation (Figure 2a–c) representing the bedrock upon which part of the historic centre of the city was built, whereas TRU8 was collected from an ashlar of a remnant of the southern defensive Roman dry walls in opus quadratum dating back to 3rd–2nd century BCE (Figure 2d–f). Other samples (TRU1, TRU2, TRU3, TRU5, and TRU7; Figure 3) are all ashlars originally installed in Roman times and reused, between the 14th and 16th centuries, mostly at the base of some younger historical buildings and on the external walls of the Fortezza Albornoz. The reuse of these spongy stones through time is highlighted by the fact that, independently from the period of installation, these stone lithotypes are all characterized by the size extensively characterizing the Roman period (59 × 59 or 59 × 74 cm) to build the defensive dry-stone walls (opus quadratum; [8]). TRU9 and TRU10, come from portals of two important oratories: Oratorio delle Grotte (Figure 4a–c) and Oratorio della Morte (Figure 4d,e), both decorated in the 17th century AD and attributed to the sculptor Bartolomeo Ammanati [29]. Based on the size of the spongy stones, the calcareous tufas of Oratorio della Morte seem to derive from the reuse of the Roman ashlars (Figure 4d,e). By contrast, the calcareous tufas of Oratorio delle Grotte are characterized by blocks of smaller and heterogeneous dimensions, as well as a wider range of size among the encrusted vegetal elements (Figure 4a–c), thus not suggesting the typical features of the original Roman ashlars.

Table 1. Summary of the investigated samples, radiocarbon ^{14}C ages, and isotopic data ($\delta^{13}C$ and $\delta^{18}O$) measurements.

	Samples	*Radiocarbon Age ^{14}C BP*	*DCP-Corrected Age ^{14}C BP **	*Calibrated ^{14}C Age (BP) ** (1σ)*	$\delta^{13}C$ (‰ *vs.* V-PDB)	$\delta^{18}O$ (‰ *vs.* V-PDB)
			Ashlars from defensive Roman walls (3rd–2nd century BCE)			
TRU6	Remnants at Corso Garibaldi	5600 ± 35	5385 ± 35	6185 ± 76	−9.87 −10.88	−9.89 −9.59
TRU8	Remnants at Palazzo Battiferri	8384 ± 45	8168 ± 45	9125 ± 79	−8.68 −8.66	−9.02 −7.75
			Reused Roman blocks in the historical palaces and fortress (14th–16th century AD)			
TRU1	Via San Girolamo	6469 ± 35	6253 ± 35	7173 ± 69	−5.76 −7.26	−6.99 −7.52
TRU2	Via San Girolamo	4731 ± 35	4516 ± 35	5167 ± 81	−9.26 −9.60	−9.21 −9.63
TRU3	Via San Girolamo	6785 ± 35	6570 ± 35	7478 ± 40	−10.24 −8.55	−9.72 −7.70
TRU5	Piola San Bartolo	7373 ± 35	7178 ± 35	7987 ± 34	−10.14 −9.20	−11.22 −10.15
TRU7	Fortezza Albornoz	4427 ± 35	4212 ± 35	4744 ± 68	−5.99 −4.32	−7.00 −6.62
			Portals (17th century AD)			
TRU9	Oratorio delle Grotte	1488 ± 35	1273 ± 35	1212 ± 49	−8.12 −8.69	−6.16 −7.56
TRU10	Oratorio della Morte	7278 ± 40	7064± 40	7890 ± 45	−8.84 −8.13	−8.31 −7.10

* ^{14}C age corrected for the Dead Carbon Proportion (DCP), see text for details. ** BP = Before the present assumed as 1950 CE.

Radiocarbon Measurements and Isotopic Analyses

The macro-contaminants present in the samples were identified by observation under an optical microscope and mechanically removed; afterward, the samples were treated with H_2O_2 to remove the most external layer. The extracted material was then subsequently converted into carbon dioxide by acid hydrolysis with H_3PO_4, and then reduced to graphite by reduction. Hydrogen was used as a reducing agent and iron powder as a catalyst. The amount of graphite extracted from the samples (>1 mg) was sufficient for an accurate experimental age determination. The radiocarbon concentration was determined by comparing the measured values of the ^{12}C and ^{13}C ion beam currents, and the ^{14}C counts with the values obtained from standard Sucrose C6 samples supplied by the International Atomic Energy Agency (IAEA). Conventional radiocarbon ages were corrected for isotope fractionation effects and machine and processing background. To correct the measured ages for isotopic fractionation, the $\delta^{13}C$ term was obtained from the beam currents measured with the AMS system, while the formulae reported in [30] were used. Correction for the background was carried out by analysing ^{14}C-free IAEA C1 standard (Carrara Marble) chemically processed in the same way as the samples. For the determination of the experimental error in the radiocarbon datings, both the scattering of the data around the average value and the statistical error resulting from the ^{14}C count were considered. The resulting conventional radiocarbon ages were corrected for the proportion of dead carbon and then converted into calendar ages (Table 1) by using the OxCal version 4.3 software, and the last internationally accepted calibration curve for atmospheric data [31]. The measured $\delta^{13}C$ and $\delta^{18}O$ values were normalized to the V-PDB (Vienna Pee Dee Belemnite) scale. IAEA 603 (calcite) and CO-8 standards were used for normalization. For each sample, two aliquots were extracted and analysed to obtain an estimation of the variability within each sample.

Figure 2. Remnants of defensive Roman walls which are present in the historical centre of the city (**a**–**f**). Places are located in Figure 1 and reported in Table 1 according to the label numbers (TRU). The wall reported in (**e**) at Palazzo Battiferri, is no longer visible due to renovations of the garden.

Figure 3. Blocks of calcareous tufas of the Roman period reused in some historical palaces (**a**–**f**) and Fortezza Albornoz (**g**,**h**). Places are located in Figure 1 and reported in Table 1 according to the label numbers (TRU).

Figure 4. The two important portals of the Oratorio delle Grotte (**a**–**c**) and Oratorio della Morte (**d**,**e**) where the calcareous tufas were employed as ornamental stone. Places are located in Figure 1 and reported in Table 1 according to the label numbers (TRU).

3. Results and Geological Insights on the Calcareous Tufas

3.1. General Features of the Samples

Macroscopically, the investigated spongy stones consist of freshwater calcite, mostly encrusting continental vegetation with very variable sizes of reeds, twigs, leaves, leaf impressions, and roots (from millimetric to decimetric in length). These phytohermal stones are characterized by an irregular framework of micropores and centimetric voids variably interconnected (Figures 2–4). Petrographic investigations on few thin sections (Nikon Opthipot2-Pol microscope; Figure 5a,b) show the presence of micritic calcite incrustations at places with a mosaic distribution of sparitic crystals of calcite (Figure 5a). The high presence of irregular voids is the main feature of this spongy stone characterized by a porosity ≥50%. A minor presence of clastic components such as quartz, feldspars, and rounded fragments of micritic bioclastic rocks was also detected. In some architectural structures, where calcareous tufas are present, we also performed a non-destructive test directly on the buildings, using the Schmidt hammer (L-type model with an impact energy of 0.735 Nm). This rebound hammer test, evaluating the apparent uniaxial compressive strength (indirect resistance, termed Qua), is also frequently used on stones installed in buildings [32]. The measurements carried out on the calcareous tufas show a Qua ranging from 33.4 to 45 MPa (Table 2) which can be considered values of moderate-strength stone [33]. Some physical features of calcareous tufas coming from both building stones and outcrops along the Metauro Valley (Canavaccio locality), reported by [8,10], show a dry unit weight (γ_d) between 1.14 and 1.68 Mg/m^3; a specific gravity (γ_s) of 2.69 Mg/m^3; and a porosity (n) ranging between 37 to 57%.

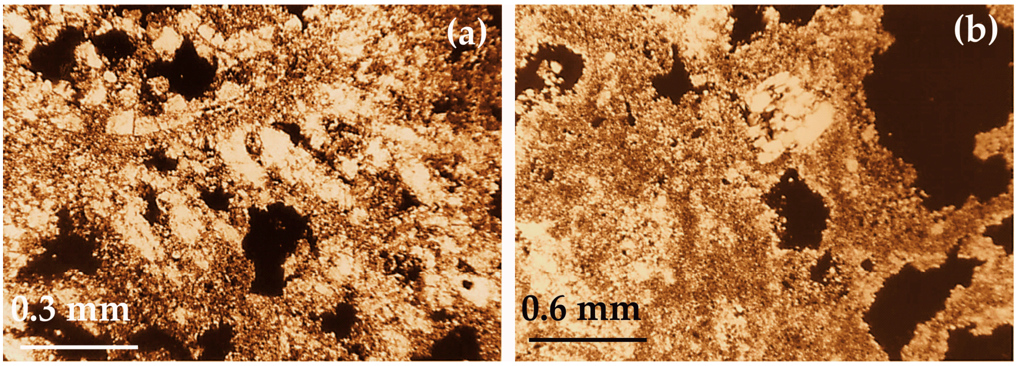

Figure 5. Representative microphotos under polarized light (crossed Nicols) of the studied calcareous tufas. (**a**) 100×; (**b**) 50×.

Table 2. Relation between the rebound index (Schmidt hammer) and apparent uniaxial compressive strength according to [34] (σc = 0.775 · R + 21.3).

Location	Rebound Index (R) *	Apparent Uniaxial Compressive Strength σc (Qua, MPa)*
Corso Garibaldi	15.6	33.4
San Girolamo	25.1	40.7
Piola San Bartolo	30.2	44.7
Fortezza Albornoz	20.7	37.4
Palazzo Peroli	22.0	38.3
Via Saffi	21.3	37.8
Oratorio delle Grotte	30.6	45
Oratorio della Morte	17.4	34.8

* Average values.

3.2. *Radiocarbon Datings and the Holocene Framewok*

For two paired and coeval carbonate and organic samples, a ^{14}C concentration of 0.9842 ± 0.0043 and 1.0109 ± 0.0041 was measured, respectively. As expected, the ^{14}C content of the organic fraction correspond to the current ^{14}C level in the atmosphere while the carbonate fraction appears depleted in ^{14}C due to the incorporation of ^{14}C-free carbonate. By these measurements, a DCP of 2.6% was estimated and used to correct all the other radiocarbon data. Radiocarbon dating reported in Table 1 show a geological age of the building stones of calcareous tufas spanning from 9125 ± 79 and 4744 ± 68 cal yr. BP, except for one sample (TRU9) which is younger (1212 ± 49 yr. BP). The oldest range of radiocarbon datings is in agreement with common Holocene ages of calcareous tufa dams available from Umbria (Central Italy) [35–37] and with the aggradation of calcareous tufa dams which started, in the Marche valleys, prior to 8260 ± 80 yr. BP along the Chienti River basin and continued, at least up to 4840 ± 65 yr. BP, in the Esino River basin [38]. There is a general agreement that there was an Early to Mid-Holocene calcareous tufa maximum and a major decline in site activity between 4000 and 2000 cal. yr. BP [6], mainly due to both the trend towards a dryer Mediterranean climate at the end of the Atlantic period and the anthropogenic factors. Dabkowsky [39], based on reviewing 62 calcareous tufa sites in Europe (comprising those from Italy), agrees that there is a general decline from ca. 5000 cal. yr. BP of these fluvial continental deposits after a maximum during the Atlantic climatic optimum, due to human impact on landscapes for the development of agricultural and land management practices (Bronze Age). Although the "late-Holocene calcareous tufa decline" became a paradigm (e.g., [40–43]), at least for spring-fed proximal or lacustrine calcareous tufas, reliable evidence of deposits developing until the present day is emphasized by several literature data [39,44–50].

3.3. δ13 C-δ^{18}O Data and the Physical–Chemical Constraints

Stable isotope data performed on the nine samples (Table 1) show variation ranges of δ^{13}C and δ^{18}O between −10.37 and −5.15 ‰ *vs.* V-PDB and −10.68 and −6.81 ‰ *vs.* V-PDB, respectively (Figure 6). Negative δ^{13}C and δ^{18}O values of all the analysed samples agree with the overall isotopic range of calcareous tufas. In fact, hydrothermal travertines stricto sensu are generally characterized worldwide by δ^{13}C positive values [13,16].

Stable isotope values of the calcareous tufa mainly derive from the composition of the spring water equilibrated with the isotopically light soil-derived CO_2 contained in the recharging meteoric waters. The typical range of δ^{13}C values in calcareous tufas is −11 to −5‰, reflecting the outgassing of the already-light ^{12}C of meteoric and soil derivation [42]. The preferential absorption of ^{12}C by vegetation through photosynthesis should play a minor role in the overall isotope carbon fractionation, distribution, and removal in the freshwater system [45,51,52]. The typical δ^{18}O values of calcareous tufas generally range from −12 to −3 ‰ vs. V-PDB, also reflecting the composition of the spring waters, directly linked to the local climatic regime and the local meteoric water line [53]. In this way, the overall negative values of the carbon and oxygen stable isotopes in the calcareous tufas are the result of the local meteoric and soil-derived karstic waters and a minor input of heavier recycled carbon (e.g., from the marine limestone bedrocks) with a negligible active involvement in the chemical biogenic precipitation of $CaCO_3$. By contrast, the values of the carbon and oxygen stable isotopes of travertines stricto sensu are much wider (and extending to the positive field of δ ^{13}C and δ^{18}O) than those of the calcareous tufas, likely reflecting the higher temperature of waters, higher depth of circulation and mixing between meteoric water, and CO_2-rich fluid of geothermal, volcanic, and/or metamorphic origin [16].

Vadour [54] and Goudie [55] emphasized a maximum calcareous tufa development in Europe and the Mediterranean region during the warm and humid Atlantic period (Holocene Atlantic climatic optimum; 7500 to 4600 cal. yr. BP) with a sharp decline by the start of the Sub-Atlantic period (2700 cal. yr. BP) which can be due to several factors. These authors cite changes in the precipitation discharge rate to be a major reason for the decline of calcareous tufas, coupled with changes in water chemistry driven by a decrease in carbonate contents within soils caused by postglacial leaching, deforestation, and consequent changes in nutrient availability. Many other studies (e.g., [56,57]) agree that calcareous tufa deposition was controlled by environmental factors and reached a maximum during warm and wet interglacial periods. Some other hypotheses such as variations in the atmospheric CO_2 concentrations controlling the rate of the calcareous tufa growth or the role of groundwater temperature on calcium carbonate dissolution within the aquifer have been also proposed [56,58].

Although the paradigm of "late-Holocene calcareous tufa decline" is consistent, concerning Central Italy, a wetter environmental trend is emphasized by δ^{18}O in speleothems from 1800 to 1200 yr. BP [59,60] and this could support a restart of the development of calcareous tufa growth in that period as well.

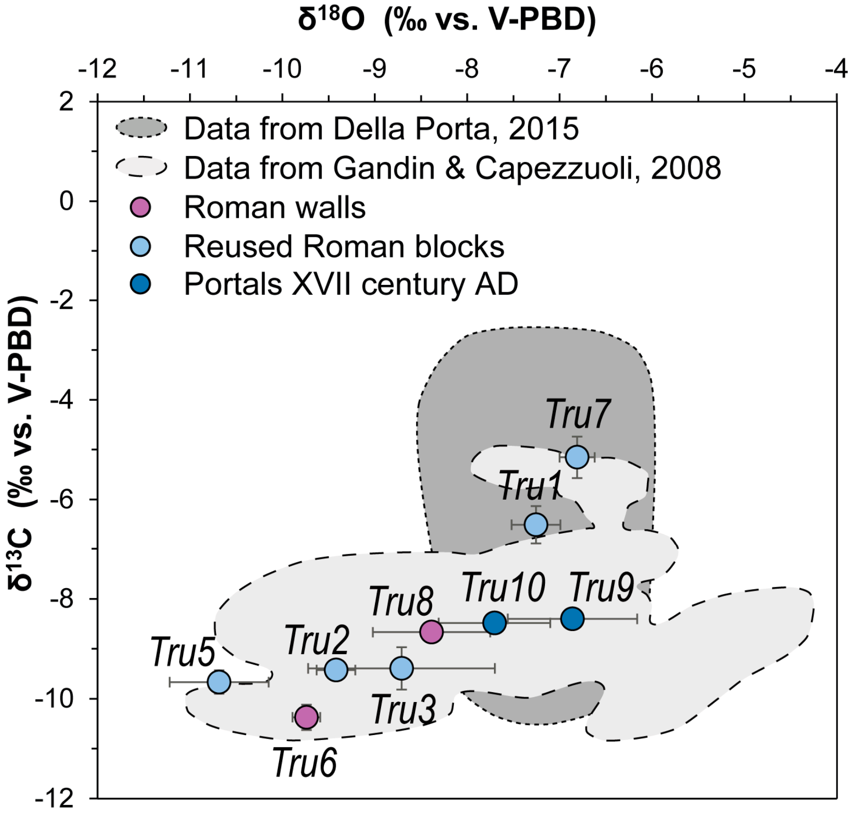

Figure 6. C vs. $\delta^{18}O$ (‰ vs. V-PDB) diagram of the analysed samples compared to literature data. The circles indicate the mean value of two measurements for the same sample; the bars indicate the isotopic variation represented by the two min–max values. The shape of the light grey field is due to the merging, in only one field, of different geographic areas (Spain, Westerhof, Dinaric area, Belgium, UK and Poland; [13]), whereas that of the dark grey field comes from the compositional variation of fluvial calcareous tufas [61].

4. Discussion on the Calcareous Tufa Stone Heritage

When visiting the UNESCO historical centre of Urbino, it is common to pay attention to the presence of carbonate stones with a spongy appearance. They are calcareous tufas used as ashlars, building and ornamental stones, and monumental portals of churches and oratories. Although they are very rich in voids (high porosity, between 37 to 57%), these calcareous tufas show good lithification, a specific gravity (γ_s) of 2.69 Mg/m^3, and an apparent uniaxial compressive strength (Qua) of 33.4 to 45 MPa, allowing architectural use. The roughness of the calcareous tufa surfaces should have been a feature that the Romans first appreciated to build defensive walls in *opus quadratum*, as highlighted by their use in Urbino in the dry-stone walls of the 3rd–2nd centuries BCE. Furthermore, the low dry unit weight (γ_d) between 1.1 and 1.7 Mg/m^3 of this spongy stone should have made transportation from the exploited areas easy and convenient.

Eight out of nine samples of calcareous tufas found as building and ornamental stones were geologically formed between 9125 ± 79 BP and 4744 ± 68 yr. BP, i.e., the main Holocene time interval of the development of calcareous tufa in Central Italy [35–38]. It should be very likely that these Holocene calcareous tufas, found in the Romans walls, were reused successively and occasionally, both as single blocks as restoration works in historical buildings or as ornamental stones in the Oratorio della Morte. By contrast, the radiocarbon dating of TRU9 at ca. 1200 yr. BP for the portal of Oratorio delle Grotte rules out the reuse of blocks from the Roman walls and some distinguishing features (smaller dimension of blocks, coarser vegetation elements; Figure 4a–c) agree with this inference. Although establishing the quarrying sites of the calcareous tufas of the historical centre of Urbino would be very speculative, it is worth noting that at about 8 km from Urbino (near the Canavaccio locality), an active deposition of calcareous tufas along the scarp between the 3rd-order fluvial terrace and the left bank of the Metauro River was reported [10]. Here, contact springs at the boundary between alluvial sediments and the underlying impermeable bedrock occur. The spring, located near the axis of a syncline structure (Figure 7), is fed by $CaCO_3$-oversaturated deep waters, uprising along a back-thrust structure [62,63] through the bedrock which is fractured because of the Middle Pleistocene extensional tectonics phase [64].

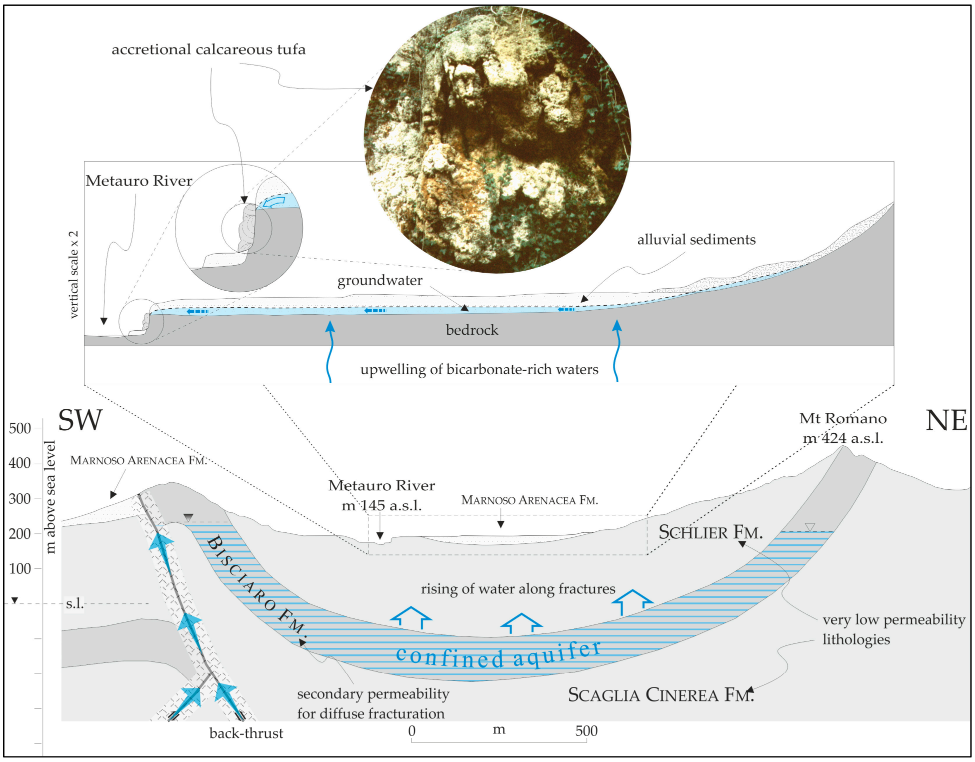

Figure 7. Sketch showing the local geological and hydrogeological conditions leading to present-day calcareous tufas formation along the Metauro Valley, near Canavaccio (modified from [10]).

In this area, a settlement dating back to the Roman period and very close to the via Consolare Flaminia, was found, also emphasizing the presence of different types of furnaces attesting to an intense production of bricks [65]. In addition, on the geomorphological fluvial terrace, very close to the present-day deposition of the perched springline calcareous tufas (Figure 7), an abandoned house (probably from the 19th–20th centuries) was mostly built using squared blocks of this lithotype. A clear relationship between the building stones used in the above rural house and the adjacent perched springline calcareous tufas can be inferred. Moreover, in the walls of the Santa Barbara church (from the end of the 12th to 14th century), about 2 km from the perched springline outcrops of the calcareous tufa described above, spongy stones are widely used (Figure 8). Unfortunately, the dense vegetation and the bad exposure of the calcareous tufas along the scarp of the fluvial terrace of the Metauro River prevented a stratigraphic sampling that needs to be planned in detail for the complex logistics. However, work is still in progress on these outcrops of calcareous tufas (at only 8 km from Urbino) which can be considered good candidates to test the provenance of the carbonate spongy stones found in the UNESCO historical centre.

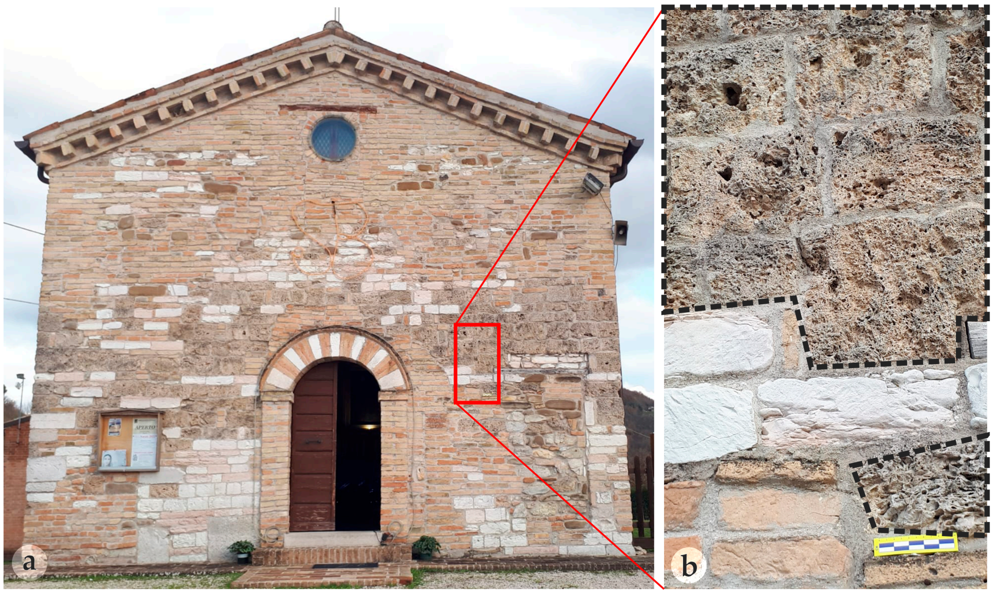

Figure 8. (**a**) Santa Barbara church (from the end of 12th to 14th century) partially built using calcareous tufas highlighted in the inset (**b**).

5. Summary and Conclusions

The physical features and stable isotope data (all negative values of $\delta^{13}C$ and $\delta^{18}O$) of the investigated spongy stones definitively prove their geological origin as calcareous tufas and not hydrothermal travertines. Eight out of nine samples, dated with radiocarbon between ca. 9100 and 4700 yr. BP closely match the Holocene Atlantic climatic optimum, coincident with the maximum growth rates of the calcareous tufas in the Mediterranean regions and northern Europe [66]. These calcareous tufas are so peculiar that they were reported as spongy stones by famous historians and scientists such as Bernardino Baldi and Francesco Rodolico. They were used since the Romans (along with bricks and other sedimentary rocks) in the dry walls in opus quadratum dating back to the 3rd–2nd century BCE. All the calcareous tufas in the historical centre of Urbino represent reused blocks and ashlars from the Roman walls, except those used in the Oratorio delle Grotte, dated at 1200 yr. BP, which are characterized by blocks of different dimensions and very heterogeneous sizes of encrusted vegetal elements. It is worth noting that the calcareous tufas, used since the foundation of the city of Urbino, can be defined as a moderate-strength stone [33], characterized by high and variable porosity. This study contributed to the cultural heritage (stone) valorisation of the UNESCO historical centre of Urbino using the correct petrographic classification and unravelling the geological origin of such a peculiar building and ornamental stone. Calcareous tufas are lithologically different from the other carbonate stones used in the Urbino historical centre but share with them challenges in planning conservation strategies, being potentially involved in the colonization of bacteria and formation of black crusts. The provenance of the investigated calcareous tufas from the Marche or Umbria regions is very likely, but establishing the precise quarrying sites could be a speculative effort at the moment because of the lack of a geochemical or textural fingerprint of the calcareous tufas from different Central Italy outcrops. Perched springline calcareous tufas near Urbino, along the Metauro Valley, are, however, under investigation, representing good candidates as source areas.

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