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Mineralogical Analysis of Viterbo Tuff Using X-Ray Diffraction and Raman Spectroscopy

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***Abstract* – This study investigates "Tufo di Viterbo", a natural stone of significant interest in the cultural heritage field widely appreciated as a building material. The mineral composition and crystalline microstructures of Viterbo Tuff were analyzed using X-ray Diffraction (XRD) and Micro-Raman scattering (MRS) techniques. This work provides valuable information that could be helpful for the artistic heritage preservation and environmental science communities, potentially enabling the formulation of enhanced strategies for extending the durability of this important natural resource. Additionally, the comprehensive mineralogical analysis of "Tufo di Viterbo" can provide instrumental evidence supporting or corroborating its natural radioactivity levels, thereby enhancing our knowledge of its geological and environmental significance. This research was carried out as part of the PRIN 2022 PNRR ATHENA project, funded by the European Union through the Next Generation EU initiative.**

I. INTRODUCTION

For centuries, the "Tufo di Viterbo" (hereafter, VT), a distinctive volcanic rock, has played an important role in shaping the architectural and artistic identity of Central Italy, notably within the province of Viterbo and the broader Lazio region. Its relative ease of extraction, workability, and light coloration have facilitated its extensive utilization in historical edifices, defensive structures, religious monuments and ornamental features [1].

Beyond its visual appeal and structural properties, the inherent porosity and thermal insulation characteristics of VT have historically rendered it a practical and locally sourced construction material.

Despite its pervasive applications and historical significance, a comprehensive understanding of Viterbo tuff's mineralogical composition and microstructure remains incomplete. Therefore, acquiring further knowledge in this domain is essential for the development of effective conservation strategies, particularly considering ongoing environmental degradation, weathering processes and the long-term effects of exposure [2-3].

Furthermore, the detailed characterization of its intrinsic properties is essential for assessing its natural radioactivity levels, a noteworthy consideration for both public safety and the preservation of cultural heritage [4].

To address these knowledge gaps, this study employs non-invasive analytical methodologies, specifically X-ray diffraction and micro-Raman spectroscopy, to investigate the mineralogical composition and microstructural features of VT. XRD and MRS analyses yield valuable data that can inform conservation efforts, assess the durability of construction materials, and support the sustainable preservation of the region's architectural heritage [5-6].

II. MATERIALS AND METHODS

A. Geological Framework

The pyroclastic deposit commonly referred to as "VT" – also known as ignimbrite C or locally as "red tuff and black scoria"– is part of the Sutri Formation (see fig.1) and is particularly rich in zeolitic minerals such as phillipsite and chabazite. This lithofacies is primarily linked to explosive eruptions from the Vico Volcano, a key volcanic center within the Roman Comagmatic Province (RCP), a NW–SE trending alignment of ultrapotassic volcanic districts and monogenetic centers that have developed along the Tyrrhenian margin of central Italy since the Middle Pleistocene [7]. The formation of the VT is part of the broader volcanic evolution of the Lazio region, which was shaped by the activity of several major centers, including the Vico Volcano to the south, the Cimino Volcanic Complex to the east and the Vulsini District to the northwest.

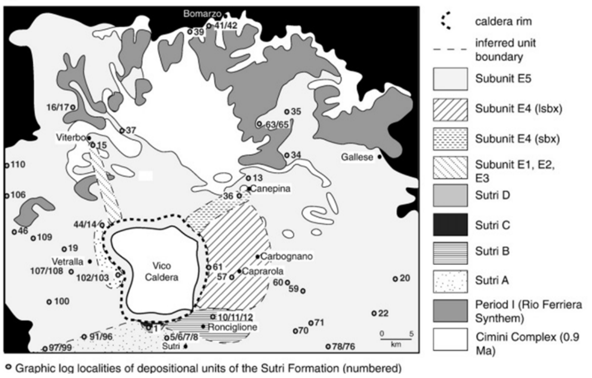

Figure 1. Geological map of the Sutri Formation (151 ka) indicating the regional distribution of depositional units A–E and exposed older volcanic and sedimentary rocks, from [8].

These centers were active during the Pleistocene and produced a wide range of pyroclastic materials –ash, lapilli and pumice– that accumulated and lithified into extensive ignimbritic deposits. The physical and mineralogical features of the VT, including its colour variability, porosity and zeolite content, reflect the nature of the eruptive sources, magma composition and depositional environments [9]. Among the most significant contributors was the Vico Volcano (active between ~500 and 90 ka), which produced voluminous ignimbrites such as the zeolite-rich Tufo Rosso a Scorie Nere [10]. The older Cimino Volcanic Complex (active from ~1.35 to 0.8 Ma) generated lithologies commonly known as Peperino [11], while the Vulsini District (active from ~0.8 Ma into historical times) added further pyroclastic sequences [12]. The VT represents a complex volcaniclastic unit shaped by successive eruptive phases and multiple source areas. Its stratigraphy often shows distinct layering and clast inclusions indicative of different eruption dynamics. Furthermore, post-depositional processes such as weathering, hydrothermal alteration, and pervasive zeolitization have significantly modified its original properties, enhancing its mineralogical complexity and influencing its geotechnical behavior [1].

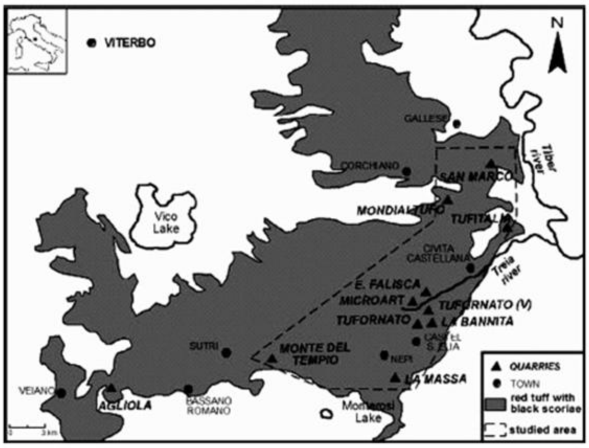

Figure 2. Map of quarries distribution [13].

B X-Ray Diffraction

X-ray diffraction (XRD) analyses were performed using a PANalytical Empyrean Diffractometer, employing Cu Kα radiation and a Bragg–Brentano (θ–θ) goniometer equipped with a solid-state PIXcel detector. For the XRD analysis, approximately 1 g of finely powdered sample was used. Data were acquired at 40 kV and 40 mA with XRD patterns recorded from 2° to 70° (2θ range) using a step size of 0.026° and a counting time of 20 seconds per step. Raw data were processed with software to remove the Cu $K\alpha_2$ component and a digital filter was applied for background correction. The identified peak positions were then compared to the ICDD JCPDS database to determine the crystalline mineral phases present in the analyzed samples.

C. Micro-Raman Scattering

Micro-Raman spectroscopic analyses were conducted using a portable "BTR111MiniRam™" spectrometer (BW&TEK Inc). The instrument employs a 785 nm diode laser as the excitation source and incorporates a thermoelectric cooled charge-coupled device (CCD) detector for signal acquisition. A BAC151B Raman microscope was integrated with the system, and the laser beam was focused onto the sample surface through a 40× or 80× objective lens, resulting in a working distance of

3.98 mm and a laser spot size of 50 or 25 µm, respectively. A maximum laser power of approximately 90 mW was delivered to the samples. Spectra were recorded within a wavenumber range of 60 to 3150 cm^{-1}, with an acquisition time of 10 s and a spectral resolution of 8 cm^{-1}. To enhance the signal-to-noise ratio, 18 spectral scans were accumulated for each measurement. Instrument performance was optimized and verified through a calibration procedure performed prior to each measurement, utilizing the characteristic Raman band of a silicon chip at 520.6 cm^{-1}.

III. RESULTS AND DISCUSSION

Figure 3 shows the XRD pattern of VT, revealing the presence of several crystalline phases: chabazite (Cbz), calcite (Clt), and sanidine (Snd) (see Figure 3) [13-17].

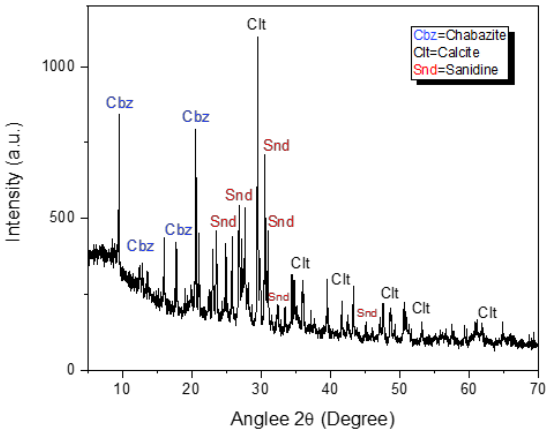

Figure 3. XRD pattern of the Viterbo Tuff sample, illustrating the crystalline identified phases. The prominent peaks indicate the presence of chabazite (Cbz), calcite (Clt) and sanidine (Snd), as labeled.

Chabazite exhibits peaks at 2θ=9.4°, 13.8°, 16.0°, 17.7°, 20.7°, calcite at 2θ=29.4°, 35.9°, 39.5°, 43.0°, 47.5°, 48.5°, 57.0°, 61.0° and sanidine at 2θ=23.4°, 27.2°, 30.5° 32°, 34.1°, 46°. The sharpness of these peaks indicates that the minerals are well-crystallized and show minimal signs of weathering or alteration. Such a mineralogical composition is typical of volcanic tuffs, formed from consolidated volcanic ash.

The identified mineral phases –chabazite, calcite and sanidine– suggest a formation history involving volcanic activity and secondary hydrothermal processes.

Chabazite, a zeolite mineral indicative of secondary alterations and potential radionuclide adsorption, is particularly known for its capacity to contain trace amounts of natural radionuclides, such as uranium and thorium [18-19], thus serving as a key factor in the tuff's natural radioactivity.

Calcite, a carbonate mineral, indicates the presence of calcium, while sanidine, a feldspar, denotes the feldspathic nature of the tuff.

Calcite and sanidine also contribute to the overall radioactivity levels due to their potential to incorporate trace amounts of these elements within their crystal structures. As confirmed by the XRD analysis, the mineralogical composition indicates a complex history involving both primary volcanic processes and secondary hydrothermal alterations. These findings are essential for understanding the formation and evolution of the VT as well as for assessing its potential uses in construction and other applications where natural radionuclide levels must be evaluated.

XRD analysis confirms that the VT sample contains chabazite, calcite and sanidine. These well-crystallized minerals suggest the sample is of high purity, with notable implications for natural radionuclide content. This composition enhances our knowledge of the tuff's geological history and supports its application in various geological and practical fields.

Figure 4 displays the micro-Raman spectrum of the VT, revealing the presence of calcite, evidenced by a noticeable peak at ~ 1084 cm^{-1} [19], along with small features at ~ 277 cm^{-1}, all related to the most stable polymorph of calcium carbonate ($CaCO_3$).

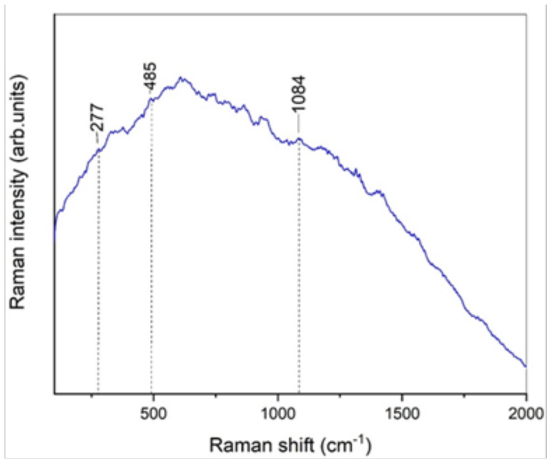

Figure 4. Representative micro-Raman spectrum of the Viterbo Tuff.

In particular, the band at ~ 277 cm^{-1} can be attributed to lattice vibrations involving translations and rotations of the carbonate groups within the crystal lattice. Instead, the feature falling at ~ 1084 cm^{-1} can be associated with the ν1-symmetric CO_3 stretching. In addition, the presence of Chabazite group zeolites is revealed by the observation of the peak at ~ 485 cm^{-1} and this band is attributed to vibration of the Si-O-Si, Si-O-Al and Al-O-Si bonds [9]. In this case, MRS results are in good agreement with the XRD findings.

IV. CONCLUSIONS

Based on the results of our comprehensive X-ray diffraction (XRD) and micro-Raman spectroscopy analysis, this study provides significant insights into the properties of VT. Our key findings can be summarized as follows: (I) The identification of chabazite, calcite, and sanidine as the main crystalline phases offers a fundamental understanding of VT's composition and its formation history, which is influenced by volcanic and hydrothermal processes. (II) The presence of chabazite, a known host for natural radionuclides, coupled with the potential for trace radioactive elements within the calcite and sanidine structures, highlights the crucial need to consider the tuff's natural radioactivity levels in future applications. (III) Ultimately, this detailed mineralogical and molecular characterization provides valuable information for researchers aiming to enhance the durability of VT, ensuring its long-term preservation as an integral component of Italy's cultural and architectural heritage.

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