SOLUTION AND PRACTICE

CHAPTER 17

INNOVATIVE, MULTIDISCIPLINARY APPROACH FOR RESTORING PAINTINGS IN HYPOGEAL ENVIRONMENT: ETRUSCAN *TOMBA DEGLI SCUDI* (4TH CENTURY BC) IN TARQUINIA

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Abstract

The Tomba degli Scudi, an important Etruscan hypogeum from the 4th-century BC, is situated in the Monterozzi necropolis of Tarquinia, Italy, and it is acknowledged as a UNESCO heritage site since 2004. The restoration of its mural paintings epitomizes an exemplary interdisciplinary collaboration, encompassing restorers, archaeologists, and scientists. As we embarked upon the restoration, collaborative discussions precipitated significant revelations in conservation, archaeology, and biology. This collaboration elucidated the conservation history, the unique execution technique, and thorough examinations of environmental parameters. The inaugural phase of this initiative was generously financed by Fondo per l'Ambiente Italiano, the Italian Environment Fund, and the Soprintendenza Archeologia, Belle Arti e Paesaggio per l'Area metropolitana di Roma, la provincia di Viterbo e l'Etruria meridionale, focusing on the atrium murals. Subsequently, murals in the sepulchral chamber were rehabilitated. Given the distinct nature of the hypogeal environment, the methodologies and material selection demand meticulous consideration, ensuring alignment with pre-Roman mural traditions in the Italic region. Simultaneously, an exhaustive historiographic assessment furnished comprehensive insights into the conservation history of the hypogeum. Rigorous analysis and restoration accuracy led to a groundbreaking revelation-depictions of human entities used modular templates for individual body components, most potentially crafted from sturdy materials. These templates, which manifested in four scales, corresponded to the hierarchical status of the depicted characters. Historically, the employment of such modular templates, termed *patroni* and *antibola*, was recognized exclusively from the early Middle Ages onward in the western and eastern art traditions, because no prior evidence of this painting modality existed. Consequently, this discovery infers that the inception of this technique predates prior assumptions by approximately a millennium, thereby refining our understanding of technological transitions from Classical Antiquity to the Middle Ages. An important and innovative aspect of this project resides in the exhaustive microbiological examination. Although the Tarquin hypogea had been intermittently probed during preceding restoration efforts, the bacterial and fungal communities, which sustain a nuanced and fragile equilibrium within these environments, had not been rigorously and holistically studied. In this endeavor, a microbiological assessment was executed before, during, and post the restoration stages. The outcomes were compared against data from other hypogea, transforming the Necropolis tombs into genuine scientific research hubs. Notably, the biological examination of the white biological deposit in the paintings was identified as moonmilk, which is an exceptional microbial-derived calcite that conserved the murals instead of impairing them. However, several preservation challenges emerged, especially regarding post-restoration disinfestation practices. Thus, a targeted study of bacterial communities yielded novel insights, heralding a new conservation approach. Concurrently, a pioneering method integrating ultraviolet fluorescence with 3D techniques was deployed. An essential dimension of the project was investigating the interplay between the preparatory strata of the paintings and the pictorial film. This discourse precipitated intriguing procedural decisions, proffering a foundation for subsequent deliberations on pictorial integration in archaeological settings.

Keywords: Restoration, Tomb, Hypogea, Etruscan, Mural Painting, Preparatory Drawing, Biodegradation, Diagnostics, 3D model, Karst phenomena

1. Introduction

The outcomes of the extensive restoration work that recovered the precious Etruscan murals from the 4th-century B.C. are discussed in this section. Rigorous experimental undertakings yielded revelations that recalibrated the conservation strategies for hypogeal settings and changed our understanding of the Etruscan mural techniques applied during its creation in the 4th century BC. The tomb under study is a distinguished Etruscan hypogeum within Tarquinia's Monterozzi necropolis, recognized as a UNESCO heritage site since 2004. As of March 2022, the site has transitioned under the aegis of the nascent Archaeological Park of Cerveteri e Tarquinia (Fig. 1a–d). Geographically, these cities align with the ancient Etruscan territories of *Caere* and *Tarchna*, nestled north of Rome, proximate to the western coastline of central Italy. Tarquinia's vast necropolis houses 6,000 rock-hewn graves, among which 200 contain painted depictions, reflecting a temporal expanse of six centuries from the 7th to the 2nd Century BC (Steingraber, 1984; 2006; Marzullo, 2017).



Figure 1. a. Necropolis of Cerveteri; b. Necropolis of Tarquinia; c. Cerveteri, *Tomba dei Riliev*i; d. Tarquinia, *Tomba della Caccia e della Pesca*.

Since the late 1980s, these painted tombs have been hermetically sealed and equipped with thermally insulating portals to maintain the requisite thermohygrometric conditions crucial for their preservation (Fig. 2 a, b). Additionally, these doors feature an antifog mechanism, enabling visitors to observe the paintings unobstructed.



Figure 2. Examples of thermally insulating doors: earliest prototypes installed (a) most recent type (b): equipped with full glass.

Temperature fluctuations—along with alterations in humidity—pose considerable threats, which are attributed to surface dehydration and internal crystallization of soluble salts. This pertains to the foundational layer, preparatory sections, and the mural facets of rock. Restricting visitor access further safeguards against inadvertent microbial introductions. Maintenance activities, executed at regular intervals, involve minimal personnel donned in protective Tyvek[®] attire, minimizing their duration within the hypogeum.

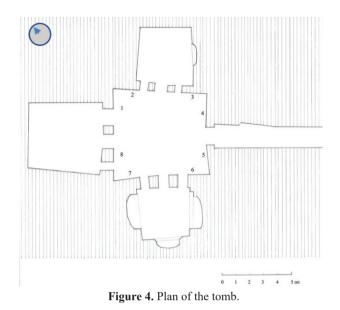
The restoration endeavor was initiated in June 2016. Spearheaded by the *Soprintendenza Archeologia, Belle Arti e Paesaggio per l'Area metropolitana di Roma, la provincia di Viter- bo e l'Etruria meridionale* (the Office of the Ministry of Culture in charge for the protection and management of the site before the creation of the Archaeological Park) with a valuable contribution from the FAI (*Fondo Ambiente Italiano*), promoted the restoration of the walls in the *atrium* of the tomb (Fig. 3).



Figure 3. Tomba degli Scudi. South-east walls: before restoration (left) and after restoration (right).

2. Execution technique

The *Tomba degli Scudi*, attributed to the late Classic era (circa 340 BC), was unearthed in 1870. Notably, it remains inaccessible to the public, given its location beyond the designated visitor area of the Monterozzi necropolis. The tomb entrance is facilitated *via* an elongated dromos that converges at the central *atrium*. Positioned 10 m subterranean, the architectural design of the tomb is similar to that of a typical Etruscan domicile. A central *atrium*, equipped with a dual-incline roof and supported by a *columen*, serves as an ingress to three additional chambers of irregular quadrangular configurations. These burial chambers communicate with the *atrium* through a primary doorway flanked by twin windows (Fig. 4). Among these chambers, both the *atrium* and the primary burial section are adorned with plaster and are further embellished with mural depictions, with the ceiling of the *atrium* being ornate as well.



These illustrative renderings display significant exemplars of the figurative motifs characteristic of grand aristocratic tombs of that epoch. These artworks extol the stature and virtues of the *Velcha* lineage, encapsulating the pivotal moment when the departed embarks on their ethereal voyage to the netherworld, epitomized by a symbolic funeral banquet encompassing the entire familial clan (Maggiani, 2015). The art conservation endeavor within the *Tomba degli Scudi* transpired in dual stages. The inaugural phase coincided with interventions in the *atrium*, elucidating the foundational artistic methodology and the pivotal technique of transcribing preparatory sketches onto walls. The subsequent stage accentuated correlations

2.1. Preparatory layers

with the concurrent milieu of pre-Roman Italic mural artistry.

The hypogeum was excavated by ancient Etruscans in a type of hybrid sandstone, termed *sabbione*. This material is devoid of adhesive cement and is solidified only through water and compression (Cirigliano *et al.*, 2021), which renders it friable and thereby simplifying excavation. Within the *atrium* and the primary burial chamber, the plaster was applied onto the rock surfaces, both on walls and ceilings, to render them uniform. The density of the plaster oscillated between 0.5 and 3 cm, with the ceiling of the burial chamber exhibiting a less refined finish. This plaster was composed of lime and *macco*, which is a porous and brittle,

coarsely milled, pale-yellow calcarenite. Macco's prevalence in Tarquinia's tombs underscores its recognition and preference among artisans. It apparently supplanted sand, which is the byproduct of hypogeum excavation. This plaster façade received an overlay of white lime, discernible against the background of the murals and in the portrayal of female forms (Fig. 5).



Figure 5. Couple *Velthur Velcha* and *Ravnthu Aprtnai*, detail of the North-west wall in the *atrium*. Lime covering plaster is used as the color of background and female complexion.

In various chambers, the layers exhibited divergent thicknesses—more robust and applied with expansive brush strokes in the *atrium*, yet more slender within the Burial chamber. Despite its consistency and the lack of visible fine cracks, subsequent analysis on certain samples (utilizing gas chromatography—mass spectrometry; GC—MS) disclosed an absence of organic additives (refer to Chapter 5). Microscopic evaluations on the TSP8 sample from the *atrium* (Fig. 6 a and b) revealed the stratified coatings, commencing from the plaster—distinguished by its granular texture and the *macco*-induced yellow hue—succeeded by a streamlined, cohesive layer of white wash and the overlying paint film.

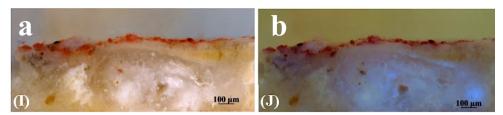


Figure 6. Microphotographs of cross-sections at 100× magnification under (a) visible and (b) UV radiation; *atrium*, north-west wall, flesh tone of the arm of *Vel Velcha*.

Historically, Etruscan mural renditions predominantly employed the *secco* method until the mid-4th century BC when the *fresco* technique was introduced. Herein, pigments, devoid of mediums or binders, were dissolved in water and layered atop a base composed of varied clays, occasionally integrated with a distinct limestone (Cecchini, 2012; pp. 159–183). The advent of lime in painting is traced back to the 5th century BC, serving primarily for crafting plasters of fluctuating thickness to standardize the foundational rock. However, during the latter half of the 5th century, lime facilitated the creation of a plaster substrate whereupon color was still applied using the *secco* method. The preservation state of these artworks attests to the rudimentary nature of this technique, perhaps representing an initial, albeit subpar, and endeavor to mimic Greek *fresco* painting technique. Since the 4th century, a preliminary layer, now forged from lime, re-emerged.

The *Tomba degli Scudi* belongs to this category; it diverges from the traditional *fresco* classification, given that the pigment adorns an already desiccated and superficially carbonated lime layer.

Although certain examples of Apulian and Lucan rock painting exhibit an earlier comprehension of Greek artistic methodologies—potentially due to their direct interactions with Greek settlements in Taranto and Paestum—in Etruria, there appears to be a more tenacious adherence to age-old techniques (Brécoulaki, 2001; Porcelli, 2021). Moreover, the methodology employed in the tombs of the 3rd century BC, including the *Tomba dell'Orco II* (latter half of the 4th century BC)—often perceived as *fresco* artistry—warrants reevaluation in light of the presence of a lime layer.

2.2. Preparatory drawing transposition technique

During the restoration of the *atrium* walls, spanning from June 2016 to December 2018, investigations delved into the techniques employed by ancient Etruscans to transpose preparatory sketches onto walls. These inquiries sought traces of methodologies previously identified

in tombs from the corresponding era, specifically any engraved marks or drawings. However, examination of the decorated surfaces within the Burial Chamber of the Shields unveiled no engraved inscriptions on the plaster. Instead, there existed a faint brush-drawn depiction utilizing a diluted red ochre.

Upon analysis, a consistent pattern among the portrayed forms in the atrium's painting was observed. Detailed examinations exposed a unique method for the transference of the preparatory layer, incorporating repetitive silhouettes or templates across various figures. Such technical augmentations have been extensively documented in Etruscan mural artistry since the 7th century BC, primarily for crafting intricate geometric or naturalistic decorative elements. Illustrative instances of these "lesser images" (Vlad Borrelli, 1991) encompass the ducks depicted in Veio's eponymous tomb, avian figures amidst garlands and ducks in the *Tomb del Cacciatore*, dolphins, and the wave *motif* in both the *Tomba della Scimmia* and *Tomba delle Leonesse*, respectively. The motifs discerned in the *Tomba della Scimmia* and *Tomba François* were assembled utilizing entire figures and occasionally inverted silhouettes (Bianchi Bandinelli, 1939).

In case of the *Tomba degli Scudi*, the investigation culminated in a remarkable revelation: the portrayal of human entities was achieved through templates representing individual anatomical sections. The impeccable alignment of extremities, torsos, and crania was demonstrated post the digital rectification of mural images using a prevalent photo-editing software, Photoshop (Fig. 7). Initially, our strategy explored the contours of primary figures onto transparent tracing paper, with the endeavor unfolding directly on the murals on-site. However, owing to the delicate state of the original plaster, this methodology was deemed untenable. As an alternative, digital images were comparatively evaluated on a computer interface. Captured using a full-frame Reflex camera, these high-resolution images were snapped with the camera positioned equidistant from the wall. To simulate an authentic digital workspace, the dimensions of the murals were meticulously measured and verified in situ. Subsequent image scaling and rectification were accomplished employing Adobe Photoshop CS6.

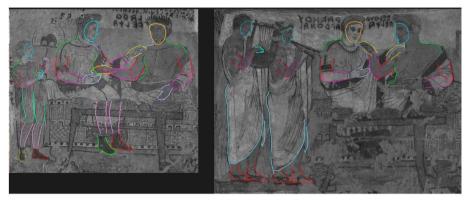


Figure 7. Left: panel 1; right: panel 2 (refer to plan p. 5). Each template of the paintings is visualized in one color.

The research underscored the likelihood that such templates were crafted from a rigid material, with each template presenting four distinct sizes. These variations reflected the hierarchical exploration of the depicted individuals (Tomassetti, Arrighi, 2019). The concept of templates, compartmentalized into individual anatomical components and tailored to illustrate varied postures, was an unprecedented finding. Historically, the deployment of modular stencils, termed *patroni* and *antibola*, has been attributed exclusively for paintings from the early middle ages onward, evident in both western and eastern artistic traditions. No antecedent instances of such an approach were documented. This revelation propels the inception of modular design techniques back by approximately a millennium, refining our comprehension of artistic methodologies traversing from Classical Antiquity through the Middle Ages (Andaloro, 2002). This discovery subsequently charts a renewed trajectory for understanding the transference techniques of preliminary sketches in Etruscan mural art. Additionally, the findings indicate a correlation with medieval practices, where template dimensions were modulated to dictate hierarchical distinctions among the illustrated subjects. Each anatomical component manifested in four scales: a standard size representing the Velcha lineage; a 65% reduction for servants, winged entities, and the custodian of the sella curulis; a 75% diminution for musicians; and an enlargement to 113% for the Velthur-Ravnthu pair (Fig. 8). This rigid hierarchical order was consistently maintained (Table 1).



Figure 8. Different percentages scaling in servants, musicians, Velcha's family and ancestors.

Table 1. Template sizes: at 100% for the <i>Velcha</i> family members, reduced to 65% for servants, reduced to 75% for musicians and increased to 113% for ancestors.				
Body Parts	Standard Size 100% (height x width)	Reduced To 65%	Reduced To 75%	Increased To 113%
Three-quarter face	15×10 cm	9.75 × 6.5 cm	11.25 × 7.5 cm	16.9 × 11.3 cm
Profile face	15 × 7.5 cm	9.75 × 4.9 cm	11.25 × 5.6 cm	16.9 × 8.5 cm
Shoulder A	10 cm	6.5 cm	7.5 cm	11.3 cm
Shoulder B	15 cm	9.75 cm	11.25 cm	16.9 cm
Chest profile	20 cm	13 cm		×
Forearm	15 × 7.5 cm	9.75 × 4.9 cm	11.25 × 5.6 cm	16.9 × 8.5 cm
Arm	20×7.5 cm	13 × 4.9 cm	15 × 5.6 cm	22.6 × 8.5 cm
Frontal hand	12.5 × 7.5 cm			
In profile hand	$12.5 \times 5 \text{ cm}$			14 × 5.6 cm
Clenched hand	10 × 7.5 cm	6.5 × 4.9 cm	7.5 × 5.6 cm	11.3 × 8.5 cm
Thigh		20 × 7.5 cm		
Calf	24 × 7.5 cm	15 × 4.9 cm		
Frontal foot	10×7.5 cm	6.5 × 4.9 cm		11.3 cm × 8.5 cm
Three-quarter foot	12.5 × 7.5 cm			
In profile foot	15×10 cm	9.75 × 6.5 cm	11.25 × 7.5 cm	16.95 × 11.3 cm
Players tunic	55 × 25 cm			
Bùccina	50 cm (diameter) 4 cm (width)			
Lituus	75 cm			

The strategic utilization of these modular templates, albeit subtly discernible, was efficacious. It facilitated expeditious sketching whilst ensuring consistent imagery. Such a method empowered artisans to meticulously calibrate character proportions, with the varied limb orientations camouflaging this systematic approach. The asymmetrical arrangement of figures within the *Tomba degli Scudi* can be attributed to the artist's intent to preserve the impeccable architectural symmetry of the *atrium* (Maggiani, 2005). Distinctive template sizes also supported the intentional representation of characters based on their societal standing. Thus, servants were portrayed as subordinate to their superiors, whereas the ancestral duo of Velthur–Ravnthu was accentuated, ensuring their immediate recognition as more eminent than their progeny—a result achieved by amplifying their dimensions.

2.3. Pictorial layer

The pictorial layer is characterized by the predominant employment of a select assortment of inorganic mineral pigments, encompassing yellow and red ochre, massicot, smoke black, and lime white. From this palette, a spectrum of red, pink, and purple shades was derived (refer to Chapter 5). In certain regions, the pigment layer is denser and more robust, whereas in others, it manifests in such a fluid manner that it culminates in conspicuous, elongated drips. This disparity is primarily attributed to the frequent amalgamation of pigments with lime, especially evident in the paintings of *atrium* and more pronounced in the depiction of complexions. The integration of lime is not guided by any technical intent linked to a purposeful carbonation process; thus, it does not conform to a deliberate pittura alla calce technique. Instead, hydrated lime functions as a pigment additive to soften ochre hues, facilitating the generation of various pink gradations. Similarly, it contributes to crafting the light-blue backdrop behind the figures when blended with vegetable black. One can discern the pigment thickness and the *ductus* of the brush strokes, particularly in the complexions, distinguishing it from the foundational preparatory layer. Conversely, in the Burial Chamber, the pigment appears more diffuse. Examination of the cross-sectional samples (TSP-7 and TSP-2), detailed in the laboratory analysis segment of Chapter 5, highlights a clear demarcation between the paint and lime preparatory layers, demonstrating the application of the secco method (Fig. 9). Given the ambient conditions, a prominent re-carbonation layer overlays the paint film, ensuring the preservation of pigments that are only solubilized in water, devoid of any calcium hydroxide mixture.



Figure 9. Left: *Atrium*, the brushstrokes of the whitewash and the pictorial layer are well-visible under raking light. Right: detail of the same wall.

3. State of preservation

The Tomba degli Scudi is a hypogeum situated 8 meters beneath the surface, carved into a hybrid sandstone known as *sabbione*. This configuration renders it a nearly isolated, confined system. Preservation conditions within such distinctive environments vary and are highly site-specific. Predominantly, humidity and temperature emerge as critical determinants influencing decay, as they dictate salt migration and karstic processes as well as govern the growth of particular microorganisms. Thermohygrometric readings were captured during the atrium restoration and subsequently during the Burial Chamber's refurbishment. These measurements, taken across varied seasons (atrium during spring and summer, Burial Chamber in autumn and winter), consistently indicated environmental stability with readings of 98%-100% RH and temperatures between 17° C and 22° C. Notable deviations were typically associated with instances when the thermally insulating doors were opened. Salt migration presents a significant concern, often resulting in the dislodgement of mural painting fragments. Such deterioration typically ensues in locales susceptible to external environmental fluctuations, encompassing temperature, relative humidity, and air circulation. Another prominent degradation source for the preparatory layers stems from karst processes, intricate chemical reactions propelled by water movement. Owing to its insular nature, stagnant air, and rock foundation, the tomb harbors a highly specialized microorganism community.

Beyond natural deteriorative processes, the tomb exhibits signs of anthropogenic damage. Since its unearthing in 1870, the tomb has experienced varied footfalls, spanning conservation endeavors, multiple graphic documentation initiatives, and military activities. The inaugural documentation campaign of *lucidi* transpired between 1872 and 1873, led by Gregorio Mariani, whose records remain instrumental in mapping degradation trajectories (Capobianco et

al. 2019; Porcelli 2021). During World War II, the *Tomba degli Scudi*, similar to other Tarquinian sepulchers, served as a storage facility, safeguarding invaluable ceramics from the local museum. After the liberation of Rome in 1944, it was first utilized by the Allied forces and subsequently by the Brazilian division as a detention cell. For a comprehensive insight into the preservation status of the tomb, the following chapter will dissect the site based on the stratigraphic layers of its mural art.

3.1. Support

Given the friable and non-cohesive nature of *sabbione*, observed deteriorations predominantly stemmed from the rock inherent geological traits and anthropogenic damages sustained over the years. Several regions displayed erosion marks accompanied by minor fissures. Historically, flooding events have deposited clay-rich soil onto the base of the walls. Notably, specific chasms, penetrating through all preparatory strata, are undeniably of human origin. The distinct morphology of these gaps suggests infliction by an instrument resembling a pickaxe or bayonet.

3.2. Plaster

The principal contributor to plaster degradation is the infiltration of water in its liquid form within the substrate. This invasion renders the plaster more susceptible, even making it malleable. Concurrently, a sequence of physicochemical reactions associated with calcium carbonate dissolution manifests a unique degradation phenomenon. This entails a significant depletion of calcium carbonate, inducing a mechanical frailty of the plaster and subsequent cavity formation beneath the pictorial stratum (Fig. 10).



Figure 10. Atrium, voids of different sizes are present underneath the pictorial layer.

Although the outermost layers largely remain preserved, the underlying plaster exhibits voids of varying dimensions, ranging from minuscule cavities to expansive hollows, undermining its structural integrity. This condition arises from a complex interplay of chemical and physical reactions, moderated by several factors that balance calcium carbonate solubilization and re-deposition. The cyclical migration of water vapor between the internal atmosphere of the tomb and the exterior of the wall might prompt partial solubilization of calcium carbonate. Additionally, it can lead to the formation of thin calcitic layers, stemming from the evaporation of walls saturated with calcium carbonate. Another distinct, localized issue is the perilous seepage of rainwater, culminating in an accentuated dissolution of $CaCO_3$ (Dreybrodt, 2012). In karstic contexts, the primary agents of this phenomenon are calcium carbonate (CaCO₃), water (H₂O), and carbon dioxide (CO₂). The inaugural component constitutes the primary ingredient of the plaster, whereas the latter two are omnipresent, both within the rock and the ambient atmosphere:

 $CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^{-1}$

 $Ca(HCO_3)_2 \leftrightarrow CO_2 + H_2O + CaCO_3$

The outlined reaction demonstrates that CO_2 molecules, upon interaction with water, undergo a transformation into carbonic acid (H₂CO₃). Subsequently, the dissociation of this acid releases HCO_3^- and H⁺ ions. These ions react with the dissolved calcium carbonate, yielding bicarbonate and calcium ions. Intriguingly, this reaction is reversible: following the acid-me-

diated dissolution of calcium carbonate into bicarbonate that is soluble, and therefore, readily removed by infiltrating water, the calcium carbonate may be precipitated from the solution. Nonetheless, this precipitation process is gradual and contingent on specific environmental prerequisites (Lerman & Mackenzie, 2018). Consequently, within the tomb, the plaster acts as the nexus for this chemical dynamic, resulting in a substantial reduction of calcium carbonate within the layer structure, and consequently, the loss of extensive painting sections. Calcite deposition may materialize as either insoluble patinas or dense concretions (Fig. 11).



Figure 11. *Atrium*, carbonate depositions of different nature and typology are re-deposited on the pictorial layer.

The patina, characterized by its glassy and pale appearance, served a protective role for the painted layer in the *atrium*. Nevertheless, it induced a slight tonal lightening and, in certain instances, exhibited flaking that compromised part of its depth. Ultraviolet fluorescence (UVF) imaging conducted during the restoration phase indicated that these deposits aligned with regions exhibiting pronounced fluorescence (refer to Chapter 5). Although visually, these zones appeared unaffected, tactile examination revealed pronounced dampness. Hypothetically, these damp zones might harbor water enriched with CaCO₃ or other compounds conducive to surface carbonate precipitation.

3.3. Pictorial layer

Similar to the prior layer, the pictorial layer exhibited a pronounced loss of material. This depletion originated from the detachment of the pictorial film—often aligning with voids in the layer beneath—and from elements intrinsically associated with the application technique. Specifically, the limited carbonation of the pigment rendered it vulnerable to aforementioned

infiltrations and time-induced mechanical and abrasive wear, yielding color loss. Moreover, the tomb walls exhibited a biological patina, termed as moonmilk (refer to Chapter 4). Its whitish, powdery appearance is attributed to its composition: a delicate layer of calcium carbonate nanofibers (Fig. 12). Contrary to potential assumptions, this biogenic layer does not harm the paintings; rather, it apparently shielded them. Notably, a direct correlation emerged: a thicker moonmilk layer corresponds to greater conservation of the underlying pictorial layer (Fig. 13).



Figure 12. Detail of the wall where the biological white and powdery patina of moonmilk has been removed on the left side.



Figure 13. Detail of the biological patina of moonmilk, where it is thicker and harder, thereby protecting rather than damaging the murals.

4. Microbiology of Tomba degli Scudi

The *Tomba degli Scudi* essentially functions as an *in situ* microbiological where our team has been working for the past seven years. The key research phases are expressed in this chapter, providing a structured approach for probing similar hypogeal settings.

Atrium: Pre-restoration. Prior to the atrium restoration, a sanitization process was undertaken. Regrettably, this precluded the possibility of microorganism sampling ahead of the biocide application. The first microbiological analysis hence highlighted a dominance of biocide-resistant microorganisms, such as *Bacillus* species and fungi (Tomassetti et al., 2017). This initial exploration revealed that the treatment selectively eliminated more susceptible species, creating an imbalance within the microbial ecosystem.

Burial chamber: Pre-restoration. Throughout the restoration, professionals noticed an unusual white deposition on the tomb walls and ceiling. The wall paintings were obscured by a white, feathery carbonate layer, a calcite deposit known as moonmilk (Mura et al., 2020). Commonly found in karst kaves, moonmilk is composed of calcite nanofibers, each less than 1 μ m in width (Fig. 14) (Mura et al., 2021).



Figure 14. Burial chamber after the restoration. Two microbiological samples for each wall were studied.

In the Burial Chamber, the genesis of the white *patina* was investigated. Historical records provided no indications of prior interventions. Classical microbiological analysis coupled with a metagenomic approach unveiled a multifaceted microbial ecosystem responsible for the moonmilk formation within the tomb (Cirigliano et al., 2018). This finding showcases a rare instance in which microorganisms seemingly offer protection through the calcium carbonate patina instead of degrading the mural paintings (Fig. 15).

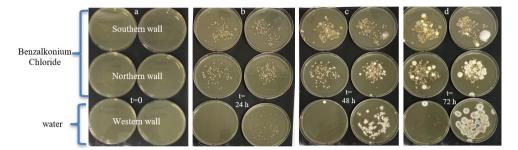


Figure 15. Two microbiological samples for each wall were directly tested for growth on complete medium plates (YPD, yeast extract, bacto-peptone and glucose). Southern and Northern walls were treated with benzalkonium chloride, whereas the Western wall was treated with water. (a) Two swabs for each wall were pressed on plates (time, t = 0). Growth continued for 72 h, and plates were imaged every 24 h (b, c, and d, respectively). The walls treated with benzalkonium chloride hosted a rich microbial community when compared with that of the wall treated only with water.

Atrium: Post-restoration. Although it became evident that biocolonization aided in mural painting preservation, moonmilk removal was deemed essential both for conserving the paintings in their original state and facilitating further investigations. However, post-moonmilk extraction from the atrium triggered a rapid microbial proliferation. Several months post-restoration, a biofilm enveloping over half of the wall surfaces was observed. Microbiological assessments ascertained that the biofilm primarily comprised a *Rhizobium* strain, typically found in soils and subterranean environments. After a comprehensive evaluation, the progression of this colonization was studied without the removal of the biofilm removal or biocide application. Expecting an eventual balance with the native hypogeal microbial ecosystem, systematic microbiological inspections of the mural paintings were performed. Spanning four years, the observed biofilm vanished, giving way to the indigenous microbial community. Furthermore, the microbial resistance to biocides from wall samples was scrutinized: a considerable proportion demonstrated minor sensitivity to Biotin T and resistance to benzalkonium chloride. Avoiding biocides proved prudent. Culturable strains were also assessed for their calcium carbonate precipitation capabilities. Some species exhibited biomineralization potential, hinting at the likely reappearance of moonmilk in the future (Cirigliano et al., 2022).

Burial Chamber: Post-restoration. Informed by the post-restoration outcomes of *atrium*, we initiated an experiment in the Burial Chamber to evaluate the activity of the commonly employed biocide, benzalkonium chloride. Post-restoration, two walls received a benzalkonium chloride treatment, whereas the northern wall was water-treated (Fig. 16). Direct growth on plates from samples (two from each wall) was observed over four days, and this procedure

was replicated. Astonishingly, a greater diversity of species was derived from the treated walls compared to the untreated (Fig. 16). In the control, the northern wall, the predominant species was *Penicillium*, an expected outcome owing to its ubiquitous nature and the probable dispersal of spores by restoration activity. Subsequently, the cultured microorganisms were subjected to biocide sensitivity tests (Figs. 16 and 17). Demonstrating varied sensitivity to biocides, these tests utilized extremely high biocide concentrations, surpassing typical environmental treatment levels. The findings indicated the biocide ineffectiveness in the Burial Chamber, revealing considerable microbial resistance.

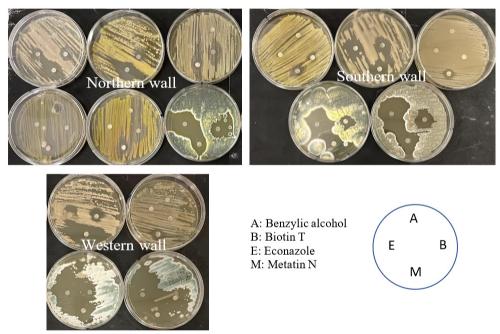


Figure 16. Biocide sensitivity test. Representative strains isolated from the mural paintings were grown on YPD plates in presence of paper disks soaked with 5 mL of the 1:10 dilution solution of benzylic alcohol, biotin T, econazole, and metatin N.

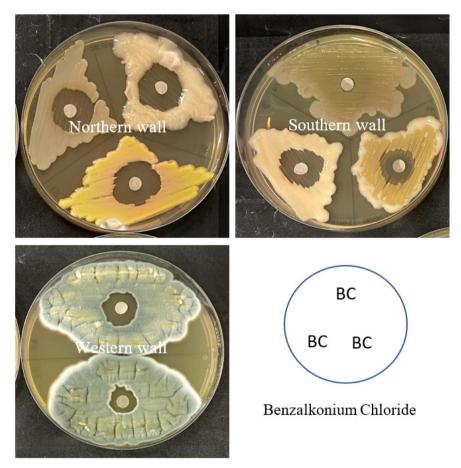


Figure 17. Biocide sensitivity test. Representative strains isolated from the mural paintings grown on YPD plates in presence of paper disks soaked with 5 mL of the 1:10 dilution solution of benzalkonium chloride.

After six years of microbiological exploration in the *Tomba degli Scudi*, encompassing pre- and post-restoration phases of the *atrium* and Burial Chamber, valuable insights for all hypogeal environments were obtained. The predominant concern in these sites is biodeterioration. This survey illuminates the complications stemming from microbial proliferation post-biocide treatment. Advisedly, the hypogeal sites carved in the rock should not undergo biocide treatments. Such treatments neither resolve issues, rather they exacerbate mural painting conditions by favoring the growth of bacterial strains. Essentially, biocide treatments are counterproductive. Subsequent to sanitation, microbial recolonization is inevitable given the inherent, stable hypolithic microbial community within the walls [5] rigliano et al., 2021; Ronca et al., 2023). Proper intervention necessitates a holistic, interdisciplinary strategy that

integrates biology and geology. Each cultural heritage location possesses a delicate balance between its microbial community and rock composition. We hypogeal tombs, the thermohygrometric values should be monitored, and restrict visitor access. Light exposure should be minimal to curb cyanobacteria and algae proliferation. Since the 1980s, in the Necropolis of Tarquinia, thermally insulated doors equipped with an anti-fog system were installed at the entrance of the tombs to stabilize the microclimates. Additional doors are situated at the dromos entrance, serving as a buffer and further enhancing thermal insulation. Beyond the aforementioned measures, the commitment remains to periodically assess the microbiological state of the tomb, and when required, undertake regular cleaning.

5. Innovative 3D diagnostics and laboratory analysis

The initial phase of our investigative approach for the wall painting in the *Tomba degli Scudi* encompassed documentation via 2D ultraviolet fluorescence (UVF) imaging, further complemented by an advanced 3D method. This technique is instrumental in elucidating the conservation status of surfaces and, specific to the tomb, in detecting potential biological agents across various painting regions (Lanteri & Pelosi, 2021). UVF assessments were conducted pre and post surface cleaning and treatments to analyze the impact of restoration interventions.

The outcomes of the acquisition and subsequent processing are presented in Fig. 18-20.

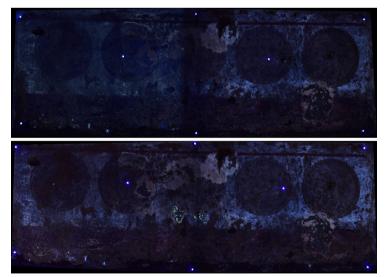


Figure 18. UVF orthophotomosaic of the right wall before (above) and after the restoration (below).

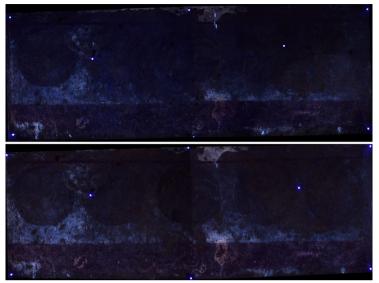


Figure 19. UVF orthophotomosaic of the left wall before (above) and after the restoration (below).

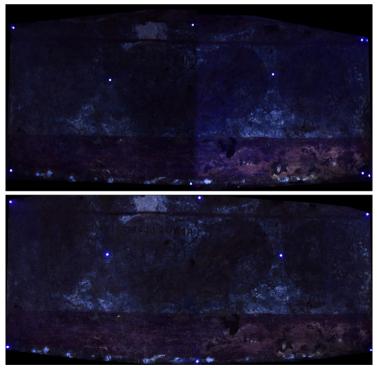


Figure 20. UVF orthophotomosaic of the central wall before (below) and after restoration (above).

Predominantly, UVF images exhibit a dark hue, especially noticeable in the shields, signifying a lack of fluorescence. However, certain regions radiate an orange fluorescence, most conspicuous in the bottom right image of the rear wall, potentially indicative of biological activity (compounds resulting from the metabolism of biological entities). The white-blue fluorescence, prominently visible on the rear wall image, might be attributed to salt deposits on the surface. The light-blue fluorescence is possibly linked to the *scialbo* layer (pure lime) which is absent in the shields, but was accentuated post-restoration. Pioneering the 3D UVF model, we acquired 30 photograms subsequently processed through Agisoft Metashape®. This software facilitates photogrammetric processing of digital visuals, including aerial and close-range imagery, to produce 3D spatial data coupled with high-definition photorealistic rendering. Employing a comprehensive Structure from Motion (SfM) method, the software merges digital photogrammetry with advanced computer vision capabilities [Lowe, 2004]. This culminated in the creation of a 3D photorealistic model of the tomb, with an illustrative view presented in Figure 21. An interactive model can be accessed *via* this link: https://sketchfab.com/3d-models/tomba-degli-scudi-tarquinia-7a183dcbe1e84bb199babcc0b30c3905

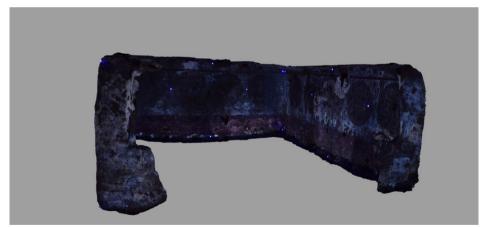


Figure 21. View of 3D model of Tomba degli Scudi, with white targets visible.

The investigation of the wall paintings encompassed various laboratory techniques aimed at identifying materials (both pigments and binders) and discerning the stratigraphic design of the decoration. Specifically,

 X-ray fluorescence and µ-Raman spectroscopies were employed to respectively pinpoint the chemical elements and compounds linked to pigments in certain designated areas of the wall paintings;

- Fourier-transform infrared spectroscopy (FT-IR) and gas chromatography coupled with mass spectroscopy (GC-MS) served to detect both inorganic and organic binders;
- Stratigraphic analyses on cross-sections were conducted to examine the sequence of ground and painting layers under both visible and UV radiation.

The primary elements ascertained through XRF spectroscopy indicated the utilization of ochre, earths, and calcium carbonate as dominant pigments. The μ -Raman spectroscopy verified this, revealing hematite (red), goethite (yellow), and carbon black for the darker shade. Carbon black, containing lighter chemical elements, remained undetected by XRF. Moreover, μ -Raman identified calcite in all inspected sections, affirming the initial hypothesis posited through XRF analysis where calcium was the predominant element. Finally, the μ -Raman detected the organic compounds, which are yet to be specifically identified but appeared to be linked with the metabolic activities of biological entities.

FTIR analysis demonstrated the ubiquitous presence of calcium carbonate, primarily as calcite, with some aragonite (Mazzocchin et al., 2006) in the wall paintings. Notably, it also discerned minor amounts of proteic and lipidic substances potentially tied to present biomass (Zucconi et al., 2012). Additionally, FTIR detected minimal traces of silicates (related to original materials) and gypsum (associated with restoration efforts). The absence of organic binders received further confirmation from GC-MS. The employed methodology, drawing from recent studies (Casoli & Santoro, 2012; Groppi et al., 2021; Annarilli et al., 2022), yielded two chromatograms per sample: one from fatty acid derivatives and another from amino acid derivatives. Based on the derived results, the detected lipid and protein content, fluctuating between 0.03 and 0.06 μ g/100 μ g of sample, cannot be ascribed to a deliberately added organic substance because of the minute quantities of identified analytes. The comprehensive results affirm that the painting technique eschews organic binders. To buttress this claim, cross-sections from painting micro-samples were further analyzed, as discussed in the subsequent section (Fig. 22).

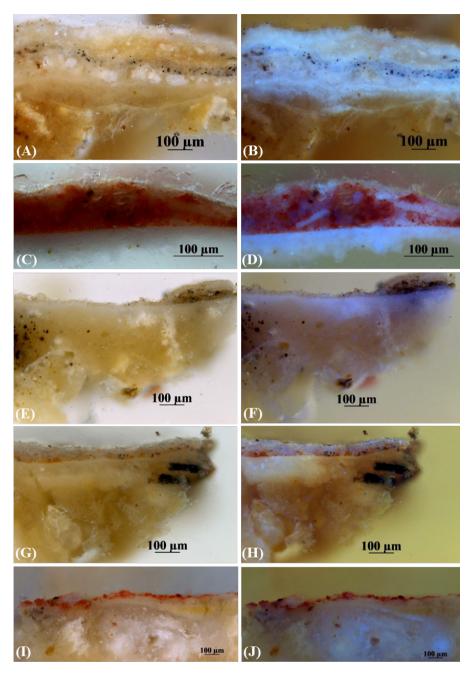


Figure 22. Microphotographs of the cross-sections at 100× magnification under visible (A, C, E, G, and I) and UV radiation (B, D, F, H, and J). Examined samples: *atrium*, south-west wall, gray, light-blue background (A–B); *chamber*, south-west wall, red frame (C–D); *atrium*, north-west wall, *scialbo* (E–F); *atrium*, north-east wall, brown color (G–H); *atrium*, north-west wall, flesh tone of the arm of Vel (I–J).

- G–H, stratigraphic sequence from the base: *intonaco* containing fragments of carbon black, *scialbo*, slender painting layer with minuscule black particles, possibly incorporated to intensify the reddish-brown hue, and a calcium carbonate surface layer exhibiting a pale blue fluorescence.

- I–J, stratigraphic sequence from the bottom: thick *intonaco* layer, *scialbo*, thin painting layer.

6. Restoration

After careful investigation of the conservation history and the factors contributing to degradation, the restoration approach entailed a rigorous assessment of the most fitting materials and techniques to employ. The primary objective in any restoration endeavor is to identify the materials that are harmonious with the originals. The selected materials and methodologies must align with the characteristics of the initial constituents utilized for the preparatory layers. Subsequently, the process demanded the identification of restoration materials and products, ensuring their chemical nature aligns with the demands of a hypogeal environment, permitting solely the introduction of inorganic constituents. All organic components, including acrylic or natural resins and gums, are vulnerable to rapid metabolism by microorganisms. Moreover, a 0.3% benzalkonium chloride water solution was consistently integrated into every stage to counteract external microbial colonization.

6.1. Cleaning

Given the dearth of prior restoration endeavors in the painted chambers of the tomb, the cleaning procedure was relatively straightforward. This phase primarily focused on eradicating the delicate moonmilk patina obscuring the artworks. The tasks involved addressing minor regions of carbonate concretions and clay deposits at the base of the wall, remnants of historical rainwater infiltrations. The moonmilk, being a biogenic deposit not chemically adhered to the substrate, was cleared using a simple aqueous medium. Generally, the carbonate concretions were malleable and could be mechanically removed; however, specific sections (half wall to the right of the entrance door and long inscription above *Velthur Velcha* wall) in the atrium necessitated preliminary softening using buffered ion exchange resins (anionics).

For eliminating moonmilk patina, a 1% benzalkonium chloride water solution was chosen. Application was done using a gentle synthetic bristle brush, with minimal agitation to the surface to lift the patina that rendered the surfaces coarse. In areas where the conservation state permitted comprehensive cleaning, residual moonmilk deposits were eradicated using low-pressure nebulizers and soft sponges, methodically dissolving and blotting the sediment. Supported by the biocidal properties of benzalkonium chloride, the subtle surfactant potential of the product chemical composition aided in dispelling the patina, mitigating prolonged interaction with the fragile plaster and pictorial layer substrates (Figs. 23 and 24).



Figure 23.Cleaning tests with the removal of calcite depositions. (Left) north-west wall and (right) south-east wall of the tomb.



Figure 24. North-east walls before (below) and after restoration (above).

6.2. Stabilization and infillings

The pronounced decohesion evident in the plaster necessitated meticulous attention from the inception of restoration efforts. It is unfeasible to return plaster to its original state, and it is equally challenging to ensure enduring protection throughout its entire depth using conventional wall painting restoration products. Filling the superficial porosity risks disrupting the delicate equilibrium established over many centuries. Given the restrictive range and supply of restoration products, the decision was made to utilize a class of products that could fulfill the specified criteria: filling and reinstating the cohesion of the material, which was substantially depleted of its binding matrix. Furthermore, it was paramount to prevent additional material loss and ensure the adherence of the pictorial layer to the plaster. A hydraulic mortar (Ledan TB1/ICR®, Tecno Edile Toscana) was selected, specifically designed for injection and tested explicitly for Tarquinia's wall paintings. After a span of 15 years, the impeccable state of conservation of the mortars was evident, showcasing their complete compatibility with the substrate and substantial longevity, even in especially challenging conditions such as humidity, salt presence, and microbial activity. By filling the majority of cavities and reestablishing chemical bonds between the plaster aggregates, degradation has been contained and even reduced. This is a provisional state, pending targeted environmental research and the installation of a system designed to mitigate water infiltration. To safeguard the aforementioned delicate balance and regulate the mortar penetration within the plaster, the mortar concentration required fine-tuning. After conducting preliminary tests to ascertain the product fluidity, two dilutions with demineralized water (ratios of 1:4 and 1:6) were devised. These dilutions were implemented both for in-depth consolidation and for re-adhering flakes to the uppermost layers. To address voids in the *sabbione*, yellow quartz sand, resonating with the rock substrate in hue and grain size, combined with a colloidal aqueous dispersion of nanometric silica (typically employed for consolidating clay and various stone materials) was utilized. In this context, it functioned as a binder for the sand, and when diluted in demineralized water at a ratio of 1:6, this dilution was significantly higher than what is traditionally employed for stone consolidation. This proportion was determined following empirical evaluations, aiming to replicate the consistency of the sabbione.

To address the voids in the plaster, numerous tests were conducted within the hypogeum under optimal temperature and humidity conditions. These were aimed at determining the right balance of binders and aggregates to mirror the mechanical strength of the severely compromised original plaster. The composition is as follows:

- Medium mechanical strength hydraulic lime (Saint Astier NHL 3.5)- 1 part;
- Slaked lime- 0.5 parts;
- Macco- 3 parts;
- Ground limestone (travertino)- 5 parts.

6.3. Aesthetic presentation

The aesthetic presentation of the painted surfaces underwent thorough consideration. In an archaeological context, the reintegration of artworks is consistently a nuanced and debated matter. This is particularly relevant for the *Tomba degli Scudi*, given the significant extent of gaps and the prevalence of visible preparatory layers. The various gaps in the *sabbione*, plaster, and pictorial film complicate the discernment of the painted images, resulting in an apparent disarray. Consequently, the fillings must serve both a conservational and aesthetic purpose. They need to secure and stabilize the fragment edges, and simultaneously enhance the artwork's appreciation by aiding in the discernment of distinct layers and restoring them to their intended levels. Given these considerations and the varied conservation challenges, once the methodology was established, the restoration was executed in phases. Each gap was assessed individually and collectively.

On the foundational level, which comprises the fragile sandstone support known as sab*bione*, only the edges of significant and deep gaps were stabilized, primarily for conservation reasons. These minimal infillings were crafted using yellow sand, closely resembling the original in both color and grain size, and bound with a sparse amount of a 1:6 water-diluted colloidal silica solution. This high dilution of the binder produced a mortar that was both malleable and of low mechanical strength, reflecting the properties of the original material. This level was maintained incomplete was backed by the intent to preserve the historical integrity and state of the artwork, especially considering the overall deterioration of the paintings and the specific origins of these gaps. Notably, a number of these gaps can be traced back to distinct, documented historical events. The upper plaster layer saw only selective infillings, corresponding to its original elevation (Fig. 25). Although the sottolivello unico technique (entailing the unification of all infilling levels of a layer-wall, arriccio, plaster, intonachino, etc.—to a singular elevation for distinction from other layers) is commonly employed for wall paintings, it was deemed unsuitable here. Such a method would have substantially altered the visual representation of the artwork conservation status. Following the infilling of the preparatory layers, an initial surface assessment facilitated decisions regarding pictorial reintegration. Primarily, the tone of minute gaps and abrasions in the paint film was subdued. The light hue of both the original and filled plaster made the gaps more prominent than the actual painted images. To prevent the lacunae from drawing undue attention, their tone was slightly reduced, referencing specific areas where the plaster naturally appeared darker. Only stable, water-diluted powder pigments were employed for pictorial touch-ups. The decision to forego water colors or other conservation-specific colors was established during the initial

2016 restorations, to exclude any organic material, such as Arabic gum, which could potentially serve as a habitat for microbial colonization. Additionally, an additional binder is not required given the porous nature of plaster.



Figure 25. *Ravnthu Aprtnai* on the South-West wall. The deeper losses of the plaster have been partially infilled for conservation reasons and to make the image easier to read. They were then glazed with natural inorganic pigments to have a single tone of that level.

7. Conclusions

The extensive research and restoration efforts in the *Tomba degli Scudi* set a precedent but require further research for conclusion, suggesting avenues for future interventions to conserve painted tombs in the Tarquinia necropolis. Currently, the onset of rapid climate change poses emergent challenges in art conservation. An acute understanding of degradation mechanisms and informed choices in restoration techniques become paramount. Such reflections gain further importance as innovative conservation strategies become vital to safeguard these delicate and invaluable artifacts for forthcoming generations, echoing the richness of Italian art. The *Tomba degli Scudi* exemplifies the indispensability of multidisciplinary research undertaken by domain specialists in ensuring precise and efficacious outcomes. Thus, owing to the unique environments housing these artworks, each conservation scenario demands a

tailored approach. Additionally, the exploration of the painting technique has spurred intriguing queries. These will be probed further in upcoming studies, aiming to deepen our grasp of Etruscan mural artistry, especially the Tarquinian style, within an expansive Mediterranean framework.

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References

- Andaloro M. (2002). Archetipo, modelli e sagome a Bisanzio. In: *Medioevo: i modelli*. Atti del Convegno internazionale di studi, Parma, 27 settembre – 1° ottobre 1999, a cura di C. A. Quintavalle, Milano 2002, pp. 569 – 574.
- Annarilli, S., Casoli, A., Colantonio, C., Lanteri, L., Marseglia, A., Pelosi, C., Sottile, S. (2022). A Multi-Instrument Analysis of the Late 16th Canvas Painting, "Coronation of the Virgin with the Saints Ambrose and Jerome", Attributed to the Tuscany-Umbria Area to Support the Possibility of Bio-Cleaning Using a Bacteria-Based System. *Heritage*, 5(4), 2904-2921.
- Bianchi Bandinelli, R. (1939). Le pitture delle tombe arcaiche, in: Clusium, Roma, 1939, pp. 23 28.
- Borrelli Vlad, L. (1991). Cartoni, modelli, disegno preparatorio nelle pitture delle tombe etrusche, in: Miscellanea etrusca e italica in onore di Massimo Pallottino, Roma 1991, pp. 1179-1192.
- Brékoulaki, H. (2001). L'esperienza del colore nella pittura funeraria dell'Italia preromana VIII secolo a.C., Napoli 2001.
- Casoli, A., Santoro, S. (2012). Organic materials in the wall paintings in Pompei: A case study of Insula del Centenario. *Chemistry Central Journal*, *6*, 107.
- Cecchini, A. (2012). Le tombe dipinte di Tarquinia. Vicende conservative, restauri, tecnica di esecuzione, Firenze, 2012.
- Cirigliano A., Tomassetti M.C., de Kruif N.F., Cavallo I.F., Maras D.F., Mura, F. and Rinaldi T. (2022). Microbial recolonization of the mural paintings after restoration in the Etruscan Tomba degli Scudi in Tarquinia. In: *Biological Risk for Hypogea. Shared data among Italy and Republic of Korea*. Edited by Giulia Caneva & Yong Jae Chung. Editor Nardini, Florence.
- Cirigliano, A., Mura, F., Cecchini, A., Tomassetti, M. C., Maras, D., Di Paola, F. M., Meriggi, N., Cavalieri, D., Negri, R., Quagliariello, A., Hallsworth J.E. and Rinaldi T. (2021). Active microbial ecosystem in Iron-Age tombs of the Etruscan civilization. *Environmental Microbiology*. 23 (7), 3957-3969.

- Cirigliano, A., Tomassetti, M. C., Di Pietro, M., Mura, F., Maneschi, M. L., Gentili, M. D., Cardazzo, B., Arrighi, C., Mazzoni, C., Negri R., Rinaldi. T. (2018). Calcite moonmilk of microbial origin in the Etruscan *Tomba degli Scudi* in Tarquinia, Italy. *Scientific Reports*, 8:15839.
- De Kruif, F.N. (2021). Il restauro della Tomba degli Scudi. Un nuovo approccio alla conservazione preventiva e al controllo della colonizzazione biologica in ambiente ipogeo [tesi di laurea magistrale], Viterbo, Università degli Studi della Tuscia,2021.
- Dreybrodt, W. (2012). Processes in karst systems: physics, chemistry, and geology (Vol. 4). Springer Science & Business Media.
- Groppi, F., Vigliotti, D., Lanteri, L., Agresti, G., Casoli, A., Laureti, S., Ricci, M., Pelosi, C. (2021). Advanced documentation methodologies combined with multi-analytical approach for the preservation and restoration of 18th century architectural decorative elements at Palazzo Nuzzi in Orte (Central Italy). *International Journal of Conservation Science*, 12(3), 921-934.
- Lanteri, L., Pelosi, C. (2021). 2D and 3D ultraviolet fluorescence applications on cultural heritage paintings and objects through a low-cost approach for diagnostics and documentation. Proc. SPIE 11784, Optics for Arts, Architecture, and Archaeology VIII, 1178417, 1-11.
- Lerman, A., & Mackenzie, F. T. (2018). Carbonate minerals and the CO2-carbonic acid system. Encyclopedia of Geochemistry; Encyclopedia of Earth Sciences Series; Springer: Cham, Switzerland.
- Maggiani, A. (2005). Simmetrie architettoniche, dissimmetrie rappresentative. Osservando le pitture della Tomba degli Scudi di Tarquinia, in Pittura parietale e pittura vascolare. Ricerche in corso tra Etruria e Campania, Atti della giornata di studio, (Santa Maria Capua Vetere, 28 maggio 2003), Gilotta F., Napoli 2005, pp. 115-132.
- Marzullo, M., Grotte Cornetane. Materiali e apparato critico per lo studio delle tombe dipinte di Tarquinia, Voll. I e II, Milano, 2017.
- Mazzocchin, G.A., Orsega, E.F., Baraldi, P., Zannini, P. (2006). Aragonite in Roman Wall Paintings of the VIIIa Regio, Aemilia, and Xa Regio, Venetia et Histria. *Annali di Chimica*, 96, 377-387.
- Mura, F., Cirigliano, A., Bracciale, M. P., Rinaldi T. (2020). Characterization of Nanostructured Calcium Carbonate found in two ancient Etruscan tombs. AIP Conference Proceedings. 2257 (1), 020011.

Mura, F., Cirigliano, A., Maras, D., & Rinaldi, T. (2021). Analysis of moonmilk nanofibers in the Etruscan tombs of Tarquinia. In *AIP Conference Proceedings* (Vol. 2416, No. 1, p. 020014). AIP Publishing LLC.

- Porcelli, G. (2021). Il restauro dei dipinti nella camera sepolcrale della Tomba degli Scudi e lo studio della tecnica esecutiva nell'Italia preromana del IV secolo a.C. [tesi di laurea magistrale]., Viterbo, Università degli Studi della Tuscia, 2021.
- Ronca, S., Mura, F., Brandano, M., Cirigliano, A., Benedetti, F., Grottoli, A., Reverberi, M., Maras, D. F., Negri, R., Di Mauro, E., and Rinaldi, T. (2023). Biogenic calcium carbonate as evidence for life, Biogeosciences, 20, 4135–4145, https://doi.org/10.5194/bg-20-4135-2023.
- Steingraber. S., Catalogo ragionato della pittura etrusca, Milano, 1984.
- Steingraber, S., Affreschi Etruschi. Dal periodo Geometrico all'Ellenismo, Venezia, 2006.
- Tomassetti, M. C., Arrighi, C. (2019). Early Evidence of Modular Templates Used to Draw Human Figures on Mural Paintings: The Etruscan Tomba degli Scudi in Tarquinia, in *Studies in Conservation*, published online: 23 May 2019, http://doi.org/10.1080/00393630.2019.1616151, pp. 1 – 7.
- Tomassetti, M. C., Cirigliano, A., Arrighi, C., Negri, R., Mura, F., Maneschi, M. L., Gentili M.D., Stirpe M., Mazzoni C., Rinaldi, T. (2017). A role for microbial selection in frescoes' deterioration in *Tomba degli Scudi* in Tarquinia, Italy. *Scientific Reports*, 7: 6027.
- Zucconi, L., Gagliardi, M., Isola, D., Onofri, S., Andaloro, M.C., Pelosi, C., Pogliani, P., Selbmann. L. (2012). Biodeteriorigenous agents dwelling the wall paintings of the Holy Saviour's Cave (Vallerano, Italy). *International Biodeterioration & Biodegradation*, 70, 40-46.