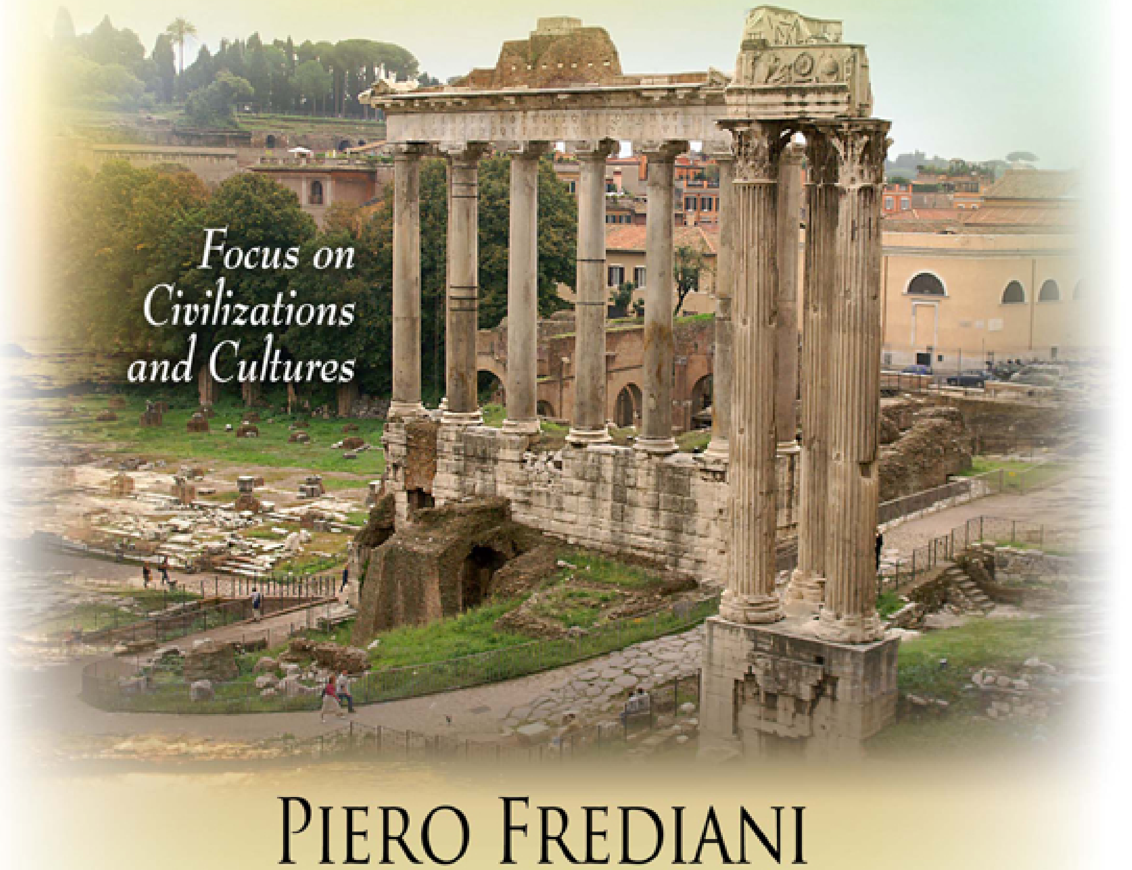
Cultural Heritage

Protection, Developments and International Perspectives



Focus on Civilizations and Cultures

Piero Frediani
Marco Frediani • Luca Rosi
Editors

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FOCUS ON CIVILIZATIONS AND CULTURES

CULTURAL HERITAGE

PROTECTION, DEVELOPMENTS AND INTERNATIONAL PERSPECTIVES

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PIERO FREDIANI
MARCO FREDIANI
AND
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EDITORS

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PREFACE

This book affords problems concerning the protection of cultural heritage by several points of views. First of all theories devoted to explain and justify the preservation of cultural heritage as a cult of ancient monuments, as a part of our history and finally the economics value involved in cultural heritage preservation. Svoboda report in the first chapter some collateral theories of heritage preservation Over the time we have moved from a pure cult of monuments to new forms of consideration of the monuments that take into account the economic benefits of a proper management of cultural heritage. In fact at the beginnings the care of historical monuments was due to an effort to preserve material relics of past ages. It can be identified with the medieval respect for holy places and the related religious piety. If, at that time, the reconstruction or preservation of a monument was to be carried out, the decisive argument that pushed the entire process forward consisted in its underlying idea, namely in the answer to the question “Why?“. It is therefore obvious that initial forms of monument care were dependent upon the sheer *reason why* a concrete building should be preserved. However, a strong and sophisticated system of justification built upon well-based arguments was developed over time to found monument care as a causality which, out of the natural cycle of creation and ruin, extracts selected objects and brings them back to presence again. Within the modern ages, this emotional basis was further complemented with the newly accentuated rationality of monument care. The rational appreciation of the quality and value of monuments introduced market forces to the care of historical monuments, thus employing the agent that sets in motion the ever-growing crowds of tourist, ensures the flux of capital, and hopefully a large number of resources must be utilized in monument care. Then, this rationality poses the question that is closely linked to the related elementary aspect of economics: What should be protected, how, and for whom? The conflict of the two above-outlined approaches can be illustrated by the actual history and development of monument care reaching up to the current systems of complex protection.

The conservation of cultural heritage involves its documentation and in the following chapter Nunez discusses some aspect of the data. Humans can build real masterpieces that amaze mankind for centuries. However, they can also destroy everything created by their actions, not only during armed conflicts, which still plague part of the world today, but also through daily actions that cause deterioration of these works. If we add the damage caused by natural phenomena such as freezing-taw cycles, earthquakes, volcanic eruptions and floods, etc., it becomes clear that plans to safeguard cultural heritage must be established.

Preservation plans start with the acquisition of as much data as possible, to document the cultural heritage and to be able of restoring it to its original state.

The Athens Charter for the Restoration of Historic Monuments was adopted in 1931 and highlights the need to establish a cultural heritage protection plan. This necessity was later confirmed by the Venice Charter of 1965, and more recently in its latest version (2008). All of these charters express the need to document cultural heritage for its conservation. Some methods for capturing and managing spatial information on cultural heritage, in a broad sense will be described in the third chapter. They focus on two areas that can help to achieve aims: the data capture methods before restoration work, and how to manage and present these data in order to compile the most comprehensive documentation possible. This chapter is devoted to geospatial documentation. Geospatial information is used in the preservation and restoration of monuments and buildings, etc. Traditional data capture techniques, such as conventional photogrammetric and topographic surveys, and the latest sensors, including terrestrial laser scanners and Unmanned Aerial Vehicles will be presented and discussed.

In the third chapter Frediani et al. present the role of synthetic polymers in the conservation of cultural heritage, with a special attention to outdoor exposed monuments. Deterioration of monuments and historical buildings has recently undergone to an important acceleration due to natural and anthropic changes in the climatic conditions and presently it has grown to a particularly evident degree. The rate of decay depends on intrinsic properties of the stone (mineralogical composition, stone texture and structure, porosity, etc.) but also on extrinsic factors that include climatic conditions, atmospheric composition, localization of the object, use and care given to it, and so on. The deterioration of stone materials occurs even in the absence of pollutants and it is important to quantify how natural or anthropic factors affect and accelerate the degradation of the material.

Atmospheric conditions in urban areas, mainly due to air pollution, greatly promote decay processes of stone materials, especially for those outdoor exposed. Damage of cultural heritage coming from air pollution has two main sources: pollutant gases improve the corrosivity of the atmosphere (acid rains) and black particles deposited on the surface cause its darkening. In recent years several studies have been developed with the purpose of setting up appropriate protective able to reduce the ruinous effects of the atmospheric pollution in combination with the change of the climatic parameters. It’s well known that almost all of these phenomena require the presence of water for their action or the water may strongly improve their influence. A variety of efforts have been undertaken over the years to preserve or protect these structures and in particular protective agents have been selected from commercial products developed for the protection of the surface of civil buildings. These materials however do not fully meet the requirements for they application on historic or artistic stones so new and specific materials are proposed. An evaluation of the state of art of polymers employed for this special application is reported in this chapter examining the requirements of the products for their use as protective for cultural heritage, their performance, stability and the class of protective polymers employed up to now. A final paragraph is dedicated to new trends in development of polymers coming from natural sources.

Novel nanocomposite UV - cured coatings, based on photopolymerizable siloxane-modified acrylic formulations with the addition of organo-modified Boehmite (OMB), are proposed by Frigione and Corcione as potential protective coatings for porous stones and wood elements. The OMB nanofiller has been dispersed into an optimized acrylic-based formulation in the presence of a proper photoinitiator for UV-curing. This represents the first example of use of Boehmite-based UV-cured nanocomposite in the field of Cultural Heritage.

The advantages offered by UV-cured coatings with respect to traditional heat-cured ones mainly reside in the attainment of superior performance achievable in lower time. The use of a nanocomposite protective coating will guarantee better surface properties and durability characteristics.

Characterization of the innovative liquid photopolymerizable siloxane-modified acrylic formulations, both in presence or absence of OMB nanoparticles, is presented, in order to assess the suitability of the proposed products for the specific applications. A wide experimental characterization of the solid coatings, applied on different substrate and photo-cured by using a medium pressure Hg UV lamp, is illustrated, in order to assess the attainment of the expected superior properties in terms of transparency, hydrophobicity, surface resistance, glass transition temperature, among the most important. An accelerated weathering procedure is run to evaluate the weathering resistance of the coatings.

Novel nanocomposite obtained as organic-inorganic epoxy-based hybrids has been also proposed by Lionetto and Frigione as potential adhesives for Cultural Heritage consolidation. A considerable interest has been devoted to organic–inorganic (O-I) hybrids, which present unique characteristics arising from the combination of organic and inorganic components. Recently, epoxy-based O-I hybrids, consisting of epoxy resins with interpenetrating silica domains, have been optimized by the authors. The methodology for their production is based on the sol-gel technology, involving the hydrolysis and condensation of metal alkoxides in aqueous solution, which is able to bind chemically, at nanometric scale, the organic phase with the inorganic one. These novel hybrid systems present superior properties then those of the parent resins. The presence of nanostructured co-continuous organic and inorganic domains, in fact, allows to achieve higher glass transition temperatures, greater mechanical properties and enhanced adhesion to different substrates. Thanks to their peculiarities, these epoxy-based hybrid systems have been investigated by the authors as potential “cold-cured” adhesives, i.e. cured at ambient temperature and used in Cultural Heritage for restoration of artefacts and consolidation of masonry structures. The main interest in cold-cured epoxy-silica hybrids lies, in fact, in the possibility of overcoming the main limitations of conventional cold-cured epoxy resins, currently used as adhesives and matrices for FRP (Fiber Reinforced Plastics) in the restoration and repair of ancient masonry structures. They require, in fact, long curing times, while, due to the incomplete cure, the glass transition temperature (Tg) of the final products can only achieve values about 10-20°C higher than the temperature used for the curing process. Moreover, the Tg of cold-cured epoxies can decrease to even lower values through the absorption of water via their strong association with OH and NH groups.

The properties of the organic–inorganic epoxy-based hybrid systems, will be analysed highlighting their potential as efficient adhesives for Cultural Heritage, structural and non-structural, applications.

Another aspect of conservation has been afforded by R. Horlings with an introduction to archaeology and protection of maritime cultural heritage in Ghana. Although Ghana is home to several World Heritage sites and it is involved in national and international plan for protection and development of cultural heritage, currently it has no provisions for the protection of the equally significant maritime heritage. Maritime activities over the past 500 years played an indelible role in international trade and relations along the coast, and archaeological materials provide testament to the many facets of history played out in the maritime arena. Ongoing maritime archaeological investigations along the Ghanaian coast necessarily highlight the question of what is or can be done to protect and preserve these non-renewable national and international heritage resources. A brief overview of archaeological research serves to illustrate both the fascinating maritime past of this region, and the precarious situation of submerged cultural heritage.

The following chapter reports by Pizzo et al. the required analyses on waterlogged archeological wood prior to start on the conservation of this material. Wood has been largely employed in the pasts thanks to its good mechanical and physical properties, easiness of use, workability, considerable availability and cheapness. Therefore, wood artifacts are an important issue to be considered in the modern approach to conservation of Cultural Heritage. Among the wooden objects deserving attention, waterlogged archaeological wood represent a highly interesting case. In conditions of almost complete anoxia, as occurs when remains are preserved under water, this material is altered only limitedly, in a manner that does not compromise the exterior integrity of objects. However, waterlogged wood is internally attacked by microorganisms (bacteria and fungi) and environmental factors. These agents both appreciably decay the wood tissue, by changing its cellular structure and its chemical and physical properties. In fact, almost always (it mostly depends on the extent of decay) the altered material needs to be treated before it can be displayed in a museum, and the conservation procedure must be based on the correct evaluation of its state of preservation. This chapter reports the characteristics of waterlogged archaeological wood decayed at various levels, by analyzing a large number of samples of different wood species and burial times, and coming from several archaeological excavations undertaken in Italy. The chapter also analyses how a correct diagnostic evaluation can be obtained only after an integrated multidisciplinary approach, making use of quantitative and reliable data. Described evaluations can be carried out by simple and broadly used techniques, which, however, have to be accurately regarded before to establish the state of preservation of the material. More in detail, microscopy allows both identifying the used timber and observing the present anatomical structure, thus recognizing the decay agents and which part of cell walls they degraded. Chemical analyses allow quantifying the depletion of structural polysaccharides caused by the decay process, and the other possible changes in chemical structure of wooden tissue. Physical characterization allows evaluating the mass loss after decay and the increase in water content (i.e., increase in porosity) in present material.

Furthermore, to attain consistent evaluations, able to establish how specific factors (such as the wood species) affect the resistance against alteration, the various physical and chemical parameters need to be combined among them in order to increase both readability and usefulness of data. In such a way the “effective” chemical parameters can be used instead of the raw ones (directly coming from chemical measurements), which allows them to refer to the presumed original mass of wood (i.e., before burial and therefore before any process of decay) rather than the mass of degraded, ash-rich, archaeological material. This also allows for a direct comparison of data referred to materials even in highly different states of preservation.

A correct diagnostic evaluation helps in understanding the new properties of decayed wood and, in perspective, lets to classify the material according to its true level of decay. Analogously, a correct grading of this material could make possible to tailor the treatment method on the basis of the decay class.

This chapter is mainly oriented towards conservators, and in general towards who is in charge of the following and possibly the setting up of a conservation process, from retrieval to the phases driving to the real treatment, in the attempt of giving the right importance to the preliminary diagnostic analysis.

In the following chapter other methodologies are proposed to evaluate the state of conservation of cultural heritage will be presented. Capitani et al report some application of advanced nuclear magnetic resonances on cultural heritage as an extension of the other methodologies reported in the third chapter by Frediani et al. In recent years Nuclear Magnetic Resonance (NMR) techniques have been increasingly applied to investigate, characterize and monitor objects of interest for Cultural Heritage. These techniques are considered as non-destructive because the sample can be investigated without any chemical pre-treatment and can be fully recovered after the analysis. NMR allows light to be shed on pictorial techniques used by artists, and can provide knowledge about materials constituting artefacts. High resolution NMR spectra are the fingerprint of organic materials such as paper, wood, textiles, parchments, adhesives, varnishes, binders, natural and synthetic resins, as a consequence, the knowledge of the causes of degradation of artifacts may also be achieved through the study of the chemical-physical transformation and structural modifications caused by ageing. NMR also provides an insight into the molecular structure of inorganic materials such as pottery, stones, and glass. NMR is not confined to a few specific applications, but its use can be successfully extended to a wide number of different issues regarding Cultural Heritage.

A breakthrough has surely been the recent development of portable NMR instrumentations. These devices can be applied directly on large objects such as *frescoes*, monuments, and in general any buildings fully preserving the integrity and the dimension of the object under investigation. The measured NMR parameters are important to establish the state of degradation of the objects, to evaluate the performances of consolidation and water repellent treatments on porous materials, to monitor the detachment of the painted layers from the support, to quantitatively map the dampness in wall paintings. A further development of portable NMR devices is the availability of sensors to obtain hydrogen driven NMR stratigraphy with microscopic spatial resolution. These devices may be useful to investigate the layer structure of paintings, obtaining information on the working practice and techniques of the artist, and helping to select correct and suitable conservation and restoration procedures. Study cases are also reported to show how NMR spectroscopy, NMR relaxometry, and portable NMR can play an important role in the Cultural Heritage field.

Another methodology, the X ray fluorescence spectrometry as a diagnostic tool to evaluate the state of conservation of illuminated manuscript is reported by Guerra and Carvalho. The capabilities of Portable X-ray Fluorescence Spectrometry to characterize illuminated manuscripts and the complementary techniques, Raman and SEM-EDS Spectroscopy will be described. The use of these techniques is essential for the understanding of the artists working methods, which aids conservation and restoration of the manuscripts.

As a case study, the Renaissance foral charters, from the 16th century, belonging to the Portuguese National Archive will be studied in detail. A complete characterization of parchments, pictorial materials and metallic coatings used in the production of illuminated manuscripts will be performed. Scientific identification of: i) inks used in the written texts; ii) pigments used in the illuminations and letterings used in the production of colouring materials and inks, will be carried out. The results of this work will be a key step in the work of conservation and restoration to be undertaken in many illuminated manuscripts, such as the aforementioned charters, which can present very high degrees of deterioration and need urgent intervention.

Another approach to preservation of cultural heritage will be reported by Pasquarella et al. This authors suggest an integrated system of biological and microclimate monitoring to preserve cultural heritage in indoor environments (museums, libraries, archives, etc.) These objects are exposed to the phenomena of *biodeterioration* caused by specific groups of biological agents called *biodeteriogens*. Several factors may affect the process of biodeterioration, depending on the chemical and physical characteristics of the materials, the state of conservation of the artefacts, the environmental conditions and the nutritional availability for biological agents. The biological components of air (*bioaerosol*) can be a potential biodeteriogen for cultural property. In the case of organic artefacts, they can be identified in a specific fungal and bacterial microflora. Once deposited on the surface of cultural objects, these microorganisms can find favourable nutritional and environmental conditions, thus becoming biodeteriogens. Certain classes of airborne particles contain allergens or toxins, and can be a risk to the health of operators and visitors. The prevention of biological risks is based on a thorough knowledge of aerobiological particles and the factors that affect their circulation, survival and growth in a specific environment, associated with a careful control of microclimatic parameters. Such an integrated system of biological (air and surfaces) and microclimatic monitoring, based on a methodological model, represents the basis for studying the complex environmental artifact- human matrix in order to understand, assess and prevent biological risks. The proposed approach relies on the analysis of: 1) airborne microorganisms with active and passive methods; 2) the surface of cultural objects with non-destructive and non-invasive techniques based on nitrocellulose membrane filters; 3) fungal spores with a spore trap (Hirst type) and microscope; 4) surface and airborne allergens with immunoenzymatic assays; 5) airborne particles, with a laser particle counter. Microbiological environmental pollutants are identified by means of direct culture and molecular biology techniques. 6) Indoor microclimatic conditions (air temperature, relative humidity, air velocity and distribution, light, temperature of surfaces) related with the conservation of cultural property and the risk of contamination by biological agents are also analysed. The effect of ventilation strategies on the microclimate can be evaluated using computational fluid-dynamics (CFD) tools. A multiphysics approach combined with CFD is used to assess air ventilation and microclimate. Transient simulations, based on experimental data and run on three-dimensional models of the studied environment, allow to define preservation and maintenance criteria. CFD plays an important role in the prediction of damage and risk, as it helps evaluate the efficiency, adequacy and reliability of any Heating, Ventilation and Air Conditioning (HVAC) system and its maintenance criteria, thus providing critical indications for indoor air quality control and energy saving. Studying both the biological and microclimatic quality of cultural heritage environments is fundamental to define adequate conservation methods and standards, and to protect the health of operators and visitors. The methodology proposed is also a useful tool for managing cultural heritage sites and choosing the best environmental control strategy when retrofitting buildings, especially in all cases where a historical building is modified to become a museum, library or archive.

In the following chapter Dionisio et al face a problem caused by a non-civil behavior of many citizens, that is “When graffiti is not art: the damage of alkyd sprays on calcareous stones employed in Cultural Heritage " . In order to evaluate the damage of alkyd sprays on calcareous monument stones, limestone and marble samples of renowned building materials and ornamental stones in the Portuguese architecture, *Lioz* and *Branco,* were submitted to artificial graffiti. The harmfulness was assessed in relation to the variation of water vapour permeability, static contact angle, water microdrop absorption, chromatic changes and surface contact roughness. For evaluation of the degree of the aerosol's penetration into the stone and the morphological surface changes, the scanning electron microscopy was used. Apart from the aesthetics aspects, which threaten the historical significance of the monument, the current research has shown that alkyd sprays used in graffiti interact with the stone substrate by reducing the water vapor permeability of the stones and thus leading to water condensation just underneath the paint. Moreover a significant reduction of the roughness of the stone surfaces is generated by the application of these paintings, creating a smooth and uniform overcoat that modifies surface texture and the details intentionally left in the original work. The water repellency of the stone surfaces is also significant incremented. An increase knowledge of the interaction of alkyd sprays with stone materials will provide valuable insight and greater understanding of the vulnerability of stone to graffiti vandalism, namely to some Portuguese monument stones.

In the final part of this book the threat posed by global warming, rising seas, and coastal erosion to archaeological, historical, and other types of *tangible* cultural heritage sites located along the world's coastlines are presented. Thomas reports that for the smaller oceanic islands, most notably on low-lying atolls, sea-level rise is of immediate concern as present-day inhabitants have few options in relocating to higher ground. Unlike people who might consider moving off island, cultural heritage sites cannot easily be relocated to safer areas. Moreover, the strong "sense of place" experienced by Pacific island societies, and no doubt other insular communities, which includes overlapping cultural and natural assets of the land- and seascape, highlights the need to preserve and protect these sites. Using a case study from Micronesia (Kiribati), it is argued that *tangible* cultural heritage should not limited to strengthening cultural identity in a rapidly globalized world, but could also serve as a benchmark in providing long-term perspectives on environmental change, integrate itself with biodiversity conservation, create local opportunities for heritage tourism, as well as articulate with the use of traditional material culture and skills in modern-day contexts.

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Chapter 1

COLLATERAL THEORIES OF HERITAGE PRESERVATION: FROM A CULT OF MONUMENTS TO THE ECONOMICS OF CULTURAL HERITAGE

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ABSTRACT

In European culture, the beginnings of the care of historical monuments as the effort to preserve material relics of past ages can be identified with the medieval respect for holy places and the related religious piety. If, at that time, the reconstruction or preservation of a monument was to be carried out, the decisive argument that pushed the entire process forward consisted in its underlying idea, namely in the answer to the question “Why?“. It is therefore obvious that initial forms of monument care were dependent upon the sheer *reason why* a concrete building should be preserved. However, a strong and sophisticated system of justification built upon well-based arguments was developed over time to found monument care as a causality which, out of the natural cycle of creation and ruin, extracts selected objects and brings them back to presence again.

Within the modern ages, this emotional basis was further complemented with the newly accentuated rationality of monument care. The rational appreciation of the quality and value of monuments introduced market forces to the care of historical monuments, thus employing the agent that sets in motion the ever-growing crowds of tourist, ensures the influx of capital, and generally opens a large number of resources to be utilized in monument care. Then, this rationality factor poses the question that is closely linked to the related elementary aspect of economics: What should be protected, how, and for whom? The conflict of the two above-outlined approaches can be illustrated by the actual history and development of monument care reaching up to the current systems of complex protection.

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INTRODUCTION

If the problems of cultural heritage and its protection are to be discussed, we need to start from a peculiar paradox characterizing today's care of monuments: Although the number of protected objects keeps increasing, the past to which these objects date is less and less distant. Even around the mid-19th century, works of art dating back to the Baroque period (and thus no less than 150 years old) were not regarded as historical monuments. Roughly forty years later, in the 1890s, a clerk of the Vienna-based office for the preservation of national monuments describes the inventory of St. Wenceslas Church in Nikolsburg (now Mikulov) as "artistically worthless" owing to its Baroque origin. Then, only some 70 years elapsed before Villa Tugendhat in Brno was added to the list of national monuments (today, it is a UNESCO-listed world heritage site), a mere 37 years after it had been completed.

Looking around, we can see substantial evidence of the intensified interest in monuments; though not devoid of difficulties, the current protection of historical landmarks is at its hitherto most advanced stage in terms of the quality, extent, and general support. The idea of progress built upon the ruins of the old world, the concept known from the French or Russian revolutions and the later devised "Plan Voisin" by Le Corbuisier, already seems to be outdated. The care of historical monuments emerged out of the clashes within the 19th and 20th centuries as the victor. Together with making the past present, the preservation of the memory of various cultures constitutes today a universal and generally shared aspect. The question of why this is so can be denoted as one of the most interesting problems within the current studies of culture. In searching the proper answer to this question, we may utilize the concept of monument values, which was implicitly developed over centuries and explicitly formulated by many monument care theorists, beginning with Alois Riegl or Max Dvořák and ending with David Throsby or Massimiliano Mazzanti. The long road to the present respect for monuments began at the moment when the symbolic value prevailed over the utility value and ends today, at a time when the former value augment the latter one.

DEFINITION OF MONUMENT VALUES

Objects referred to as monuments have always been most endangered by two circumstances: The effect of time, which has always led to decay, and active destruction caused by war or dismantling (during which a monument was exploited to provide construction material such as masonry, brick, and precious metal). Any monument as an evidence of the past was exempted from the natural cycle of creation and ruin only when protected by special measures. The beginnings of the cult of antique objects and their conscious preservation can be related to the symbolic and cultic value of monuments, to the notion of "pietas, which means not merely devoutness; it includes loyalty to parents, to family and to the homeland. But above all, piety manifests itself in the attitude towards religious traditions.

Sacred shrines, the graves of martyrs, and indeed relics … are the object of piety.“ [1, p. 76]. Such protection, which enabled the preservation of a monument, either was conducted by the *patria* or had a religious character.

An example of the first type of protection aimed at antique objects is shown already in the Bible [2], where Jehoiada the priest and his people “rebuilt the temple of God according *to its original design* and reinforced it.“ (2 Chronicle, 24, 13). The second type of protection can be exemplified by emperor Hadrian’s (117 – 138 CE) decree on the protection and preservation of monuments, mainly those of Pharaonic Egypt and classical Greece. “However, this action needs not necesarily be interpreted as conscious attempts at heritage managements. This may be motivated by a mixture of religious, philosophical, political, and aesthetic objectives.“ [3, p. 2]

A similar approach initially persisted during certain phases of the Middle Ages. Through this period, only artefacts of primarily religious or, in the least, high symbolic value were purposely preserved: The continuity of the material symbols was required for the continuity of the cult. In this context, the statue of St. Foy of Conques may be referred to as an example. The statue was originally a reliquary bust, in which the face of the saint was formed by a Gallo-Roman male mask incorporated in the Christian reliquary. However, as the growing piety of the saint around the year 1000 required a bigger figure, the bust was enlarged to constitute a full-figure sitting statue, visually impressive both from a distance and laterally; yet, with all the modification performed, it was also necessary to preserve the visual and material continuity [4, p. 136]. Similarly, the identification of an old building with a new one or, in the least, some reference to ideological continuity with an older tradition were made possible by the incorporation of spolia, namely the re-use of earlier building material or decorative sculpture on new monuments. This custom dating back to late Antiquity enabled the architects and builders to “maintain the continuity of existence of consecrated Christian institutions through the survival of some aspect of the replaced structure in the replacing one“ [5, p. 461]. In its beginnings, the use of spolia is connected with the largest buildings of emperor Constantine’s era: St. John Lateran’s Basilica, Old St. Peter’s Basilica, and the Arch of Constantine. The motivation behind such usage of older constructional elements or decorations did not primarily consist in economic reasons, let alone any “lack of artistic imagination, or superficial haste“, as noted by B. Brenk [6, p. 104-5, or 7]. Spolia should “be considered seriously as a new artistic medium which by the character of tradition and time-honored norms could be transmitted to a building: a new aesthetics, operating not with the concept of the brand-new but rather with the concept of reuse“. [6, p. 105]. Similar motives characterized also the application of spolia in later centuries; here, Palatine Chapel in Aachen or the reconstructed St. Peter’s Basilica may serve as prominent examples. Marbles from Rome were used not only on the Italian peninsula, but also in Constantinople, Aachen or Westminster [8, p. 9]. Importantly, high symbolic and cultic value consisted in relics and related objects of art, which essentially provided physical evidence of the past. Thus, multiple reliquaries (shrines) were created to prove the physical existence of saints; thanks to their – whether real or reputed - historical value, the reliquaries were held in high esteem, and the protection and piety directed to relics were partially transferred to the shrines. To exemplify this statement, we could refer to the crown of thorns, a relic for which La Sainte-Chapelle was built. By comparison, the Chapel of the Holy Cross in Karlštejn, Bohemia, appears to have been no less costly, being a reliquary that enshrined not only a large number of panel paintings but also many relics.

The set of these relics also included a painting of Crucifixion which, in its corresponding sections, most probably concealed tiny fragments of both Christ‘s cross and the sponge given to Jesus by one of the soldiers. Karlstein castle was a treasury for the most extensive collection of Passion relics in western Christendom [9].

However, already in the Middle Ages, the protection of objects having symbolic value came to be extended to comprise certain other categories that - according to the outlook of the time - were worth preserving, not least for their aesthetic characteristics and effects. Medieval sources refer to the taste of the lover of art objects, which is firmly vested in sensual perception. Alcuin admits that it is easier to adore “objects of beauty“ than God; however, if these objects are enjoyed with the underlying aim to better love God, then this propensity to *amor ornamenti* can be reasonably supported. And if spectacular churches are thus not to be subject to contempt, it is understandable that due time and energy should be spent on preserving and restoring these buildings or objects [10, p. 14]. The Middle Ages were not a period of moralistic denial of sensually perceptible beauty. Beauty was a value if consistent with the truth, good, and other attributes of divinity [10, p. 26]. For this reason, the work of abbot Suger expressed love of the beauty of the House of God and contained a rich description approaching the art treasures of Saint-Denis, a description written to prevent the eventuality that “...Oblivion, the jealous rival of Truth, sneak in and take away the example for further action“. Here, we can identify the first evidence of monument care embodied in the effort to protect objects of the past not only as witnesses to historical events but also as aesthetic and practical agents constituting applicable examples for future artistic creation.

As outlined within Suger’s text, relics of the past were valued throughout the Middle Ages especially for being a memory and information storage medium. If (still within the boundaries of the discussed period) we set about searching for an aspect substantiating the care of historical monuments, we could use the analogy based on the justification of the most significant storage medium of the times – the painting. From the papacy of Gregory the Great, there had existed the well-established message summarized by Thomas Aquinas within his authoritative substantiation of the essence present in Christian paintings: “first, for the instruction of the masses who could not read; secondly, that the mystery of the incarnation and the examples of the saints may be the better remembered; and thirdly, that pious feelings may be excited, as men are more easily moved by what they see than by what they hear.“ [10]. It is not by mere coincidence that the medieval theory justifying the existence and defending the acceptability of paintings was, with its argumentation, transferable to the justification and defence of the monument as an individual relic. And, interestingly, current texts defending or clarifying the reason for the preservation of monuments contain similar arguments (only the sitmulation of religious piety or devotion could be effectively replaced with aesthetic feeling). Thus, today the monument constitutes a sort of secular relic, which (as correctly noted by Riegl) simultaneously becomes a peculiar cult and a living reminder of the past. Analogically to the paintings of the Middle Ages, the preserved artefacts are a privileged location of memory, joining the commonly shared meaning with the real social space, the concrete corporality, and the individual experience [4, p. 172].

New quality was brought into the care of historical monuments by the Rennaissance, mainly because the evaluation and related protection of historical locations or objects was not based on the application of symbolic values but rather on the appraisal of artistic and historical characteristics. Perhaps it would be more apt to say that the Rennaissance gave birth to a full-scale (or more generally oriented) protection of monuments [12].

And this novel approach can be well demonstrated on the example of Rome of the Rennaissance: In the Eternal City, which had succumbed to centuries-lasting decay, various methods for the protection of the numerous historical treasures were progressively sought. Already in the 6th century, at the time when the imperial court was moved to Byzantium, the financial resources supporting the maintenance of most Roman monuments dried up, and the major part of Rome fell into ruin despite the decrees repeatedly prohibiting destructive action on the buildings. “During the Renaissance, European scholars and artists rediscovered Greek and Roman antiquity. Artefacts, books, thoughts, paintings and architecture were invested with special meaning and considered models of inspiration and imitation“ [13, p. 12]. The overwhelming spirit of the time can be well shown using an observation by Francesco Albertini, which aptly read *Roma quanta fuit ipsa ruina docet*. Even though scholars and artists of the Rennaissance held Antiquity in high esteem and strove for its rebirth, little was done to preserve the monuments still standing. Thus, “the demolition of ancient remains skyrocketed during the Renaissance in Rome“ (cf. [14], [8]), since all the interest in objects of the past was easily beaten by economical approaches: if, at the time, the cost of transporting masonry could swiftly surpass the price of the stone and rock, then the dismantling of monuments was clearly the cheapest way to acquire building materials.

Moreover, the impact of the individual edicts issued by the municipal administration to ensure the protection of Rome’s monuments was limited to a great extent, and this fact is well documented by prominent buildings such as the Colosseum [15]. A more comprehensive system of the care and research of antique monuments began to emerge in the first years of the 15th century, only after the Papal Court had returned to Rome.

In 1515, pope Leo X appointed the painter Raphael the “Prefect of all marble and stone“ and invited him to commence a systematic survey of the monuments of the city. Consequently, and probably no later than this very moment, the monuments of Rome ceased to be regarded as a mere resource of cheap building materials [3, p.2]; even though there still appeared cases of misuse affecting the monuments, they already attracted wide criticism. When, a century later, pope Urban VIII of the Barberini family decided to remove the bronze roof from the Pantheon portico and had it used for the casting of 80 cannons located in the Castle of the Holy Angel (rather than having it applied for the construction of St. Peter’s baldachin, as claimed by the contemporary diarist Giacinto Gigli), the locution *Quod non fecerunt barbari fecerunt Barberini* started to circulate widely around Rome [16]. Then, Urban VIII was not much helped even by his effort to have a new roof fitted.

Within the period, the interest in monuments awoke also in the Transalpine region, where it was not based on recognizing the achievements of Antiquity but rather on the desire to learn more about local history and the available material evidence. John Leland, the antiquary of king Henry VIII, compiled a sort of topography of England, a document to be followed by William Camden’s book *Brittania* (1568), which may well have been the first preserved guide to the antiquites of a single country, comprising objects from Stonehenge and Roman buildings to the Saxon work preserved in later churches [3]. Through the 16th century, topographies appeared in a wide range of regions across Europe. In Denmark compiles Ole Worm, Flavio Biondo in Italy and Johan Bure in Sweden. Formally, the growing interest in relics of the past was accompanied by the transition to more systematic care of monuments; thus, in the 17th century, legislative measures ensuring the protection of monuments began to appear at ever more narrow intervals, and the involvement of the state in the preservation of surviving relics came to be markedly emphasized.

In 1624, the administration of Rome released an edict that “banned proprietors of works of art from selling them beyond the borders.“ Additionally, “no excavations could be undertaken without the supervision of the Papal Commissioner, and any work of art accidentally found had to be at once declared.” [17, p. 128]. As regards northern Europe, the first systematic decrees aimed to secure the protection of monuments were issued in Sweden, where, in 1666, all field monuments were declared property of the Crown and enjoyed protection as heritage of the Swedish people. The decree enumerates castels and ramparts, cairns, standing stones, tumuli and barrows [17, p. 128]. Three years later, this protection was extended to portable antiquities [3].

Besides the legislation, the 17th century also brought an emblematic watershed in the care of historical monuments: The discussions of rebuilding or demolishing old constructions then became increasingly more dominated by advocates of preservation. This ideological change can be related to the completion of two significant events which, to a certain extent, symbolized the metamorphosis of the approach to monuments. These acts of importance consisted in the reconstruction of both St. Peter’s and St. John Lateran’s basilicas; here, the former case involved total rebuilding, while the latter one was predominantly conducted with the aim to conserve the existing status.

St. Peter’s Basilica was left to decay during the Avignon captivity and the subsequent schism. Even though reconstruction work commenced in 1442, it was interrupted shortly after, and in 1506 pope Julius II finally decided that a new building would be erected. The reconstruction therefore comprised not only complete demolition of the old basilica but also inevitable destruction of other buildings, namely those that occupied portions of the space in front of St. Peter’s. Even as late as 1660 the Palazzo Branconio dell'Aquila designed by Raphael had to be torn down to make room for Bernini’s colonnade: Thus, the value embodied in a new building was clearly preferred to the historic basilica and to the work by Raphael, then already a well-recognized artist.

This act of radical reconstruction was nevertheless contrasted by the approach to the restoration of the Lateran Basilica, which was conducted between 1646 and 1650. Interestingly, the rebuilding was accompanied by the clash of two equally supported attitudes. To acquire a more detailed insight into the contradictory opinions, let us notice that “some people wanted to demolish the whole building down to the footprint of Constantine's basilica and build a completely new church. This idea was supported by 'the people, always the friends of novelty' … The second party was the preservationists. … They reminded the pope that the church was made with spolia from pagan temples, re-used as a sign of the triumph of Christianity. Rome could not be deprived of its cathedral, and the world would be appalled to hear of the demolition of the *caput et mater* before a new church could take its place.“ [18, p. 529]. Eventually, the conservationist approach prevailed and reflected itself in the preservation of the ground plan and fragments of materials used in the old church. And the manner in which these aspects of the original building were presented in the restored object was influenced too; the oval openings above the niches for the apostolic statues exposed masonry of late Antiquity, which was interpreted by many as the intention of the designer. Thus, the restored Lateran Basilica would have constituted a large structured reliquary for the early Constantine’s basilica, with the original pattern of the church preserved in both the layout and the material form [19, p. 243]. From the 17th century onwards, the idea behind the systematic care of historical monuments and creative preservation gradually gained in strength and acquired support of public authorities.

But then there also occurred a perceptible leap towards acceleration of monument care, and this was paradoxically brought by the huge wave of destruction instigated by the state administration of major European countries. The ruination and plundering of sacred objects became a part of the French revolution, German secularization, or the reforms directed by the Austrian monarch Joseph II. These excesses of progress were only several years later countered by Romanticism, which found a mighty ally in the emerging identities of individual European nations. The sentimental looking back to the past is what connected Romanticism with the interest in the elapsed periods and the effort to preserve the existing material evidence of the contemporary times. The term *historical monuments*, which can be related to the Rennaissance-based concern for the relics of ancient Greece and Rome, spawned in the 19th century the notion *national cultural heritage* applied mainly in connection with the construction of national identity [13, p. 23]. The reinforcement of nation states was accompanied by an intensified pressure to secure the care of significant national monuments, relics that indicated the actual level of the (purported or mythic) cultural maturity and historicity of the given nation. This process was obvious especially in France, where monuments came to be protected in response to the destruction and desecration of ecclesiastical relics (and their reselling as building material, which occurred in locations such as Cluny); symptomatically, the protection thus granted was justified as the care of national values. And it was France that gave birth to the terms *national monument* (Monument national) and *public museum* (Musée public). In a society where the strength of the cult had dwindled, the care of all evidence of the past was taken over by the government. Across Europe, a vital prerequisite for the construction of nation states consisted in the invention of the national cultural heritage, whose conservation became a national interest. But it was not until the 20th century that some monuments ceased to be protected as mere “parts of the national being“ (within the interpretation by Georg G. Dehio), and their preservation was transformed into an interest of the whole mankind – a transition that has been embodied since the middle of the 20th century in the introduction of a monument to the list of world cultural heritage.

Thus, out of cultural turbulences of the period, the approach was born that could be without difficulty denoted as active care of historical monuments. Thanks to the effort made by artists such as Karl Friedrich Schinkel, Viollet-le-Duc, and their followers, relics of the Gothic times were rehabilitated and restored. John Ruskin, in his long essay titled The Seven Lamps of Architecture, explicitly formulated the opinion that was to become the dogma of the future care of monuments: The monument is, above all, heritage. In Ruskin’s words, “*be it heard or not, I must not leave the truth unstated, that it is again no question of expediency or feeling whether we shall preserve the buildings of past times or not. We have no right whatever to touch them. They are not ours. They belong partly to those who built them, and partly to all the generations of mankind who are to follow us.*“ [1, p. 74].

Through the ages, a multitude of arguments had accumulated in favour of preserving old objects, and the 19th century, in which the care of monuments began to be institutionalized, already witnessed the need to systematize and evaluate the accrued requirements. What should be protected, and why? Do we protect the archetypes for future generations, as proposed by abbot Suger? Or is it more fitting to say that we conserve evidence of the past owing to its symbolic continuity value, in the same sense that the walls of the original Constantine’s basilica are secured by the Borromini architecture? Do we protect monuments for didactic purposes, following the path trodden by the Rennaissance humanists, who sought to know their history? Are relics of the past preserved as proposed by John Ruskin, namely as the property, the heritage we are obliged to pass on to our descendants? Does purism constitute the aim of restoration, or is it necessary to respect valuable contributions of all epochs?

At the end of the 19th century, the trends within the conservation and protection of monuments had produced attitudes so strong and contradictory that the time was ripe for a comprehensive theory of the care of historical monuments, a theory that could not only summarize and classify the existing knowledge but also indicate an optimal form of care. Suddenly, the crucial question of *what to protect* grew to include the new, equally important elements of *how* and *for what purpose* the protection should be done.

CLASSIFICATION OF MONUMENT VALUES

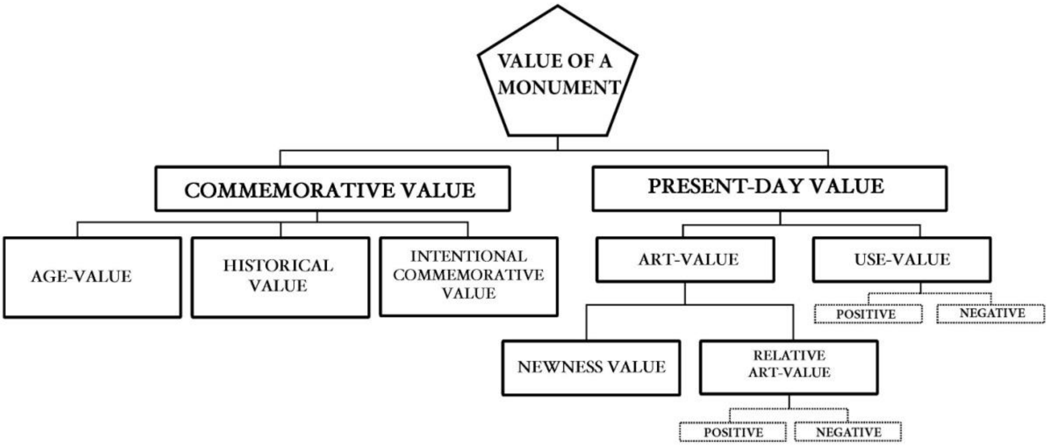
A comprehensive theory summarizing the monument values then known was proposed by Alois Riegl in his long essay *Der moderne Denkmalkultus* (The Modern Cult of Monuments: Its Character and Its Origin). This work had originally been conceived as an argumentative report justifying the plan to reorganize the care of public monuments in Austria, a report that served as the basis for the preparation of the act on monument care. Riegl captured, very carefully and in a precise manner, the long-term metamorphosis of the substance and requirements peculiar to the so-called cult of monuments, and he also described the resulting imperative of theoretical definition and practical reorganization of monument care.

Riegl’s analysis begins with the characterization of the notion of *monument*; at this point, the author also classifies monuments into intentional and unintentional. In this respect, an intentional entity is defined as “a human creation, erected for a specific purpose of keeping single human deeds or events” [20], thus being virtually a memorial or a monument of memory. This element is then contrasted by an unintentional entity, likewise created by humans yet purposed differently. Unintentional monuments came into being to satisfy practical needs of one or slightly more generations and were not intended by their builders to become relics or evidence passing to the future generations a message of the respective times and their artistic or cultural activities. Thus, these monuments were not the “privileged place in memory” but a purely practical substance, a good whose main value consisted in the provided utility (benefit); this aspect was only later, through the time, joined by values related to ageing. And it is also important to note that the perception and evaluation of unintentional objects was brought by the 19th century as a novel approach, one that necessitated changes within the structure and competences of monument care.

Riegl himself connects the basis of his work with the oldest strata of the care of historical monuments, and he most vividly does so by claiming (already in the title of his essay) that, in our presence, any evidence of the past may become the object of a cult; such cult then comes out of the age of the relic, helps to create its value, and – in a peculiar manner - further elevates the monument. However, as the text of the essay flows on, the author begins to apply exclusively the notion of *value*, which constitutes a universal expression of various types of monument importance.

In the introduction to his theory, Riegl classifies monument values into the sub-groups of the commemorative value and the present-day value. The former is a subjective construct because the acts of signifying a certain good as a monument and determining its commemorative value are based on the period-specific perception of the monument as a record (or evidence) of the past. Riegl constructs the commemorative value as the evolution of the perception of various monument values; he thus starts from the oldest one, the *intentional commemorative value*, which is natural only to intentional monuments, proceeds through the *historical value*, which began to be strongly accentuated in the Rennaissance period and comprises the data of the monument's origin communicated to us by the relic itself, and ends with the *age-value*, which is given by the non-contemporary appearance of a relic and came to be appraised within Romanticism and the later periods. To this point, Riegl relates his theory to the older tradition of monument care as well as older texts reflecting monument values. Then, however, he introduces yet another value type, the *present-day value*, which congenially anticipates further development within the care of monuments and facilitates the understanding of relics as cultural capital, a phenomenon of benefit both spirtiual and material.

The present-day value of monuments is based on present needs, respecting the principle that "most modern creations satisfy the senses and the intellect as well as if not better than older monuments". If this value is based on satisfying the senses, Riegl recognizes it as the *use-value* of a monument; however, if it starts from and reflects spiritual needs, the value is denoted as *art value* and can be further divided into the *newness* and *relative art* values.



Commemorative values consist of three significant sub-groups:

The *Intentional commemorative value* is peculiar solely to intentional monuments, which, from their moments of creation, function to perpetually commemorate a particular event or person. The aim behind intentional monuments is to make a particular point in time perpetually present, or to keep it from drifting to the past and make it perpetually present and alive in the minds of the future generations.

While the *age-value* consists exclusively in decaying and the *historical value* aims to – starting with the present day – withhold any decay, the intentional commemorative value requires the intransience and perpetual presence of the work as shaped at the moment of origination.

Any traces of disintegration must be broken and eliminated, for the reason that “the intentional commemorative value has, since the very beginning, since erection of monument, a specific purpose: never allow a certain selected moment to become the thing of the past, maintain future generations awareness of this event” [20].

The *historical value* of monuments consists in the representation by this value of a certain stage in the evolution of mankind. Generally, it is to be maintained that the higher the degree of preservation of the whole original monument, the higher the value. The motive behind the preservation of the historical value consists in striving for the inviolability of a monument. However, the aim here is not to preserve the traces of age but – with a prominent view to the contemporary beholder and the future research in the history of art – to preserve with the least possible degree of distortion the information concerning a monument. The historical value therefore attempts to conserve the status of a relic at the moment of its inclusion in the cult or monuments.

The a*ge-value* represents the appreciation of the non-contemporary appearance of a monument. This appearance or style of a monument expresses itself by a certain incompleteness, lack of wholeness, and tendency to dissolve form and colour. The criteria applied in the process of appreciating age-value embody a sort of aesthetic revolt of the 19th century, a revolt against the aesthetics of newness and progress, which dominated the century together with the rapid expansion of industry and trade. A typical example of appraising the age-value, being a value not acquired through intellectual reflection but mediated via emotion, lies in the Romanticism-based cult of the ruin.

The *present-day values* include two sub-groups:

The *use-value* inherent with a vast majority of unintentional monuments, which, for that matter, came into being for the purposes of practical use. As proposed by Riegl, the main criterion of this value is the sense of the satisfaction of practical needs. For unintentional monuments, at the present time, it is possible to derive the requirement that they are “live“ and serve a purpose, mainly because in their essence they are not defined by the *intentional commemorative value*. And the object indeed offer diverse experiences: Visiting a villa by Palladio, where every step shows traces of the family life led by the current owner, is substantially different from visiting the functionalist Villa Tugendhat, an object that – though carefully restored – has become a monument entirely devoid of such forms of life. Thus, the preservation of the use-value constitutes an exceptionally important aspect of monument care in unintentional relics.

The *art-value* was interpreted by Riegl as the appreciation of a monument from the point of view of a contemporary human being.

This value comprises two sub-groups:

The first entity consists in the *newness value*, which is shared between the art-values of the current and the past art epochs. The newness value appreciates solely the wholeness of form and colors because, as seen by the people (the crowd), the thing that is new is also beautiful. The mere dignity of the owner and his need of status presentation both require the removal of any traces of age. And the aspect of age that exposes the monument to decay and caused it to lose its newness value; this quality can be restored only through eliminating the traces of age and renewing the form and colours, namely via intervention which will provide the relic with the character of a newly conceived object.

The newness value stands in sharp and overwhelming contradiction to the age-value, since this value is founded upon the decay of the form and colour.

The second sub-group relates to the specific character of a monument, its forms and colours; these are the elements whose effect at the time they were conceived differed from the impact seen today. This effect is described as the *relative art-value*; Riegl emphasizes the non-objectivity of the value and its metamorphosis through time. As regards the relative art-value, Riegl connected his outlook with the then newly emerged view that each style is justified within its time and has its own ideal of beauty reflected in contemporary art. This value was denoted as *relative*, mainly because in Riegl's time the concept of a single canon of art providing *absolute* art-value to monuments had been refuted. In the mid-19th century, however, this opinion was still generally accepted, and the higher evaluation of monuments from certain periods was explained using the argument that the artistic production of precisely these periods came closer to the objective canon of art or the absolute art-value. In Riegl´s time - and obviously even more vividly in the current period - the feeling prevailed that there does not exist anything like absolute art value. Within the context of the care of monuments, Riegl used this notion to claim that, in different periods, different parts of relics are appreciated, and these parts are usually those that correspond to the aesthetic requirements of the time. Thus, Riegl helped to overcome the existing dogmatism in both aesthetics and style, which accentuated the so-called progressive art styles (such as the Rennaissance) and neglected those that could be labelled as regressive (such as the Baroque style). For this reason, monuments were not to be protected solely on the basis of the contemporary taste, mainly with respect to the future generations, whose taste may be subject to change). These conditions prepared the ground for further extension of monument care in such a manner that newer monuments would be included (such a industrial architecture).

Already the first sight makes it apparent that the system, conceived as outlined above, is intrinsically contradictory. Contradiction is a feature of the care of historical monuments; here, it always has to be defined which values should be preserved and which ought to recede. Thus, the preservation of the historical value is often realized at the expense of the use-value and vice versa. The fact that not all monuments can be preserved to the same extent is the defining limitation of monument care, where we regularly need to identify the aspects of the past that are to be maintained for the future. Moreover, the system is dynamical, in the very tradition of any system of values. Values "are subjected to cultural and educational processes, and may change over time" [13, p.6].

Riegl's system probably constitutes the most sophisticated approach to the identification and classification of monument values; it is a well-disposed system that reflects the metamorphosis of the general character of monuments in the 19th and anticipates the development within the 20th centuries. Even though the problem of monument values was later analyzed by a larger number of authors, none of them proposed a manner of systemization with precision to match Riegel's (cf. [21-26]).

CAPITALIZATION AND RATIONALIZATION OF HERITAGE VALUES

Characterizing the care of monuments of the past as the care of a specific system variable through time is a very complex answer to the question of what should be protected and how the protection should be carried out. However, this attitude indirectly help us to find anwers to the question of for whom, in fact, the existing monuments are protected.

We conserve monuments with the future in mind, since the future will adopt the entire group of relics together with the inherited system of values, which may possibly be further modified. “For human progress to occur, each generation must refine the values it inherited from the last, and then must pass those enhanced values on to the next generation through the socialization of its children“ [27, p. 201]. The care of monuments, though pushed ahead and requested only by a part of society, therefore seeks to maintain the memory of civilization, thus benefiting everyone not only materially but also spiritually or in the aesthetic sense. The preservation of monuments thus supports the creation of seminal aspects within the elementary outline of cultural literacy.

If the 19th century witnessed the successfully fought battle of the underlying sense behind monument care, the 20th century saw the attempts to base the care of historical monuments upon rational ground. The characteristic problem of the 20th century care consists in searching for the answer to the question of how to make the maintenance of monuments more rational, or desired and enforced by people (proprietors). And rationality – contrary to the emotivity of the earlier monument care – became the feature of the 20th century approach. The very beginnings of rationalization within the discussed field can be related to Ruskin, who, together with the notion of *heritage,* introduced the economic accent to the care of monuments; importantly, this facet was to be strengthened substantially through the 20th century by the introduction of the system of monument values. If a monument constitutes a value, then the rational approach is to preserve and multiply this value. From here, only a step remains to the current interpretation of monuments as a part of the cultural capital, which enriches us both materially and symbolically.

An indisputable contribution of Romanticism consisted in the fact that the care of monuments was realized by employing the most significant institutions of the time – the state and its laws; analogically, the main benefit brought by tourism was the ability to exploit the market and its resources as the most intensive force of the 20th century. At the moment when a tourist appeared to be willing to pay for the experience accessible through visiting a monument, he made the preservation of monument values an object of the economic interest. Thus, the preservation was secured of many relics individual or combined, and the monuments became well-marketable articles worth being invested in by both local authorities and individuals.

If we establish a connection between the roots of European tourism and medieval fairs, we will recognize that the beginnings of tourism economically benefited large spiritual centres and places located close to holy temples, sanctuaries, or pilgrimage trails, mainly those leading to the tombs of St. James and St. Peter. In the Rennaissance, artists and noblemen began to often travel to centres of culture and continued to do so in the later periods. The 17th century brought the phenomenon of Grand Tours [28], and the 19th century witnessed the genesis and development of travel agencies such as that of Thomas Cook. However, despite the marked wave of tourism sweeping through the time, travelling abroad did not cease to be an instance of luxury reserved for the higher society. International tourism gained momentum only in the mid-20th century, when its faster development was underlined by the expanding air transportation.

And these rapid processes within travelling made a significant contribution towards the eventual recognition of the fact that cultural capital can be relatively easily transformed to capital, not excluding its profits. Thus, the care of historical monuments came to be firmly associated with such terms as *tourism* or *regional* development.

Thanks to these changes, there occurred certain shift in the perception of the monument. The use-value, until then accessible mainly to the owners, metamorphosed into the market value; this change then brought profit to both individuals and companies. Therefore, the growing volumes of tourism are accompanied by the awareness of how the inherited cultural capital can be valorized, thus retroactively generating strong rational interest in the protection of monuments. For example, in Europe alone tourism accounted for 8% of total employment in 2012, and the total contribution of travel and tourism to the GDP was 8,2% (www.wttc.org). The intensive involvement of economics within the discussed field produces ever more potent interest in the preservation of those components of capital that support this segment of economy.

Yet even here it is still true that positive development poses certain dangers [29]. The tourism industry changes tradition into a show and separates monuments from their original function, which constituted a revitalizing agent. The number of people living historic centres of towns and cities deeps dwindling, mainly because the residential function of buildings has been largely replaced with service businesses, tourist attractions, and hotels. Tourism also performs the function of negative homogenization by suppressing local features and supplanting them with artificial reality. “Places have become absurd and synthetic ... made up of the surrealistic combination of history, myth, reality and fantasy that have litlle relation ship with the particular geographical setting” [30, p. 594].

The confined space of historic centres is very often overwhelmed by tourists; consequently, there occurs the paradoxical process of the enlargement of tourist areas and facilities, a procedure performed at the expense of monuments that constitute the real tourist destination and aim of travelling. This progressively means that ever more people can see ever less monuments. And the monuments lose their existence as national symbols to become *international* relics of the era of globalization; thus, the stability and continuity of the local community embodied in the monument as a symbol of home are being displaced by the variability and discontinuity of tourism.

CONCLUSION

In spite of the difficulties and everyday failures accompanying the care of historical monuments, to say that we are living in a lucky time is no exaggerated claim. The monument care of today has been built upon a remarkable symbiosis of cult and rationality, it is a well-established and respected constituent of society worldwide. The system of monument values can be described as stable, and we are capable of not only providing exact definition of the different values but also deciding which of them should be preferred. Hitherto unseen technological means are available to shift the care of monuments to top levels of quantity and quality. We are living at a time when all significant factors act in favour of monument protection. Most countries of the world are not being made to face major armed conflicts, world societies are enjoying unprecedented economic prosperity, and education based on tradition is widely held in high esteem. The spiral of social development still exhibits the tendency towards moving upward, which means that the growing standard of living increase the demand for tourism and produce economic pressure to preserve monuments as one of the forces behind regional economic growth.

Thus, further rise in living standards is supported. The demand for monuments increases steadily, and the number of objects, groups, and sets included in the care of historical monuments is being extended. Importantly, the rising levels of education enable people to appreciate evidence of the past, and the presentation of monuments contributes to the general increase in education. Moreover, prominent monuments are protected not only as national treasures but also as world heritage, and they enjoy international protection within UNESCO and various multilateral agreements. In a large number of historic places, the protection of monuments defines the character of the town or city and constitutes a decisive criterion for its further development [2]. The idea of monument care is well established worldwide and promotes the active positive approach to relics of the past, objects that create the basic outline and structure for the transfer of knowledge related to diverse cultures.

It is obvious that monument care is essentially a conservative activity and will thus experience further clashes with other progressive social streams and movements; similarly, the care of historical monuments will also be exposed to eventual civilization problems or breakdowns. In the same manner as churches or spiritual communities, monument care is made to search the balance between the effort to preserve the substance of the cult of monuments and the necessity to facilitate further development of society and reaction to possible changes. The multilayered basic of the care provides us with the hope that out past will have a future too.

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Chapter 2

DOCUMENTATION OF CULTURAL HERITAGE

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ABSTRACT

Humans can build real masterpieces that amaze mankind for centuries. However, they can also destroy everything created by their actions, not only during armed conflicts, which still plague part of the world today, but also through daily actions that cause deterioration of these works. If we add the damage caused by natural phenomena such as earthquakes, volcanic eruptions and floods, together with natural ageing, it becomes clear that plans to safeguard cultural heritage must be established. Preservation plans should include the need to gather as much documentation as possible, to be able to restore cultural heritage to its original state.

The Athens Charter for the Restoration of Historic Monuments was adopted in 1931 and highlights the need to establish a cultural heritage protection plan. This necessity was later confirmed by the Venice Charter of 1965, and more recently in its latest version (2008). All of these charters express the need to document cultural heritage for its conservation.

This chapter presents methods for capturing and managing spatial information on cultural heritage, in a broad sense. It focuses on two areas that can help to achieve aims: the data capture methods required before restoration work begins, and how to manage and present data in order to compile the most comprehensive documentation possible. The data discussed here is known as geospatial information.

Geospatial information is used in the preservation and restoration of monuments and buildings, etc. Here, we review traditional data capture techniques, such as conventional photogrammetric and topographic surveys, and describe the latest sensors, including terrestrial laser scanners and Unmanned Aerial Vehicles (UAVs).

Keywords: Architectural survey, photogrammetry, laser scanning, GIS, cultural heritage documentation

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INTRODUCTION

Knowledge about the localization, interpretation, study and evaluation of cultural heritage is one of the main requirements for its protection. Therefore, it is of the upmost importance to compile the most complete documentation possible on the historical heritage of any town, nation or culture, to document and transmit its artistic and historical value. Thus, access to this information can be ensured for present and future generations. Moreover, comprehensive documentation is absolutely necessary for the restoration and rehabilitation process.

This necessity was determined in the Athens Charter of 1931, and later confirmed in the Venice Charter of 1964, drawn up at the Second International Congress of Architects and Specialists of Historic Buildings. At this meeting, arrangements were made to establish heritage protection plans. In November 1968, during the fifteenth session of the General Conference of UNESCO, which took place in Paris, a recommendation was approved on the conservation of cultural properties (scientific, artistic, archaeological and historical monuments) that could be in danger due to public or private construction [1].

In the Paris Charter of 1972, UNESCO published a recommendation on the protection of each state’s cultural and natural heritage of each State. Article 29 establishes that each member state will draw up an inventory of cultural and natural heritage, including properties that are inseparable from the surrounding environment that contributes to their character.

More recently, the document “Terminology to characterize the conservation of tangible cultural heritage” was presented in New Delhi during the Fifteenth Triennial Conference of the International Council of Museums (ICOM-CC), held in 2008 [2].

The highest authorities are also clearly concerned with safeguarding heritage. For example, through various reference texts (agreements, declarations, recommendations, resolutions and charters), the European Council has sought to protect European cultural heritage, especially architectural and archaeological items [3]. The Spanish Ministry of Culture [4], through the Sub-Directorate General of Historical Heritage Protection and the Institute of Cultural Heritage of Spain (IPCE), has worked to expand state collections, channel methods of acquiring cultural items from museums, libraries and state archives, invest in cultural heritage, increase coordination and communication between autonomous communities, and focus on international cooperation, as well as conservation and restoration. For this reason, the Sub-Directorate General created the concept of a “*Bien de Interés Cultural*”; an item of cultural heritage. This is a legal form of protection of Spanish historical heritage for personal property and buildings. In this context, “building” is classified as: a monument, historical group, historical garden, historical site, archaeological zone, paleontological zone, ethological point of interest, archaeological park or protected archaeological space.

Other organizations have established the need to document heritage as a first step towards its preservation and transmission, while maintaining its present purpose and respecting its cultural, social and spiritual significance. Since their constitution, the International Committee for Documentation of Cultural Heritage (CIPA), which is the founding organism of the International COuncil on MOnuments and Sites (ICOMOS), and the International Society of Photogrammetry and Remote Sensing (ISPRS) have worked to keep up-to-date with technology and to guarantee their usefulness in the conservation of cultural heritage, education and dissemination.

CULTURAL HERITAGE RESTORATION AND ACTIONS

Actions are needed to preserve heritage, in order to prevent major deterioration and to guarantee stability and continuity.

Cultural Heritage preservation actions are carried out in the following fields: architecture, to restore, reconstruct or stabilize buildings; archaeology, to excavate sites and preserve excavated pieces; and art, to restore paintings and sculptures.

In the process of architectural, archaeological or art restoration, the maximum amount of information is needed to work on the objects. Objects of cultural heritage value should only be restored when absolutely necessary, and models must always be handled and reconstructed with the utmost care.

Architectural constructions are restored or rehabilitated when they are in need of conservation or repair. Restoration and rehabilitation are defined as the methods and processes that allow us to bring back different elements of the construction, its forms and original characteristics. Several techniques can be used to restore historic buildings, but they all require fully comprehensive documentation prior to action. Above all, topographic or photogrammetric surveys (*rilievos*) of the state of the building must be carried out with the highest possible precision. Such surveys require data capture techniques that are explained in this chapter.

One of the first tasks consists in locating the heritage item, which may be hidden between layers of earth or at the bottom of a lake or sea in archaeology. This is the reason why Non-destructive reconnaissance and prospecting techniques are needed to localize sites [5, 6].

In archaeology, the term “prospecting” goes beyond the geological definition of exploring underground in search of hidden sites. It includes the study of a zone of geographical interest and the use of various techniques to superficially analyse the terrain and any archaeological sites it may contain. The most common factors that affect prospecting are the accessibility and visibility of the terrain, as well as the perceptibility of sites [7].

In all cases, a preliminary analysis of potential sites is necessary. Previous information on the area of interest is examined (topographic maps, aerial photographs, toponyms and historical descriptions). Toponymy is analysed in particular, as the possible origin of a place name could indicate that a site is of special interest. Then, field work begins with a search, localization and site registry.

Excavation is still the main archaeological method. It involves not only extracting objects from underground, but also registering and leaving written and drawn evidence of everything that is found, so that the relationship between each object and its surroundings can be studied. Excavation is destructive and all unregistered items could be lost. Non-destructive exploration methods include the use of data capture techniques to visualize hidden elements without the need for excavation. This technique has its limitations, but it is complementary with, and sometimes replaces, classical excavation.

In the field of archaeology, localization, diagnostics and prospecting methods show a strong importance to allow us to protect, conserve, investigate and disseminate cultural heritage.

The process known as stratification examines the consideration of construction systems and the materials used in different stages of construction which appear found at archaeological sites.

It can help us to establish habitability and social aspects of cultures. In this field, the use of geographic information systems (GIS) has a considerable impact due to its versatility and ease of management of any type of data recovered during excavations.

In recent decades, a term has appeared that combines two disciplines: the “archaeology of architecture”. It was first used by Tiziano Mannoni [8], and refers to reconstructing the history of existing buildings through observation and documentation of the materials and construction techniques used by preindustrial artisans, and to the seriation of building systems to establish the chronological order of construction stages in different historical periods [9].

As in archaeology, the method involves analysis of stratification. It contributes to the study of construction systems and materials, and provides information on the work that has been carried out over time on historical heritage buildings. In the method, technologies based on graphic representation combined with alphanumeric databases, i.e a GIS, are of fundamental importance to obtain precise, complete documentation [10].

Art is another field in which restoration work is carried out. Before a work of art is studied, in-depth information is required about its distinctive features, including the production techniques, the state of inner layers, and possible prior interventions. If we have the maximum amount of information about an object, we can act accordingly to restore it without any damage. The techniques used in this case are based on radiology and thermography [11] and enable us to learn about the different phases in the work’s creation.

To protect cultural heritage, it is essential to gather knowledge on every aspect that facilitates its localization, dating, interpretation, study and evaluation. Information on localization may be easy to find and documentation may only require methods to capture the geometry and other characteristics.

However, the site might be hidden and require special systems to localize it so that it can be excavated and documented as required. Consequently, the next section focuses on data capture methods and on methods we refer to as “exploration”, which can be used to localize hidden heritage.

DATA CAPTURE METHODS

Scherer [12] groups report four documentation method: traditional methods, topography, photogrammetry and laser scanning. However, given the principle of obtaining coordinates, we consider that laser scanning could be incorporated into topographic methods. Thus we focus on three main groups, leaving a fourth for methods with other types of complementary sensors that go beyond the capture of visible elements, such as all the techniques of geophysical prospection and thermographic cameras.

These systems can also be classified according to the quantity and characteristics of the data obtained. In this case, we can talk about discrete and massive capture methods. In discrete methods, less data are obtained.

However, they are captured following the operator’s criteria to register all the lines to define the element. In massive methods, the quantity of information is prioritized, but the lines must be obtained from a point cloud.

The choice of measurement method should depend on the type of element that is analysed that must be documented as well as the final scale of the document.

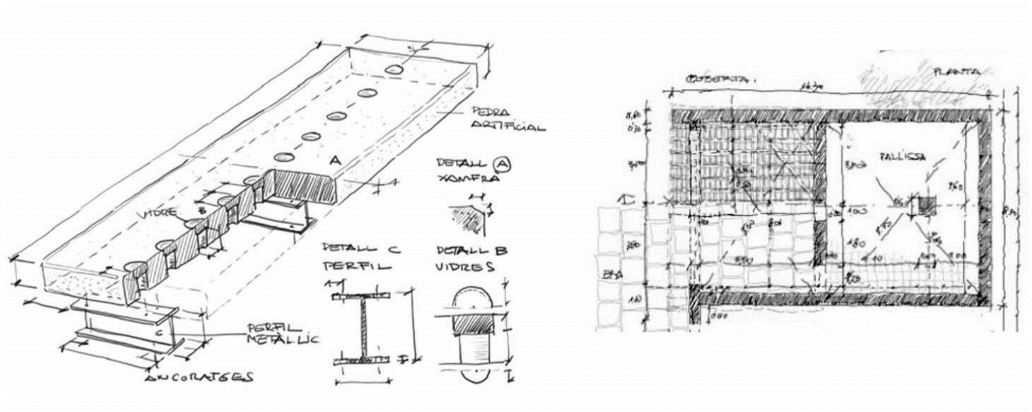

Figure 1. Sketch.

Traditional Measurement Methods

The tape measure is the main instrument in simple or traditional methods. However, it has now been replaced in certain situations by the laser distance meter. In some cases, a simple drawing or sketch is sufficient to represent the proportions of different elements of an object (see Figure 1).

Most of these methods are based on the measurement of distances in the horizontal plane to represent the planimetry, and in the elevation to obtain the gap between different elements. There are two common methods for representing elements in the plan view: trilateration and side shots -abscissa and ordinates. Trilateration involves decomposing any element into triangles from which each segment is measured. The side shots-abscissa and ordinates method consists of measuring the distance to a survey line that is generally created using another tape measure (see Figure 2). In other words, we measure on a tape that acts as the abscissa axis. Another perpendicular tape shows the measure from the abscissa to the object on the ordinate axis [13].

Each of the points can be obtained with an accuracy of around a centimetre [14].

Topography

All the topographic methods used in heritage documentation provide three-dimensional coordinates for each measured point. The instruments used vary widely, from optical tachymeters to laser scanners.

In the following paragraphs, we describe how to work with each of these instruments. Optical tachymeters measured angles more precisely than distance, and the longitude of the visuals was not excessive, which had an impact on coordinate precision. The use of an infrared light (IR) distance meter attached to a tachymeter overcame these limitations, and the subsequent integration of angle and distance measurement sensors in the same instrument led to what is known as a Total Station. The use of a laser to measure distances instead of IR is an improvement, since it allows us to measure without a prism at the point where we want to obtain the coordinates.

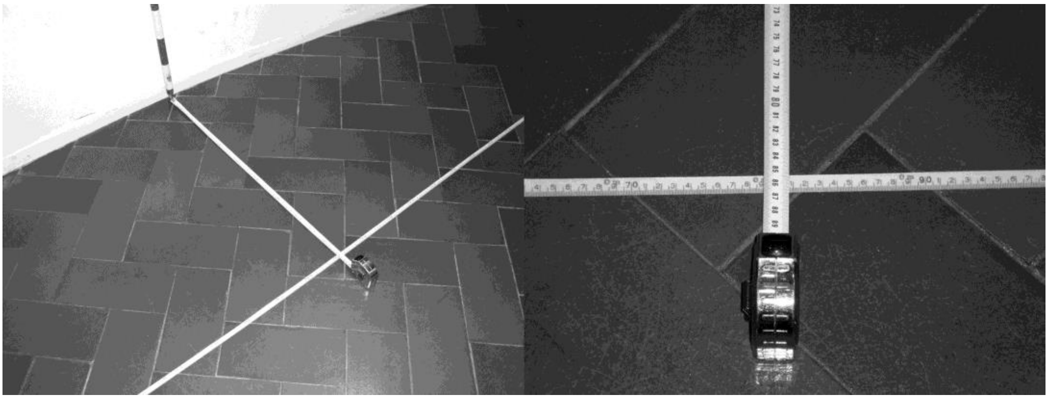

Figure 2. Side shots-abscissa and ordinates method.

This kind of survey can be used to find out the geometry of an element. However, we lose other types of information, such as the texture, material and colour, which must then be obtained from photographs. The great advantage is that it is not time-consuming, in terms of office work.

Servo Total Stations are now available, which measure horizontal and vertical angular movements and behave like laser scanners, although they are much slower. These stations are set up with a camera so photos can be taken from the point on which the 3D information is captured, to obtain information on texture.

In all of these cases, the same phases are used to obtain the data. The instrument is set up at a point where the coordinates are known and oriented towards another point where the coordinates are also known. Thus, the origin and orientation of the coordinate system are fixed. Afterwards, each point along the characteristic lines of the element is measured. The points are selected by the operator. If we work with a station that acts as a scanner, the surface of the element can be scanned along the lines, to obtain a point cloud. In this case, a capture window must be defined from a photograph taken by the station itself or by measuring the four points that define the work area. The grid spacing must be fixed both horizontally and vertically, and the station will start to measure the points automatically.

If the building's geometry cannot be defined by data captured from one station, a traverse itinerary must be observed, that gives coordinates to other station points from which the survey can be completed.

In recent years, active sensors have been used more widely in data capture. These instruments are known as terrestrial laser scanners and 3D digitizers, and can be classified into various groups, depending on the measurement method [15].

- Time-of-flight. In this case, the laser signal is concentrated in pulses that are emitted and travel through the medium until they encounter an element from which they bounce and travel back to the sensor. The system measures the time required by the light to go from the emitting source to the detector. Once the travel speed is known, the distance to the object can be calculated. This instrument provides centimetre precision for work distances in the order of hundreds of metres. Therefore, it is recommended for elements of large dimensions or landscapes.

- Phase difference. The laser signal is emitted with a determined phase and travels until it bounces on an object. Then, it travels back to the sensor with a different phase. The difference between the emitted phase and the returned phase allows to calculate the distance between the sensor and the object. In this case, a lot of points can be obtained in less time, but the work distance is reduced to maintain precision.
- Optical triangulation. In this case, the sensor has a laser emitter and a CCD sensor separated by a known distance. The laser ray impacts on the surface of the object and is gathered by the CCD. A triangle is formed between the emitter point, the receiver point and the reflected point. The triangle is calculated from the distance between emitter and receiver and the exit angle of the beam. In this case, the work distance is reduced to a maximum of a few metres, but sub-millimetre precision can be obtained from a single measurement.

In these cases, the capture is very fast but the post-process is time consuming. Georeferencing information can be obtained directly or indirectly, depending on the instrument's characteristics [15]. Some instruments cannot be stationed at known coordinates, so indirect methods must be used, such as scanning control points and targets (spheres, cylinders, etc.) or obtaining details of known coordinates that will be georeferenced once they have been identified in a point cloud. In other cases, the sensor can be set up at a point of known coordinates, or a GPS receiver can be attached to localize it. The sensor has a sight so that it can be orientated towards another point of known coordinates, so that the point cloud can be georeferenced directly. In This way all of the captures have the same geospatial reference [16].

As in traditional topography, the element cannot always be covered from one position. Therefore, we need to scan from other points. Several methods can be used to register all the point clouds:

- If the instrument can be stationed and oriented, registration is carried out directly, since the clouds are in the same reference system.
- Using control points. At least three common targets must be identified in the point clouds so that we can register them in the same coordinate system, with the spatial transformation that takes us from one reference system to the other.
- Using surface fitting [17].

Figure 3 shows an example of a survey using terrestrial laser scanning (TLS) in the Sant Sever Church (Barcelona, Spain). In this case, eleven targets, referenced with a total station, were set to capture the data. Moreover, meaningful points of the altarpiece were observed and captured, all of which allowed captures from the scanner to be transformed to the reference system established in the topographic capture of the control points.

Four bases were established. In each one, three captures were made in the vertical and horizontal positions, i.e. transverse and longitudinal positions in relation to the church.

A first data capture with 4 cm grid spacing and a second capture with a higher resolution of 1 cm were carried out for each position. The point clouds were registered with control points and the adjustment made with the orientation of 3 common surfaces (planes). The 12 available point clouds allowed us to obtain a single model with an average error of 9 mm. The final spatial model consisted of over 87 million points.

From this complete model, we could obtain a representation of the ground plans, elevations and architectural sections (see Figure 3).

Finally, we focus on structured light sensors. Although these are not scan sensors, many authors treat them as such, due to their operating system. Structured light sensors consist of two digital cameras located on the far sides of a bar and a light projector that emits a pattern of light (dots, lines, grids or circumferences) on the object. The cameras gather an image that is processed using the optical triangulation process, so that the object coordinates are obtained for each pixel of the image.

As in TLS, to complete the model of the object the sensor must be set in different positions and the point clouds registered. To achieve this, reference points must be put on the object, which in most cases consist of adhesive targets.

Figure 4 shows the result of the Venus sculpture capture. The sensor used was a 3D ATOS digitizer from GOM Optical Measuring Techniques [18]. The twelve partial captures that were obtained were registered using targets located on the surface of the sculpture. The final model has over 2 million points and allowed us to obtain a model of triangular tiles adjusted to the surface of the sculpture.

Photogrammetry

Photogrammetric techniques have been used for centuries. Meydenbauer first used this term at the end of the nineteenth century, when photographs were used to obtain architectural elevations. Due to its characteristics, photogrammetry was recommended in July 1968 by the International Council on Monuments and Sites (ICOMOS) as a technique for obtaining heritage documentation [19].

Figure 3. Architectural section obtained by laser scanning.

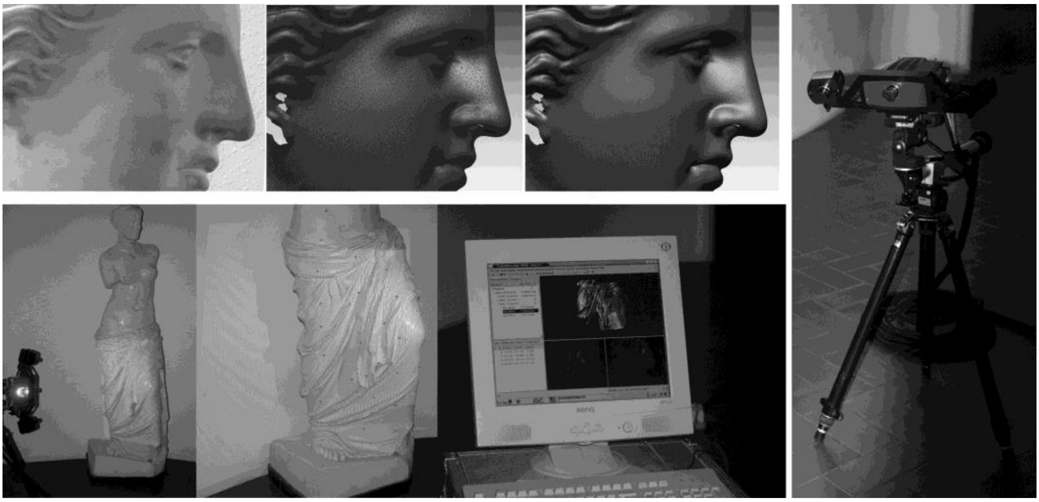

Figure 4. Top: original model, TIN and virtual model. Bottom: data capture, targets and light pattern.

Subsequently, the *Comité International de Photogrammétrie Architecturale* (CIPA) was given the mission: “To promote recording, documentation, information management and monitoring of cultural objects, monuments, groups of buildings and their environment, villages, towns, sites and cultural landscapes by the means and further development of applications of traditional surveying methods, photography, photogrammetry, laser scanning, remote sensing, information technology and management, including and integrating related disciplines and techniques” [20] (renewed on 1 January 2004).

Photogrammetric methods can be classified into three main groups according to the number of photographs used: one, two or more than two.

When the object under study is a simple surface whose elements are found on the planes, one photograph is enough to obtain the elevations. However, the photograph must first be scaled and the perspective corrected [21]. Photographic rectification is used to eliminate the photographic perspective and correct the existing displacements in the original image, caused by the inclination and the obliquity of the axis of the shot. In this case, the two-dimensional transformation that is applied is known as the projective transformation (eq. 1) and relates the two planes: the image plane and the photographed facade (Figure 5) [22].

$$x' = \frac{a_0 + a_1 x + a_2 y}{u\,x + v\,y + 1} \qquad y' = \frac{b_0 + b_1 x + b_2 y}{u\,x + v\,y + 1} \tag{1}$$

The eight coefficients can be determined if we have the coordinates of at least four points that are identifiable in the photo. However, it is advisable to know the coordinates of more points, to provide information on the quality of the results, using the least squares adjustment.

In Figure 5, the first image shows the original photograph of the partial facade of the Colonia Vidal of Puig-Reig. The second corresponds to a rectified photo in which the deformation has been corrected (only the planes parallel to the facade were corrected).

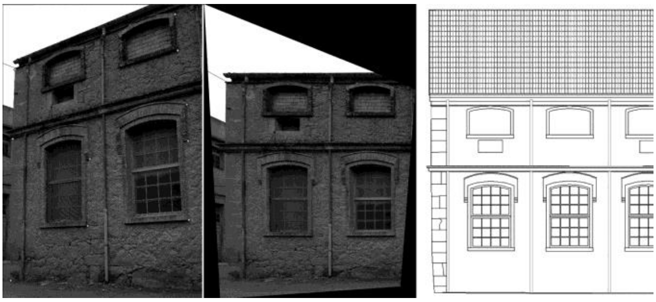

Figure 5. Original image, rectified image and vector model (Colonia Vidal, Puig-Reig).

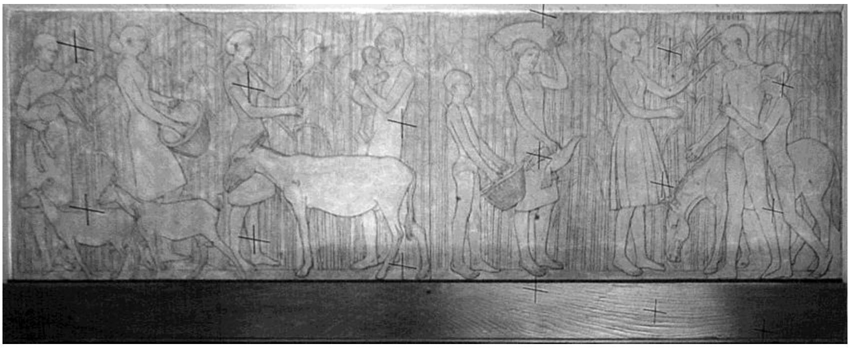

Figure 6. Rectified image of a frieze by Joan Rebull (Barcelona).

Ten control points that are spread out evenly over the facade were used in this process. After the adjustment, the largest residue obtained was below 2 cm and the RMS was 8 mm. The result was a useful metric document with a scale of 1/50. In this case, the photographs were taken with a non-metric camera with controlled distortion.

Once the digital image had been converted to a metric document, a line drawing was created to define the edges and significant details of the object. Elements outside of the facade, such as the roof, were captured by classic topography.

If the photograph is taken with a metric camera, the result is generally of better quality than that obtained with a conventional camera with known calibration, in which high residual distortions remain. Some analogical metric cameras provide better control, since they have marks printed on the original and the derived image. Figure 6 shows a corrected image obtained with a Rolleimetric 6006 camera using continuous photographic film and medium format. The marks added to the model can be seen.

When we work with complete sets (for example of facades) rather than with independent photograms, we must build a mosaic out of all the partial photographs used to complete the survey. In this process, the photographic images must be processed to unify contrast and colours and obtain a quality product.

If a three-dimensional model is required, the most suitable process is photographic restitution. In this process, at least two photographs of the element are needed, with a common zone, to obtain a stereoscopic model. The two images are named the stereoscopic pair. The camera used to take them must be calibrated and the shots have to allow good intersection of the homologue beams. In cultural heritage documentation, close-range photogrammetry is used.

In this case, to obtain a quality model, the elements must not have noticeable outlines or very different depth values, as this would complicate the establishment of a ratio between the capture base (B) and the distance to the object or depth (Z). In this situation, a base-distance ratio (B/Z) that is smaller than the aerial case is recommended [23]. The most accepted values range from 5 to 12 times the photographic base in relation to the work plane:

$$\frac{1}{5} > \frac{B}{Z} > \frac{1}{12}$$

In the photographic capture of architectural and archaeological models, the best approach is to locate the photographic base perpendicular to the optical axis. In this type of applications, the camera-object distance is very short, so the base is small. Moreover, a large depth of field (DoF) to several distances is required [24].

The coordinates of some points are needed to orientate the stereoscopic pairs and create the model. Consequently, targets or specific details of the element are measured using topographic methods to obtain the coordinates of the control points.

In close-range photogrammetry, the most common mathematical solutions in the process of determining image orientations or obtaining a model by restitution are based on collinearity equations. In this case, the coordinates of each point in the terrain are related with the coordinates of the photograph for each of the photographic positions [25].

$$\begin{aligned} x &= x_0 + \Delta x - f\,\frac{m_{11}(X - X_0) + m_{12}(Y - Y_0) + m_{13}(Z - Z_0)}{m_{31}(X - X_0) + m_{32}(Y - Y_0) + m_{33}(Z - Z_0)} \\ y &= y_0 + \Delta y - f\,\frac{m_{21}(X - X_0) + m_{22}(Y - Y_0) + m_{23}(Z - Z_0)}{m_{31}(X - X_0) + m_{32}(Y - Y_0) + m_{33}(Z - Z_0)} \end{aligned} \qquad (2)$$

where:

- x, y are the photo coordinates of the points of interest measured in each photogram
- x_0, y_0 are the photo coordinates of the principal point referred to the fiducial system
- f is the camera's focal length
- $m_{11} \dots m_{33}$ are the components of the rotation matrix
- X, Y, Z are the coordinates of the terrain points
- X_0, Y_0, Z_0 are the coordinates of the perspective centres for each position.

Another solution is based on the coplanarity condition (Terrero-Hauck condition). In this case, two photographs are related to generate what is known as a photogrammetric or stereoscopic pair.

The coplanarity condition forces both the perspective centres and an identifiable point in both photographs to belong to one plane.

$$\begin{vmatrix} b_x & b_y & b_z \\ x_1 & y_1 & -f \\ \overline{x_2} & \overline{y_2} & \overline{z_2} \end{vmatrix} = 0 \qquad (3)$$

where:

- b_x, b_y, b_z are the coordinates of the perspective centre of the right photograph, referenced to the measurement system of the left photograph
- $x_1, y_1, -f$ are the photo coordinates of the considered point measured in the left photograph, referenced to the measurement system of the left photograph
- $\overline{x}_2, \overline{y}_2, \overline{z}_2$ are the photo coordinates of the considered point measured in the right photograph, referenced to the measurement system of the left photograph.

The mixed product of these three vectors expresses the volume they generate, which should be zero. If we apply the coplanarity condition, we can determine the relative orientation parameters [26]. Once the orientation has been obtained, the stereoscopic view of the common zone of the photographic pair can be determined and the model coordinates obtained. If necessary, these coordinates can be spatially transformed to terrain coordinates in an absolute system (eq. 4)

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \lambda R \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} T_x \\ T_y \\ T_z \end{pmatrix} \qquad (4)$$

where:

- X, Y, Z are the terrain coordinates of the absolute system
- x, y, z are the model coordinates of the relative system
- λ is the scale factor between coordinate systems
- R is the spatial rotation matrix between coordinate systems
- T_x, T_y, T_z are the terrain coordinates of the absolute system.

Thus, the details of interest in the stereoscopic model can be drawn in cartographic coordinates. Alternatively, digital photogrammetric systems can be used to find and determine the spatial coordinates of all the points through automatic correlation in several photographs.

Figure 7. Restitution of the Queen Elisenda tomb (Pedralbes Monastery, Barcelona).

Figure 7 shows the process followed to restore the Queen Elisenda tomb, located in the Monastery of Pedralbes (Barcelona). The upper and lower right parts of the Figure show the stereoscopic model with overlaying vectors, while the lower left part displays the vectorial drawing. The restitution was carried out at a scale of 1/50 in continuous mode, from block-oriented models. In total, over 100 photographs with scales ranging from 1/150 to 1/250 were taken using a non-metric Nikon D300S 2.8 AF focal 20 mm camera. A total of 368 detail and control points were measured for both sides of the monument (identifiable elements such as cornices, arc vertices and sculpture details). Finally, 14 stereoscopic pairs were restituted for the inside and 10 for the outside of the church. The example was block triangulated and restituted with Image Master software from TOPCON. The final document was presented as a 1/100 scaled plan.

The results were obtained by analytical computation methods, which reduced the operator's influence and increased production. The result of the automatic correlation process is a point cloud that is similar to that which could be obtained using a Light Detection and Ranging (LiDAR) or TLS, with the advantage that characteristic lines like edges or break lines can be added prior to point cloud generation.

A large amount of commercial software for this process is now available and free software, which can produce point clouds, can be accessed on the internet. The cloud is generated once the user has uploaded a group of convergent photographs [27]. Among the free software the most extended ones are Photosynth by Microsoft and the Autodesk 123D Catch web service, and the main open-source software is visualSFM and Bundler and PMVS2. We used Autodesk 123D Catch web service to obtain a virtual model of a turtle figure at the base of a column on the Nativity facade of the Temple of the Sagrada Familia. The model was made from 50 photograms (see Figure 8), taken with a photographic Canon 450D camera with a 55 m focal objective. In all of the shots, the optical axis was perpendicular to the object, with a frame that was wide enough to gather the environment of the object, since this was used to correlate the sequential images.

To cover all of the visual obstructions, two circular itineraries were followed at different heights. The camera-object distance was kept at 1.80 to 2.00 m to obtain a representation scale and a final resolution for the uniform grid (see Figure 9). The precision of the grid was a little less than 0.7 mm in the optimal parts, and 1.1 mm in the furthest areas.

To obtain optimal results and avoid excessive contrast, the capture must be carried out with light that is as even as possible. In addition, we must take into consideration that the base document is the photograph in these systems of obtaining three-dimensional information. Therefore, the error increases with the camera-object distance. This is why the camera sensor resolution, in pixels, must be as high as possible. In our case, the sensor has a resolution of 4272 x 2848.

Other Sensors

In recent decades, cameras have been developed to capture different information from usual. The best known and most widespread are those that capture parts of the non-visible spectrum, in other words, information that is imperceptible to the human eye.

Figure 8. Camera positions for the shots of the sculpture.

Figure 9. Textured model and detail of the grid of points, obtained by correlation.

Figure 10. A 3D camera and the result of the grey-image capture and representation of distance.

In addition, some cameras have appeared that can measure the distance from the capture point to the documented object. These are similar to the sensors described in the previous paragraphs, but instead of profile scans, they obtain the distance using a matrix of points.

3D Cameras (ToF Camera)

A 3D camera or Time-of-Flight (*ToF*) camera captures images with the grey-level data of each pixel. At the same time, it provides information on the depth of the whole scene and for each pixel (see Figure 10). The light emitted needs a certain amount of time to reach the objective and reflect itself forward to the sensor. This time is directly proportionate to the distance covered [28].

The detecting element and the electronics to measure the signal are integrated in a silicon chip, called the Photonic Mixer Device (PMD). These “smart-pixel” sensors can capture entire scenes in 3D in real time.

The resolution of 3D cameras is generally low (160x120, 176x144, 320x240 or 640x480 pixels). These systems can cover distances ranging from a few metres to approximately 60 m. In comparison to the 3D laser scanner, *ToF* cameras work very rapidly, providing over 100 images per second.

They allow independent measurements of distance, colour and the reflectivity of the object.

When various measuring systems are needed at the same time (multi-cameras), multiple frequencies of illumination can be used (a different one for each camera).

Examples of these types of cameras are the Argos3D – P100 [29], developed by BLUETECHNIX (chip PMD PhotonICs 19k-S3 ToF 3D), Panasonic D-Imager, PMDCamCube, 3D-MLI Sensor, SwissRanger™ SR4000 (a 3D vision camera with time-of-flight technology) and the ARTTS Camera.

In recent years, with the development of video game consoles in 3D that are sensitive to players’ movements, controllers have appeared with inertial systems that can detect movement. Some 3D cameras have been developed along these lines, for example, the Xbox 360 Kinect (see Figure 11). This device has an RGB camera, depth sensor, multiple matrix microphones, a personalized processor that captures the movement of the whole body in 3D, and facial recognition and voice recognition capabilities. The depth sensor is an infrared projector combined with a CMOS monochrome sensor that allows the Kinect to see a room in 3D in any environmental light conditions.

Ultraviolet, Infrared, Thermal and Hyperspectral Cameras

Among the different instrumental analysis techniques that allow the measurement of physical-chemical matter properties there is the spectroscopy. This technique allows art historians, for example, to see whether the visible layers of a painting are different from lower layers or whether there are differences among the layers. This information is very useful in determining whether a painting is by an artist or a copy, and for assessing whether it has been changed by restoration [11].

Monochromatic light can be used to observe works of art, and retouching is very common. In fact, many vision applications require solutions beyond the visible spectrum, due to the characteristics of object emission or evaluated applications. These include applications that must be resolved in the range of ultraviolet or near infrared, mid-wavelength infrared and far infrared [30].

Figure 11. Xbox 360 camera.

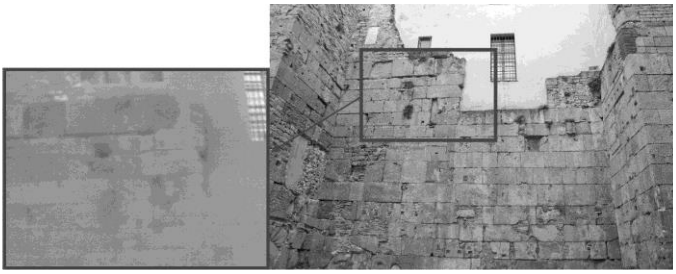

Figure 12. Part of the Roman wall in Barcelona, captured by an infrared camera.

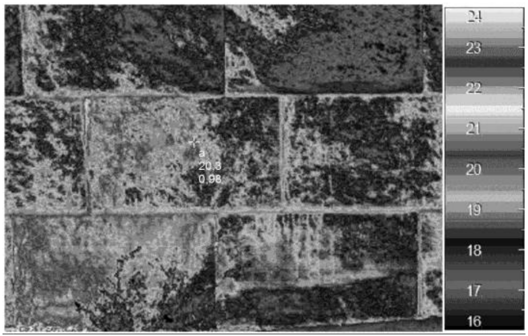

Figure 13. Part of the Roman wall in Barcelona, captured by a thermal camera.

Thermal cameras can determine the temperature of bodies from their infrared radiation. There are two ranges of wavelengths more used within thermal cameras, from 2 to 5 µm and from 7 to 12 µm. Generally, thermal cameras are monochromatic since they only work for a certain range of the spectrum that depends on which sensor is used.

Figure 12 is an image of the fourth century Roman wall in Barcelona, taken by infrared camera. Figure 13 is an image of the same wall captured by a thermal camera. Small differences in thermal energy can be distinguished. This effect is produced by the different materials used in the construction. Slight differences in temperature enable quality images to be generated, regardless of the environmental light.

Another spectroscopic technique uses hyperspectral images. Basically, hyperspectral images are a fusion of spectroscopy and the image process. A hyperspectral image contains continuous spectrum through a wide spectral range, to form a “cube” of data (image rows/ column rows/channels) [31].

GEOPHYSICAL METHODS

The methods used to detect buried structures are on-foot prospecting methods, aerial observation (B/W, colour, infrared or thermal photographs) and geophysical prospecting. The main factors that influence prospecting are the accessibility and visibility of the terrain, as well as the perceptibility of sites.

There are two main advantages of using geophysical techniques in archaeology: they are non-destructive; and they can be used to reach large study areas in short periods of time. Thus, archaeological heritage can be preserved without excessive costs.

In addition, geophysical techniques can be used in any phase of an archaeological study (including localization, delimitation, auscultation and restoration) [32, 33].

There are various geophysical prospecting techniques; the most common are electric, magnetic, electromagnetic, seismic, geo-radar, gravimetric, ultrasonic and vibration prospecting.

Electric Techniques

Electric techniques can be used for two-dimensional and three-dimensional modelling of the subsoil. Electric or resistivity prospecting uses the principle of conductivity (measurements are made with a resistometer). Most excavation sites are composed of sedimentary and construction stratigraphic units. Construction units can be revealed by adding different values of electrical resistance. Thus, diagrams can be created that represent excavation sites at ground and below-ground levels.

Electric prospecting is one of the most commonly used, non-destructive tools for characterizing underground areas, mainly due to the speed at which it obtains data, the high number of measurements that can be made, and the quality of them.

The most popular techniques are Vertical Electrical Sounding (VES), electrical tomography, and 3D electrical tomography.

Geo-Radar

Geo-radar is one of the most commonly used techniques in superficial geophysical sounding. It is based on emitting electromagnetic radiation and registering the echoes produced by the medium under analysis. Geo-radar antennas emit an electromagnetic pulse at a determined frequency. The resolution (the minimum size of a detectable object) is determined by the employed bandwidth [34].

This system gives the horizontal and vertical positions of buried objects and different structures. The most common methods are the single-frequency geo-radar and the 3D multi-frequency geo-radar. In the first case, two-dimensional sections of the underground area are obtained that are no more than a few metres from the surface. The advantages of this method are high lateral resolution, rapid data capture and low costs. In the second case, the data capture speed is higher and more detailed models are obtained.

Three-dimensional models can be obtained to give a general view of the medium under study and delimit the identifiable structures precisely. For this purpose, antennas are used that have various channels [35] separated by a few centimetres, in order to build a three-dimensional model of the terrain that is several metres wide.

Gravimetric Techniques

These techniques are based on determining variations in the field of gravity of a studied area. Variations are produced by the differences in density of the materials that form the terrain. Gravimetric techniques are used to locate cavities.

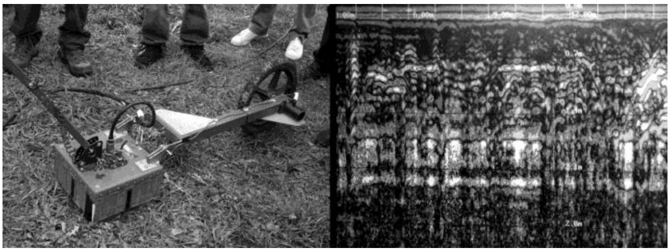

Figure 14. Data capture with geo-radar and radargram.

The most common method is microgravimetry. This consists of determining the variation of the gravitational field in a determined region, with high precision. It is carried out using measuring stations distributed in profiles or regular grids that cover the whole area of interest. Periodic readings are made at a reference point (the reference base), to obtain the instrumental bias curve.

Underground density models are generated that are geo-referenced in a detailed topographic survey to correctly identify the signal that the topographic relief produces in the measurements made in the field [36].

DOCUMENTATION

The results of the above techniques can be used on two well-differentiated levels. Firstly, data sets can be formed by compiling the data extracted from the techniques. Secondly, new information can be generated by managing the data. Data management can lead to new documentation, which in turn provides new data that can be used to work on the heritage site.

To draw up new documentation, we must be aware that data extracted from the capture methods is graphic and/or alphanumeric. This data is essential in the techniques used to work on the heritage item, for example in the restoration or rehabilitation of buildings or archaeological ruins, archaeological jobs, and the restoration of sculptures, paintings and altars, among other elements. Therefore, the documentation must be explicit and organized effectively so that it can be used by all agents involved in the work.

Graphic Documentation

The diverse, wide ranges of documents that can be generated include classic sketches on paper, drawn directly in the field, and computer files that relate spatial geo-referenced positions with historical, constructive and material data. All or some of this information can be extracted immediately when required.

Graphic documentation can be presented in various ways, for example, as a traditional graph, vector graph or raster image.

Images of architectural elements or the localization of objects in archaeology have been created using graphics of ground plans, elevations and sections, which can be directly generated from “in situ” sketches using traditional drawing methods and materials (including pencils, set squares and compasses).

These images can also be obtained through orthographic projections of three-dimensional computer models (generic CAD software that is applied or object-based). A 3D graphic computer system can be used to process information from the aforementioned capture methods.

Three-dimensional capture data can be used to create 3D models with different configurations, depending on the type of entity we want to apply: solids, surface or nets. Models are generated by the methods of restitution, management and virtual modelling of point clouds in different formats. The formats depend on the required presentation at each moment, and range from images of the 2D ground plan, elevation, axonometric projections and perspective projections to 3D models extracted from 3D printers.

One important type of documentation is the photographic image (raster), which is a resource that provides complimentary information. It can be used to extract information from 3D models in which we can appreciate not only the shape, but also the colour and the material of the cultural heritage element.

Geographic Information Systems

Cataloguing of heritage should go beyond obtaining graphic documentation that is later stored in a folder. In recent decades, there have been advances in the development of Geographic Information Systems (GIS), which can contain the properties of each heritage element. Previously, data were stored in separate documents, generally in files without links. Web applications that enable citizens to access this information have become particularly common. One example is the cultural heritage catalogue that is available on Bétera City Council’s website (Valencia, Spain) [37].

Heritage elements cannot be evaluated in isolation, they must be analysed in their surroundings and therefore they must be georeferenced, as required by heritage management departments. Thus, we can gain a better understanding by establishing the relationship between the surroundings and human elements, and by determining the heritage properties [38]. All this can be achieved with GIS.

In 1998, Moscati [39] described the objectives that could be achieved by using a GIS for archaeological cataloguing: co-operation among different institutions, preservation of the archaeological record for the general sake of science and to safeguard cultural heritage; formalization and computerization of scientific procedures; joint use of geographical, geophysical, topographical and archaeological data; integration of data and technical tools; data restitution in different formats and with different purposes; data analysis and visualization; and data diffusion through the use of multimedia systems.

In addition to the ordered storage of any type of information (geographic, raster, vector, documents, etc.), the main advantage of implementing a GIS is the opportunity to carry out a search to analyse, between other operations, various aspects of a heritage item. In architecture, for example, GIS can be used to control restoration work, as images of the zones affected by pathology can be accessed at any time, and any changes can be registered in the database associated with the project.

In recent years, many organizations that use these types of tools for urban management have benefitted greatly from being able to combine raster images, vector data and alphanumeric information.

In addition, GIS aid the process of disseminating information to citizens, through the creation of SDI nodes, although difficulties must be overcome by adapting standards [40].

However, we must take into consideration that GIS are not only for municipal management since are used to create cartography. Increasingly, GIS are used to create virtual museums with quality and better citizen access to information [41].

All documentation must have a global and integrating aspect. Information should be organized so that the management of data from documents, bibliographies, digital images, planimetrics, cartography etc. is complemented with data extraction. At the same time, we should be able to relate all data, to provide databases that are accessible and allow the integration of a GIS.

DISCUSSION

Clearly, organizations that are responsible for managing and conserving heritage in different fields and at different levels (international, state or regional) consider that metric graphic documentation and other documentation is essential to gain comprehensive knowledge about an item. This knowledge is what enables us take suitable measures in each case.

To obtain the most complete documentation possible with a suitable level of precision, complementary methods and instruments can be used to capture geometry and characteristics of cultural heritage.

In recent decades, techniques have been developed to obtain large volumes of data in 3D, including TLS or digital photogrammetry by correlation. These techniques provide metric information and data on characteristics such as texture and colour.

However, we lose definition in the determination of characteristic lines that must be obtained by superficial intersection in TLS or through restitution by an operator in photogrammetry.

These techniques are the result of advances in information technology, by which large volumes of information, in this case point clouds, can be administered. Information is processed to obtain final products, such as plans, elevations, sections and virtual models.

The progress in geographical information systems is also notable. GIS can be used to manage three-dimensional information. They work with data from different sources and formats and even with different reference systems. This improves information management and the development of operations, and facilitates consultation and analysis, so that each monument can be monitored effectively.

In addition, major advances have been made in prospecting techniques to determine and localize elements of historical heritage that have remained hidden for various reasons.

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Chapter 3

DETERIORATION AND PROTECTION OF HISTORIC AND ARTISTIC STONES: THE ROLE OF SYNTHETIC POLYMERS

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ABSTRACT

Alteration of monuments and historical buildings has recently undergone to an important acceleration due to natural and anthropic changes in the climatic conditions and presently it has grown to a particularly evident degree.

The rate of decay depends on intrinsic properties of the stone (mineralogical composition, stone texture and structure, porosity, etc.) but also on extrinsic factors that include climatic conditions, atmospheric composition, localization of the object, use and care given to it, and so on. The deterioration of stone materials occurs even in the absence of pollutants and it is important to quantify how natural or anthropic factors affect and accelerate the degradation of the material.

Atmospheric conditions in urban areas, mainly due to air pollution, greatly promote decay processes of stone materials, especially for those outdoor exposed.

Damage of cultural heritage coming from air pollution has two main sources: pollutant gases improve the corrosivity of the atmosphere (acid rains) and black particles deposited on the surface cause a darkening of the surface itself.

In recent years several studies have been developed with the purpose of setting up appropriate protectives able to reduce the ruinous effects of the atmospheric pollution in combination with the change of the climatic parameters. It's well known that almost all

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of these phenomena require the presence of water for their action or the water may strongly improve their influence.

A variety of efforts have been undertaken over the years to preserve or protect these structures and in particular protective agents have been selected from commercial products developed for the protection of the surface of civil buildings. These materials however do not satisfy the requirements for they application on historic or artistic stones, so new and specific materials are proposed. An evaluation of the state of art of polymers employed for this special application is reported examining the requirements of the products for their use as protective for cultural heritage, their performance, stability and the class of protective polymers employed up to now. A final paragraph is dedicated to new trends in development of polymers coming from natural sources.

INTRODUCTION

Alteration of monuments and historical buildings has recently undergone to an important acceleration due to natural and anthropic changes in the climatic conditions and presently it has grown to a particularly evident degree.

It is known indeed that atmospheric conditions in urban areas, mainly due to air pollution, greatly promote decay processes in stone materials, especially for those exposed to an open air.

It is however important to acknowledge that erosion of stone materials is a process that occurs even in the absence of pollutants and it is important to quantify how urban atmospheric conditions affect and accelerate the natural or background degradation of the material.

Damage of cultural heritage coming from air pollution has two main sources: pollutant gases increase the corrosiveness of the atmosphere (acid rains) and black particles deposited on the surface cause a darkening of the surface itself.

The rate of decay depends on intrinsic properties of the stone (mineralogical composition, stone texture and structure, porosity, etc.) but also on extrinsic factors that include climatic conditions, atmospheric composition, exposition of the object, use and care given to it, and so on. Therefore, in recent years several studies have been developed having the purpose of setting up appropriate protective barriers capable of reducing the ruinous effects of the atmospheric pollution in combination with the change of the climatic parameters.[1]

Many parameters may affect the damage of stone materials due to natural causes, to a combining and sometimes synergic effect of chemical, physical and biological phenomena. However it’s well known that almost all of these phenomena require the presence of water for their action or the water may strongly improve their influence.

A physical degradation phenomenon which acts on all stone surfaces is connected with the succession of frost and thaw cycles. Water absorbed inside the pores of the material freezes, and the ice crystals having specific volume higher than the liquid stress the material and cause fractures and/or decohesion with loss of material.

Another chemical-physical phenomenon connected with the presence of water is the dissolution of calcium carbonate, which may be present in stone materials as the main component or a binder. In every case the consequence is a loss of cohesion between the granules of stones.

Other phenomena of relevant importance in the decay of outdoor exposed stones are due to chemical processes: they are mainly caused by the chemical transformation of the carbonate portions of the material, by polluting substances present in the atmosphere (carbon dioxide, sulphur di- and trioxide, nitrogen oxides). Such pollutants are dissolved in the water and transformed in acids able to corrode the material. Their concentrations are particularly high in rain especially in the first time of the event or when brine is condensed on the surface of a material. Other pollutants also, such as ammonia, hydrogen chloride, hydrogen sulphide, ozone, may improve the corrosion of stone if water is present.

Damages due to a chemical and mechanical disaggregation can be also due to the biological activities of microorganisms, fungi and algae but the development of these contaminants also requires the presence of water in the materials. [2]

Soluble salts play also an important role in the deterioration of stone, especially in the Mediterranean basin. Salts contaminate stone materials by several routes, such as capillary rise of groundwater, dry deposition from aerosol by the sea (sodium chloride), air pollution in urban areas (sulfates, nitrates), and so on. Salts can cause stone decay by different mechanisms. The most important is the growth of crystals from a supersaturated solution, as a consequence of its evaporation or cooling due to environmental fluctuations. Several aspects such as type of salts, substrate characteristics and frequency and severity of environmental fluctuations, play an important role in salt weathering. Depending on the conditions, crystals can precipitate at the surface of the stone, leading to an exterior damage stain of the material (*efflorescence*), or inside the pores (*subflorescence*). In the latter case, crystal growth can exert stresses able to overcome the tensile strength of the stone (order of few megapascals). This easily happens with sodium sulphate, one of the most damaging soluble salts because it exists in two stable fases (room temperature and pressure): anhydrous thenardite (Na_2SO_4) or decahydrate mirabilite ($Na_2SO_4 \cdot 10H_2O$). It is now recognized that stone containing thenardite and exposed to water or rising humidity in a certain range of temperature, experiences both dissolution of thenardite and crystallization of mirabilite, leading to tensile stress from mirabilite precipitation damaging most of the stones. However some challenges are coming out from this research field. [3] Crystallization is not the only physical mechanism connected to salt damage in stone materials. Salts can also damage stone through the stress from the different thermal expansion (such as sodium chloride inside calcite stones). Furthermore salts can also play a role in weathering stones containing swelling clay as well as in some chemical and biodeterioration processes. In salts weathering also water plays a crucial role.

A variety of efforts have been undertaken over the years to preserve or protect stone materials and in particular protective agents have been selected from commercial products developed for the protection of the surfaces of civil buildings. [4] These materials however do not satisfy the requirements for they application on historic or artistic stones, so new and specific materials are proposed. An evaluation of the state of art of polymers employed for this special application is reported examining the requirements of the products for their use as protective of cultural heritage, their performance, stability and the class of protective polymers employed up to now. A final paragraph is dedicated to new trends in development of polymers coming from natural sources.

IDEAL PROTECTIVE AGENTS

The most desired requirements for an ideal protective agent include chemical inertness, low volatility, photo-oxidative stability, thermal stability, solubility in eco-friendly solvents even after ageing (the treatment must be reversible in order to let the removal of the product applied after some times from its application). The coating must also be colourless and no colour changes must be evidenced on the stone surface, even after ageing. High resistance of the coating materials to acid and abrasion are also of considerable importance.

One of the most desired features of a protective agent is the conservation of its characteristics in the course of time, therefore the capability to keep its properties for a long time even in heavy polluted environments. Products having long stability and duration avoid the frequent applications of expensive and laborious protection treatments.

In the case of monuments placed in an outdoor environment the main goal to be achieved by a protective treatment is to prevent water penetration inside the stone. Water, in fact, as above reported, may be considered the main medium for physical and chemical weathering of stone materials. As a consequence it is desirable to avoid or reduce as much as possible the penetration of water inside the stone, applying a water repellent product.

On the other side it is necessary to preserve the permeability of the stone to water vapour in order to let the evaporation of the water present inside the stone through the microstructure of the stone itself. Substances with high permeability to water vapour often have not a high water repellence.

This performance may be obtained if the coating material covers the surface without blocking the pores, that is the coating material should be applied using a solution having a viscosity in a range which permits wetting of the pores via capillary action. High wetting is also required to ensure a complete and uniform coverage.

PERFORMANCE EVALUATION OF A PROTECTIVE TREATMENT

The effectiveness of the protective treatments is normally evaluated measuring the changes of some surface properties of the stone samples induced by the application of the product, such as capillary water absorption, water vapour permeability, water repellency, porosity and colorimetric characteristics.

Procedures for testing these performances are available in the literature, codified by both national (UNI/NORMAL Commission) and international committees (RILEM). [5]

Water Absorption

Hydrorepellency is one of the most important characteristics that have to be granted to the stone after a protective treatment.

It can be evaluated by means of capillary water absorption, according to UNI EN 15801:2010: the porous stone material is placed on the top of a pile of water soaked filter paper (Figure 1); the water is absorbed by the stone sample by means of the upward capillary force and the amount of water absorbed is evaluated weighing the sample before and after the water absorption. The time of the experiment is prefixed, usually 20 or 60 minutes. The protective efficacy (P.E.%) of the hydrophobic treatment is calculated through the formula:

$$P.E.\% = \frac{A_0 - A_1}{A_0} \cdot 100$$

with A_0 and A_1 are the amount of liquid water absorbed by the stone sample, respectively before and after the treatment. Obviously, the value 100 of P.E.% means the best performance of a treatment.

This simple method has a very good reproducibility and is commonly used in laboratory tests, but it is not applicable *in situ*.

The Karsten pipe, the contact sponge and the contact angle methods can be other alternative tests to evaluate the absorption of water by a porous stone material. All of them are non-destructive techniques that allow *in situ* measurements.

The Karsten pipe method consists of a pipe filled with water, which is attached with a glue (plastiline) to the surface of a porous stone material: the water absorption is determined over time by measuring the decrease of the water volume in the graduate pipe. This method presents some technical difficulties that limit its practical use, such as the correct adhesion of the pipe to the surface, especially if it is not perfectly plane, or the difficulty to remove completely the glue from the surface after the test or little fragments of the stone may be taken away when the glue is removed. These difficulties affect subsequent evaluations on the same surface previously tested: i.e. if some fragments of the stone are removed the surface is damaged and the subsequent determination gives uncorrected results. In Figure 2 is reported a modification of the Karsten pipe realized to avoid some of the problems above reported.

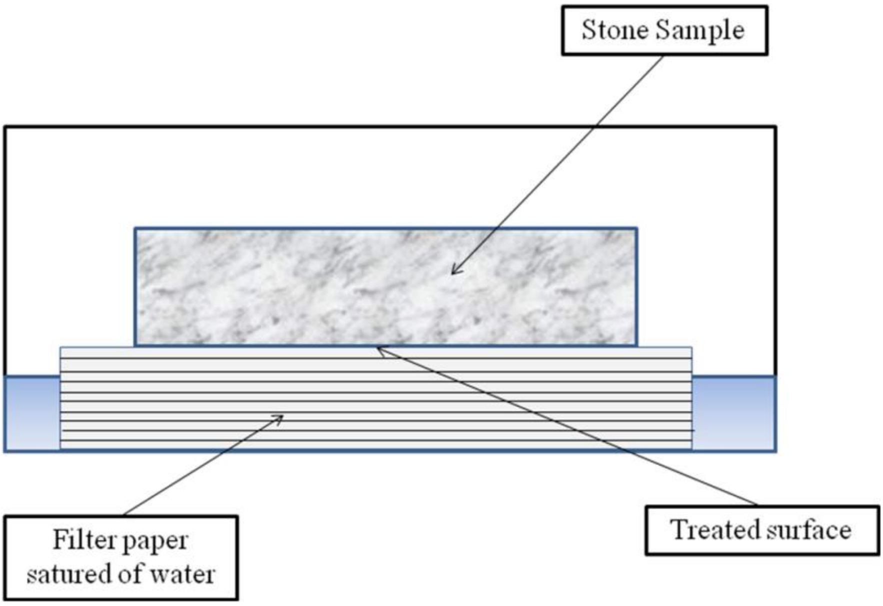


Figure 1. Scheme of the capillary absorption test performed on a stone sample.

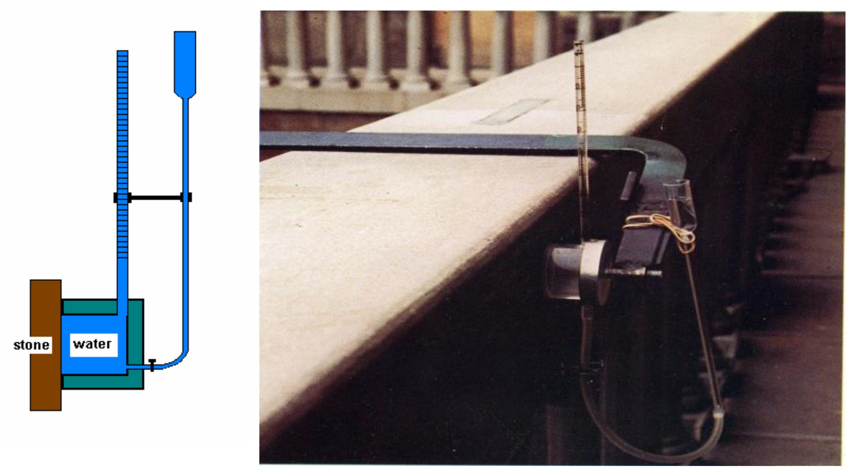


Figure 2. An “in situ” application of a modified Karsten pipe.

The contact sponge method [6] consists of a Rodac contact-plate containing a humid sponge having a thicker depth than the height of the borders of the contact plate and it can be pressed against the stone surface under a given pressure and during a given period of time (Figure 3).

The amount of water absorbed by the porous material is calculated by the different weight of the sponge before and after the test. This method is very simple and affordable and appears as a very promising method, applicable in laboratory and *in situ*, if a balance for weighing the sponge is available. The sponge method was standardized in Italy in 2011 (UNI 11432:2011).

The contact angle method measures the angle α formed by a drop of water placed on the surface of a material. As it can be seen from Figure 4, high values of α indicate poor wetting of the surface (good hydrophobicity) while low values of α indicate that the liquid water and the material of the surface have almost the same surface tension, that is a low hydrophobicity.

The measurement of the contact angle, is codified by the UNI EN 15802:2010, [7] for the sessile static contact angle on stone surfaces whose roughness is previously reduced or standardised by means of abrasives and later treated with a protective agent. It is not simple to be performed, and it has some limits [8]: the reduction of the material roughness by abrasion is successful for highly compact materials, like limestones. Moreover, a real monumental surface cannot be abraded, so the protective treatment will give different values among test samples and real cases.

Figure 3. Some examples of “in situ” contact sponge measures and the kit available from CTS, Altavilla Vicentina (Italy).

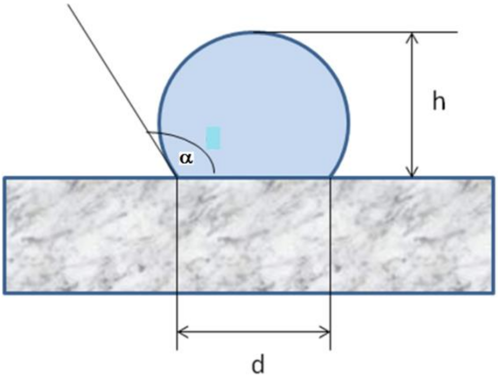


Figure 4. Contact angle (α) of a liquid on a surface.

Besides, the measure of the static contact angle performed on a not ideal surface that is heterogeneous and/or rough, gives very partial information. The measure is substantially equivalent to the evaluation of the advancing contact angle, the highest among the possible values of the contact angles, and it allows only to verify the presence of the protective, not its efficiency. The effectiveness of a protective agent on the stone is better understood by considering its receding contact angle in water, rather than the advancing contact angle, but unfortunately the receding angle is not obtainable through the static method.

The VIECA (Vibration-Induced Dynamic Contact Angle) technique is reported in literature [9] to obtain the equilibrium contact angle on heterogeneous and rough surface. It consists in the production of capillary waves on a drop of liquid in order to obtain the relaxation of the liquid meniscus and the value independently from the speed of meniscus movement and from the micro-roughness and heterogeneity of the surface.

In any case, from the knowledge of the equilibrium angle of the protective polymer and the measure of the advancing and receding angles on the protected stone, it is possible to determine the efficacy of a protective product and the minimum amount of polymer to obtain a homogeneous protection.

An indirect and non-destructive technique to evaluate the protective treatment is Magnetic Resonance Imaging (MRI). It has been successfully applied to evaluate the kinetic of the diffusion of liquid water inside treated (hydrophobic treatment) or untreated stone samples. By MRI tomography it is possible to follow the rise of water inside the sample, through the pores present in the stone sample placed in contact with a water source. Vertical sections of the sample, analysed at given time intervals, show the progressive gradient of water inside the sample [10] (Figure 5). Other Nuclear Magnetic Resonance (NMR) techniques have been employed in recent years to investigate, characterize and monitor several Cultural Heritage objects. Some of these techniques does not require any chemical pre-treatment of the sample and sometimes may be used without any sample collections. A breakthrough has surely been the recent development of portable NMR instrumentations. These devices can be applied directly on large objects such as *frescoes*, monuments, and in general any buildings without any manipulations of the object and measures may be important to establish the state of degradation of the objects, to evaluate the performances of consolidation and water repellent treatments on porous materials, to monitor the detachment of the painted layers from the support. Furthermore using particular hydrogen sensors it is also possible to obtain stratigraphy with microscopic spatial resolution of paintings. One of the following chapters of this book will be devoted to advanced nuclear magnetic resonance presenting several applications of these new techniques. Unfortunately these instruments are quite expensive and not easy to use by non-expert technicians.

Water Vapour Permeability

The residual permeability of a treated stone is a very important parameter, because the water eventually present in the pores of the stone could be entrapped inside the material leading up to degradation problems, such as freeze-thaw weathering and solution-dissolution of salts. This test may be performed on laboratory samples, while it's not possible to do an *in situ* test.

The water vapour permeability of a standard stone sample may be evaluated measuring the mass of water vapour crossing through a surface at 30°C per 24 h. The tests may be performed using the "small cup" method [11] (Figure 6). The residual permeability (R.P.) is calculated from the permeability measured on the same sample before (P_0) and after (P_1) the treatment by the formula:

$$R.P.\% = \frac{P_1}{P_0} \cdot 100$$

A significant reduction of the water absorption and a relevant residual permeability to water vapour are generally considered as a good performance of hydrophobic treatments. [12]

Colour Variations

Another recommended test to assess the performance of a protective treatment is the evaluation of the colorimetric characteristics of the stone surface before and after a treatment. A good product does not modify the visual aspect (colour, brightness, etc) of a treated surface, neither after treatment, nor after ageing.

The CIELAB is one of the most popular methods adopted to evaluate object colour [13] (Figure 7): L* indicate lightness while a* and b* are the chromaticity coordinates. These three parameters are the three colour attributes and can be put together to create a three dimensional solid. Hue forms the outer rim of the solid with $L^* = 0$ yields black and $L^* = 100$ indicates diffuse white (specular white may be higher), its position between red/magenta and green (*a**, negative values indicate green while positive values indicate magenta) and its position between yellow and blue (*b**, negative values indicate blue and positive values indicate yellow). The asterisks (*) after *L*, *a* and *b* are part of the full name, since they represent *L**, *a** and *b**, to distinguish them from Hunter's *L*, *a*, and *b*, method. [14]

With a colorimeter, even low colour differences can be detected and expressed numerically and easily understood. In the L*a*b* colour space, colour difference may be summarised as a single numerical value ΔE, which indicates the size of the colour difference but not in which way the colour has been modified.

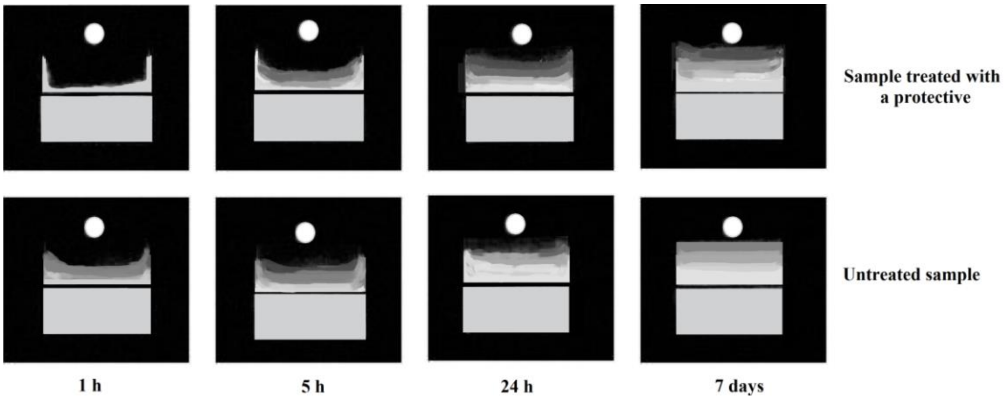


Figure 5. Magnetic Resonance Imaging of a sample treated with PB72 and TEOS and a not treated sample, after 1, 5, 24 h and 7 days of water absorption. (PB72: Paroloid B72; TEOS: tetraethyl orthosilicate).

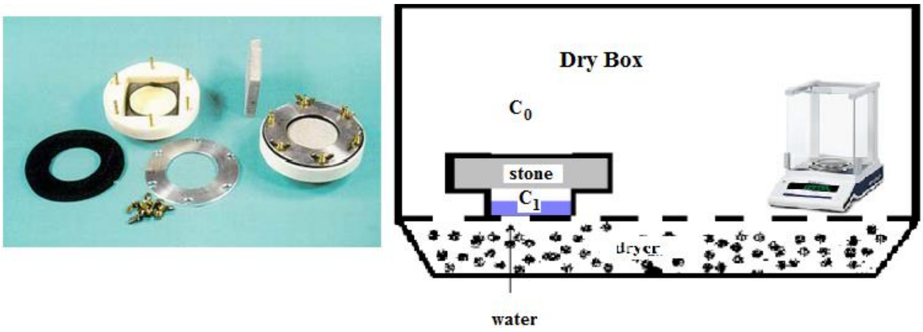


Figure 6. Some pictures of the “small cup” to evaluate the residual permeability and its arrangement in a dry box.

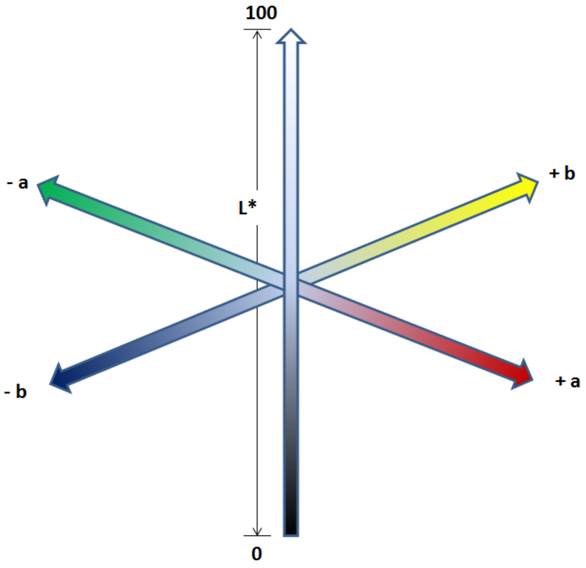


Figure 7. The CIELAB color space.

ΔE is defined by the following equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

The chromatic variations are visible to the human eye when $\Delta E > 3$, while lower values are not detectable.

This evaluation may be usually performed in situ or in a laboratory using a commercial portable instrument.

Fiber optics reflectance spectroscopy (FORS) is another non-invasive optical technique that makes possible to perform measurements on all objects even if there are non-movable. If correlated with colorimeters it gives large information because it may analyse wavelengths among UV and IR. Due to its dimension and weight, the FORS apparatus can be easily transported and used for *in situ* collecting spectra. FORS is an accurate technique for the identification of pigments and analysis of colour and its variation on paintings. It can be used also for measuring colour changes, for example after light exposure, protective treatments and detecting the presence of alteration products. [15]

Other Parameters

It is well known that the efficacy of a protective product strongly depends on the nature of the stone. A deep knowledge of the material to be protected is very important when a conservative intervention is approached. Furthermore, as the performance of the conservation treatments strongly depends on the penetration and distribution of the protective products inside the stone structure, it is essential to evaluate these parameters in order to assess the efficacy of the treatment.

Recently scientific investigation has been devoted to the study of the spatial distribution of the polymer within the porous structure of the stone.

Porosimetry is an analytical technique used to evaluate the porous nature of materials, such as pore diameters, pores distribution, total pores volume, surface area, bulk and absolute densities of the material. Techniquesrequire intrusion of a non-wetting fluid, usually mercury, nitrogen or helium, inside the material. The pore size determination is based on the equilibrium between the external pressure required to force the liquid inside pores and the opposing force due to the liquid's surface tension. By comparison of tests performed before and after the application of a product, it is possible to have an indication of the distribution of the protective inside the treated material.

Other methods to evaluate the depth of penetration of polymers inside a porous stone substrate involve direct detection of the product by instrumental chemical analysis such as Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry (SEM -EDX), X-ray Photoelectron Spectroscopy (XPS) and TeraHz spectroscopy (THz).

FTIR spectroscopy can be used with the aim of determining the depth of penetration of polymers within a porous stone substrate, [16] in reflexion mode if the studied samples have only a few µm of thickness, or in photo-acoustic mode on unaltered samples taken from historic buildings subjected to hydrophobic treatments. Depth-profiling of polymers inside stone substrates by direct determination with vibrational spectroscopic techniques (Micro-Attenuated Total Reflection Micro-ATR, diamond cell transmission, and Thermo-gravimetry-FTIR) has the advantage of providing information on the molecular structure of the polymer present inside the porosity of the stone until a few microns without any further manipulation. Otherwise it is possible to perform a micro-ATR on cross sections of a treated stone.

Scanning Electron Microscopy (SEM) can be utilized for high magnification imaging of many materials. In combination with Energy Dispersive X-ray Spectrometry (EDX) is also possible to evaluate the elemental composition of the material. The presence of a conservative treatment on a substrate can be hardly established by means of SEM observations, so EDX elemental analysis of the cross-sections of a substrate may be performed in backscattered electron mode (EDX-BSE, Figure 8 and Figure 9).

X-ray Photoelectron Spectroscopy (XPS) is used to determine quantitative elemental and chemical composition of a material. It is a surface analytical technique: the sampling volume extends from the surface to a depth of 50-70 Å. XPS can be utilized for sputtering depth profiling to characterize thin films or quantifying matrix-level elements as a function of depth. The process works by irradiating a sample with monochromatic X-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume.

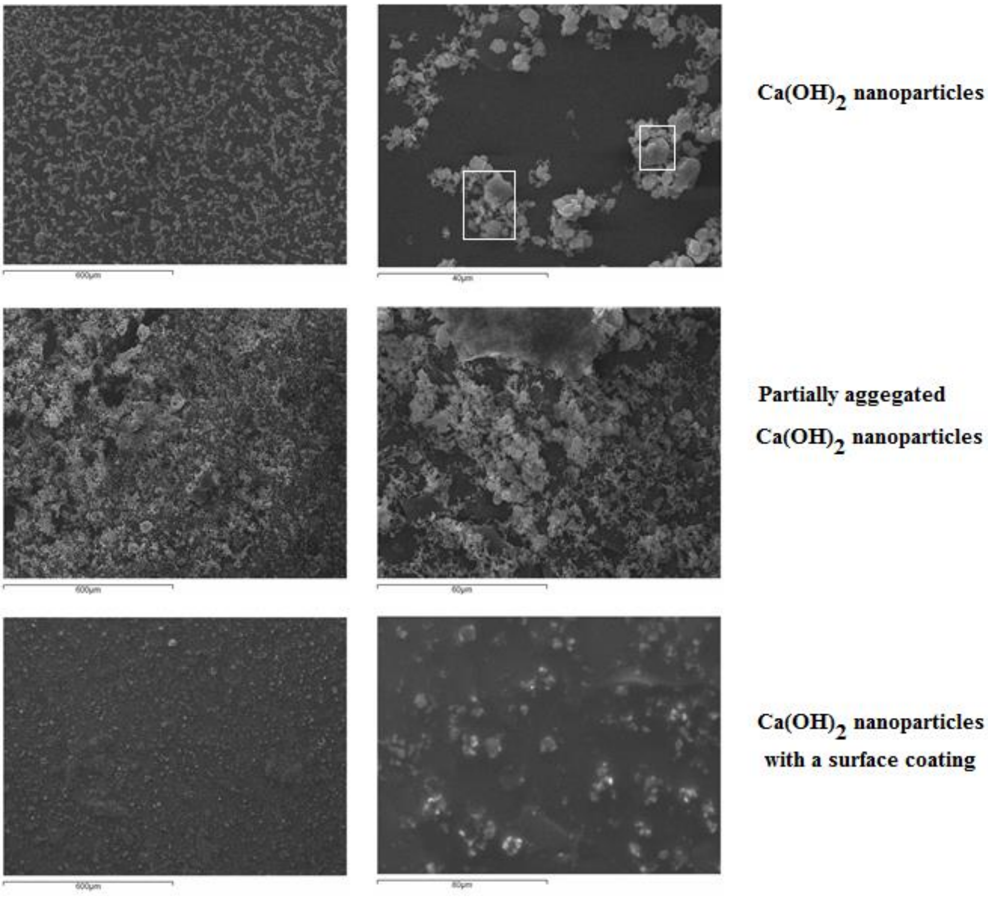


Figure 8. SEM images of lime nanoparticles (By courtesy of Luigi Dei – University of Florence).

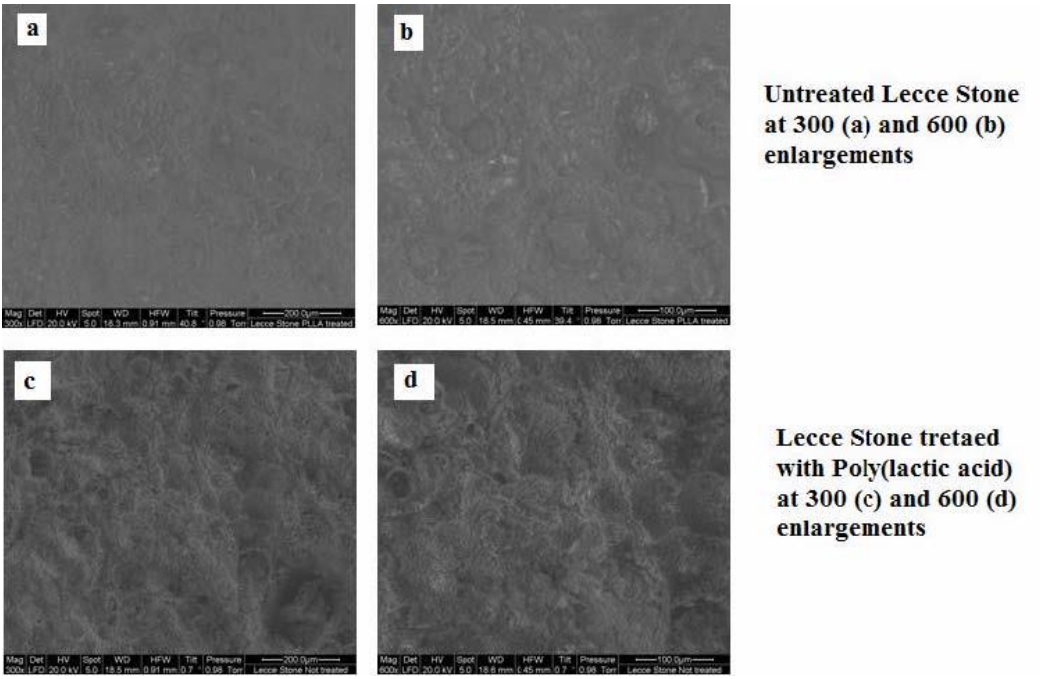


Figure 9. SEM images of Lecce stone untreated (a, b) and treated with poly(lactic acid) (c, d).

Terahertz (THz) spectra, used in reflectance or absorbance mode, can be acquired by FT-IR Spectroscopy in the region between 1.5 and 20 THz and by THz Time Domain Spectroscopy (THz-TDS) in the region between 0.1 and 3.6 THz. The ability of THz to penetrate into the medium without causing damages neither to man's health nor to the object, can allow to obtain information about the surface in a no destructive way. Moreover, it is also possible to provide three-dimensional structural information and chemical composition (THz Imaging). However this technique is very expensive and up to now only occasionally employed.

STABILITY EVALUATION OF A PROTECTIVE

In the preservation of cultural heritage items, the use of polymeric materials for the consolidation and protection of artifacts having a historical and artistic value is widely accepted. Therefore over the last decades, a good knowledge of the performances of different polymeric materials has been achieved, with regard to their consolidating, protective and waterproof properties.

In the stone conservation, the application of polymeric materials is a technique used to reduce the rate of stone decay and to preserve stone which are deteriorated by processes such as natural weathering, atmospheric pollution, inappropriate interventions, and so on.

Several criteria may be employed for the choice of a protective polymeric product: a good material should assure hydrophobicity to liquid water (water repellence), chemical and photo-chemical stability and aesthetical invariability of the stone treated in order to preserve its original colour and good permeability to water vapour. Furthermore, it is important to assure the removability from the substratum maintaining the possibility to perform future treatments with better products presently unavailable.

Polymeric materials are known to degrade by prolonged exposure to light, heat, oxygen, moisture, environmental pollutants or chemical agents such as acids, alkalies and some salts or by mechanical stress. [17] Different polymers show a different stability when exposed to photo, thermal, mechanical, chemical and biochemical stress, even if it can be often difficult to distinguish among them.

Photo-Degradation

Photo-degradation of organic polymers is mainly due to ultra-violet (UV) light. This radiation can cause the formation of radicals through breaking of the polymer-chain and/or scissions of side-chains, sometimes followed by reactions of the radicals formed with the oxygen present in the atmosphere. Such mechanisms can lead to deep modifications of the polymer structure. Other radiations having low energy such as visible or IR are less energetics and cause lower damages than UV radiations.

Many natural and synthetic polymers are subjected to degradation by UV radiation, giving a cracking of their chain and loss of their protective performances. The problem is known as UV degradation, and it is a common problem for products exposed to sunlight and the degradation depends on the extent and degree of exposure. Common synthetic polymers may be subjected to this degradation and especially those containing tertiary carbon atoms in their chain structures are easily degraded. The UV radiation activates such carbons to form free radicals, which may further react with the oxygen present in the atmosphere, giving rise to the formation of oxygen containing compounds.

The main factor determining the photo-stability of a polymer or the way of its degradation, is the strength of the chemical bonds present in the polymer. There is a connection between the energy of a bond and the wavelength of the radiation required to break this bond. Most of the bonds present in organic compounds such as C-C, C-H, C-O, don’t absorb in the near ultraviolet region while polymers such as polymethyl methacrylate, polyethylene as well as natural materials like cellulose, can be quite severely affected by UV light. These polymers have their own characteristic way of degradation and resistance to UV radiation, heat, and chemical agents. For instance, polyethylene and polypropylene are sensitive to oxidation and UV radiation, especially low-density polyethylene (LDPE) and polypropylene (PP). Polyacrylates, polyamides and polyesters are susceptible to hydrolysis and are degraded by strong acids, while polycarbonate depolymerises rapidly in contact with strong alkali.

A selection of bond dissociation energies and the corresponding wavelength required to break a bond in organic materials is shown in Table 1.

Usually, in order to evaluate polymer degradation, the product is applied on a stone and exposed to an UV light for a prefixed time that is through an artificial and accelerated ageing. The effects of UV degradation may be evaluated by IR spectroscopy, DSC and SEC analysis on sample collected after various ageing intervals. A Solar Box, that is a chamber where the polymer may be directly exposed to a UV or a solar radiation may be employed to simulate the exposition of a polymer to solar irradiation in outdoor conditions [18] (Figure 10).

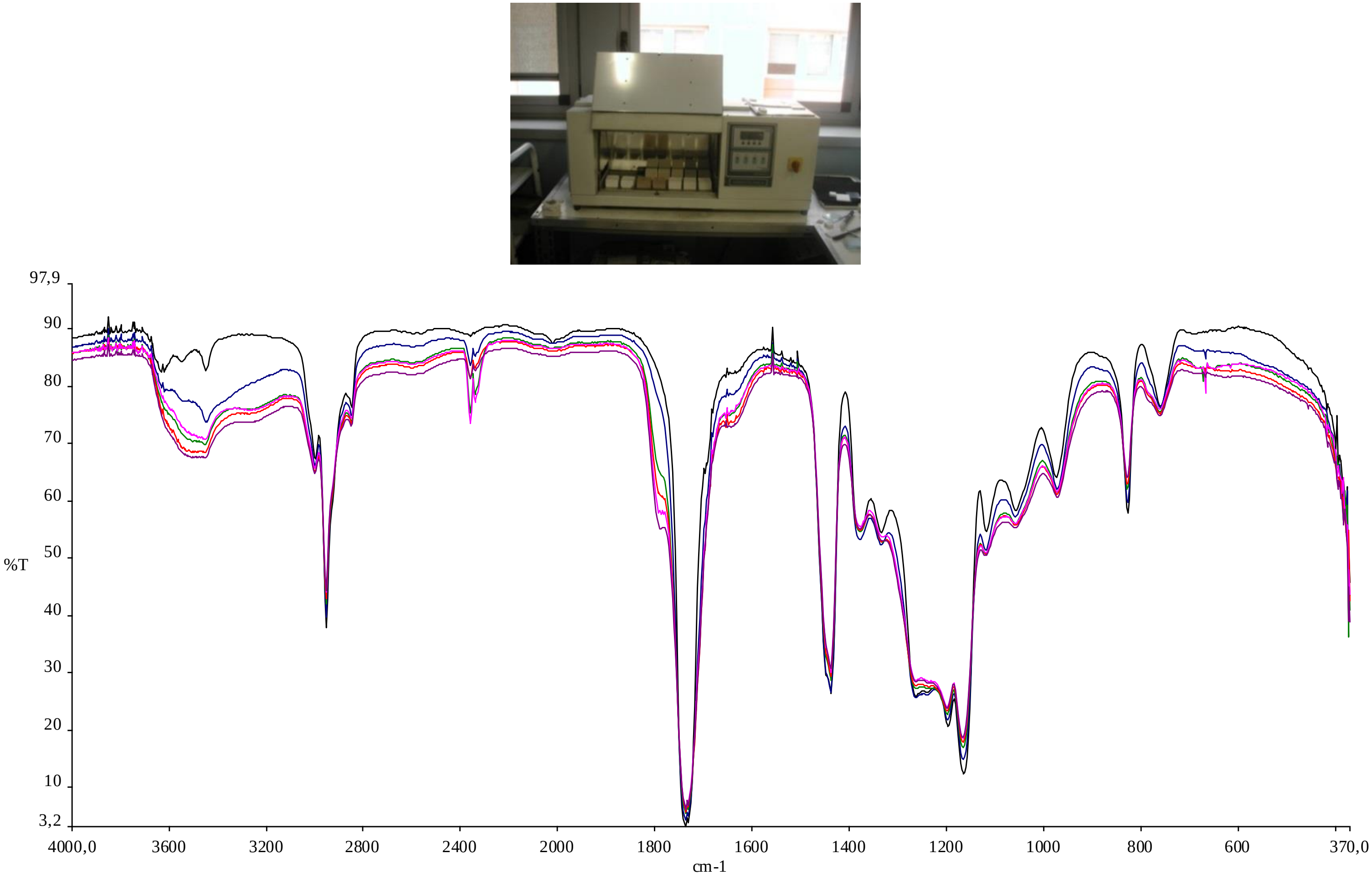


Figure 10. Solarbox Co.Fo.Me.Gra. (up) and an example of UV ageing of a polymer: FT-IR spectra of poly(methacrylate) (PMA) after some intervals of UV irradiation (0h, 72h, 250h, 500h, 750h, 1000h) (down).

Table 1. Bond dissociation energy and wavelength of breaking energy for some organic bonds

Bond	Bond dissociation energy (Kcal/mol)	Wavelength of breaking energy (nm)
C-N	72.8	392.7
C-Cl	81.0	353.0
C-C	82.6	346.1
S-H	83.0	344.5
N-H	85.0	336.4
C-O	85.5	334.4
C-H	97.7	289.7

Oxidative Degradation

Organic polymers may be degraded by oxygen, especially at elevated temperatures. Oxidation initially starts from tertiary carbon atoms, due to the low bond dissociation energy of C-H and to the relatively high stability of tertiary free radicals. Also hydrogen atoms linked to a carbon atom in α position with respect to a double C=C bond or to a carbonyl group are easily drawn up because relatively stable alkyl radicals are formed as intermediates. The reaction of the radical with oxygen gives rise to the formation of a peroxy radical followed by the formation of a hydroperoxide and another radical on the main chain. The hydroperoxide may be itself easily decomposed giving an oxy and a hydroxyl radicals. The radical on the main chain may be further degraded breaking the polymer chain, and giving another radical. This process weakens the material lowering its molecular weight. Sometimes coupling of radicals gives the formation of products having a molecular weight higher than the starting materials. This reaction gives a material having different characteristics than the starting polymer: it is more rigid, less soluble and may be physically degraded during heating/cooling processes.

Thermal Degradation

Thermal degradation is due to an overheating of the material. It may induce, a homolytical breaking of a C-C or C-H bond in many polymers, giving several free-radical reactions with negative effects on the stability and molecular weight of the material. As an example, chain scissions lead to a rapid reduction of molecular weight already in the first stages of degradation; in an opposite way crosslinking, due to the coupling of two radicals, leads to an increase of average chain lengths and consequently of the molecular weight and an increase of the polymer dispersion index.

Chemical reactions involved in thermal degradation cause also a change in physical and optical properties of the polymer: an increase of the molecular weight leads to a reduced elasticity and embrittlement, colour changes, and reduction of most of the other desirable physical properties.

The effects of thermal degradation may be studied and monitored in laboratory with a climatic chamber, where temperature and relative humidity can be chosen simulating real climatic conditions and variations in an accelerated way (Figure 12).

Mechanical Degradation

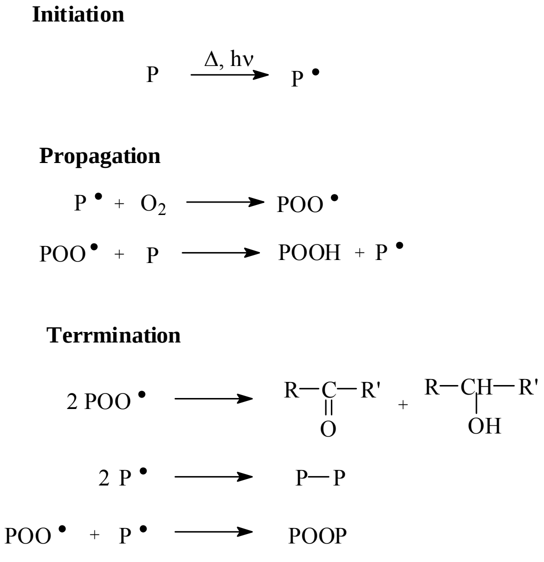
When treated stones are exposed to sunlight their temperature may increase causing a mechanical stress, since organic polymers may have thermal expansion coefficients very far from those of stone materials.

Mechanical degradation of organic polymers is often related to other kinds of degradation: as above reported, UV radiation can cause an increase in molecular weight of the polymer and due to the difference among the expansion coefficients of protective and stone materials can cause a stress and “craquelure” or irregularities on the surface of the polymer.

Other factors can lead to environmental stress, like hard leaps of temperature, or polymer migration inside the material due to a lacking of adherence between the polymer molecules and the stone substrate.

Chemical Degradation and Biodegradation

Polymers are subjected to degradation caused or accelerated by several chemical agents. Oxygen is one of the most common, as already reported in the previous paragraph on the photo-oxidative degradation.



P: polymer chain; R, R': alkyl group

Figure 11. Photo-oxidative degradation of a polymer

Figure 12. A climatic chamber and some samples inside.

Water is another important deterioration agent, since it can promote hydrolysis of esteric and/or amidic groups, in a process accelerated by acids, basis or other contaminants acting as catalysts.

Many polymers may be attacked by other pollutants such as ozone, sulphur dioxide and formaldehyde and degraded.

Another type of deterioration is due to biodeterioration, that is an ageing process of the polymeric materials mediated by a biological system such as moulds, bacteria or fungi and sometimes the enzymatic action or biochemical processes of higher forms of life. However, due to the hydrorepellency of the polymeric materials usually employed in this field, this degradation processes play a minor role.

SYNTHETIC POLYMERS FOR THE PROTECTION OF STONES

From a long time the use of a sacrificial layer, namely plaster, stucco, or paint film, was diffused as means of protecting masonry. Most often, natural organic substances, such as beeswax, oils, milk, fats and natural terpenoid resins, were used as traditional products in order to improve the hydrorepellency of stone surfaces.

Nowadays, water repellent treatments for stone materials take advantage of properties and performances of synthetic polymers, that are mostly easily available and more resistant than natural materials. Among them the most commonly employed are acrylic resins, silicone resins (alkyloxysilanes, siloxanes, silicones), epoxy resins and fluorinated polymers (Table 2).

Paraffin Wax

Aliphatic wax hydrocarbons are obtained as a heavy fraction in the refining of petroleum or by polymerization of ethylene. They are mainly constituted by linear aliphatic hydrocarbons having relatively low molecular weight. They have a high resistance to ageing and optical properties close to those of natural resins. They are mainly employed as varnishes for panel or canvas paintings. Due to the low polarity, when applied on stone materials, they easily diffuse inside the stones.

Synthetic products with a hydrocarbon structure are widely employed in the field of conservation, such as microcrystalline waxes (e.g. *Cosmolloid 80*), polyethylene glycols (*Carbowax*) and aliphatic varnishes (e.g. *Regalrez 1094*). One of the main problems when these products are employed for stone conservation is the rather low ability to interact with stone surface due to their polar structure. This leads to a migration of the product inside the stone and a loss of protection efficacy when exposed to an open air. Recently an attempt to solve these problems was made with the synthesis of polar functionalized polyolefins specifically designed for stone protection [19]. Ethylene/10-undecen-1-ol and ethylene/7-methyl-1,6-octadiene copolymers, containing polar groups, were synthetized by Ziegler-Natta catalysis. Ethylene/7-methyl-1,6-octadiene copolymer was further functionalized by hydroesterification and hydrogenation. The final products were composed by linear polyethylene chains with moieties containing hydroxy and ester groups, more compatible with the inorganic substrates. The performance of these products was tested on selected marble and Lecce stone specimens with very different porosity and pore size distribution.

Ethylene/7-methyl-1,6-octadiene copolymer (Figure 13) was obtained as an amorphous material and showed interesting film forming properties and very high water repellency. However a loss of protection efficacy was observed when exposed to artifical ageing, caused by photodegradation and oxidation reactions.

Ethylene/10-undecen-1-ol had a more crystalline character and its solubility was strongly affected by molecular weight distribution. The protective performance was higher when applied on the high porosity Lecce stone rather than on low porosity marble substrate. The product showed high stability to photo-oxidation and mantained the protection efficacy even after 1000 hours of exposure to UV radiations.

Acrylic Resins

Acrylic polymers are widely used for the formulation of protective products, due to their good adhesion, transparency and film forming properties. Acrylic resins are also used as consolidant and adhesive products, besides protective coatings.

They are thermoplastic materials, obtained from homo- or copolymerization of esters of acrylic and methacrylic acid (Figure 14). Their molecular weights are in the range 30000-100000 u.m.a.: the characteristics of an acrylic product can be quite different, according on the monomer (the acid moiety: acrylic or methacrylic, or ester moiety: methyl, ethyl, propyl, butyl, etc.) and the molecular weight.

Polymer rigidity and “rubbery grade” change according to the acid moiety (methacrylic are more hard and rigid than acrylic esters) and the length of the ester group: as an example, poly(methyl methacrylate) (PMMA) is hard and fragile, while poly(butyl methacrylate) (PBMA) is an oil at room temperature. Most of acrylic resins are soluble in common organic solvents, like ketones, esters, aromatic hydrocarbons and chlorinated solvents, and have good adhesive properties, while their glass transition temperature (T_g) and melting temperature (T_f) can be very different, giving to the product a very wide set of rigidness and hardness. These properties may be modulated selecting different monomers and modifying the molecular weight of the polymer in order to have the desired and appropriated T_g and T_f.

Table 2. Natural and synthetic organic materials used in stone conservation

Natural Organic Substances		Synthetic Organic Materials	
Classes	***Commercial names***	***Classes***	***Commercial trade***
		Paraffin wax	Regarlez 1094/1126
Oils	Linseed oil	Acrylic resins	Paraloid B72
	Walnut oil	Acrylic resins	Acryloid B72
	Poppyseed oil	Acrylic resins	Acrylic 30
Wax	Beeswax	Silicon resins	Wacker 290
		Silicon resins	RP224
Fats Resins	Animal fats	Silicon resins	Silirain
	Dammar	Silicon resins	Hydrophase
	Mastic	Epoxy resins	Water coat
		Fluorinated polymers	Akeogard
		Fluorinated polymers	Fombiln YR

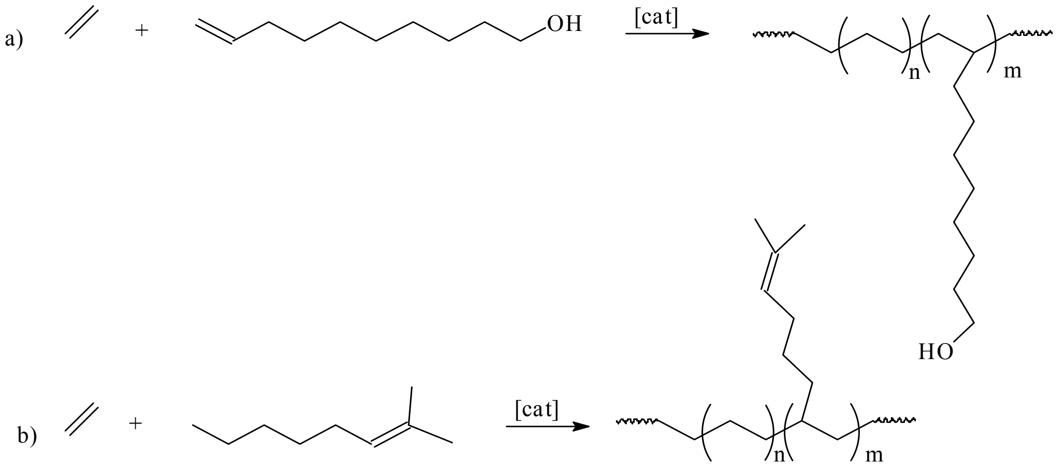
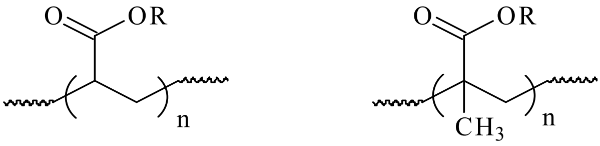


Figure 13. Schemes of ethylene/10-undecen-1-ol (a) and ethylene/7-methyl-1,6-octadiene (b) copolymerization.



R = CH_3, C_2H_5, C_4H_9, ...

Acrylic polymers Methacrylic polymers

Figure 14. Acrylic and methacrylic polymers.

Paraloid B-72 (a polymer among ethyl methacrylate (EMA) and methyl acrylate (MA) (70/30) with low amount of butyl acrylate (BA)) is a commercial product, which is extensively used since 1970 as a consolidant and protective agent (Figure 15, Figure 16). It offers a quite good hydrorepellency, high transparency, and hardness, partial reversibility and moderate stability. Other commercial products, such as Primal AC33 (a copolymer between methyl methacrylate and ethyl acrylate (MMA and EA)), Paraloid B67 (poly isobutyl methacrylate), Elvacite 2010 (poly(methyl methacrylate) (PMMA)) were pervasively used in the past decades.

Acrylic resins have some limits, as the other categories of protective products.

One of the most common problems noticed with these polymers is a low penetration of the product inside the stone material: even in the better conditions of application (a good solvent and a low viscosity of the solution), a penetration which is deeper than 1 cm is very hard to be reached. Another limit observed when acrylic resins are used as protective materials, is their keeping of the water repellent properties for a limited period of time. In order to obtain a long-lasting effect, acrylic polymers are often applied in mixture with silicon resins, or as an acrylic/fluorinated copolymer, as we'll see further on.

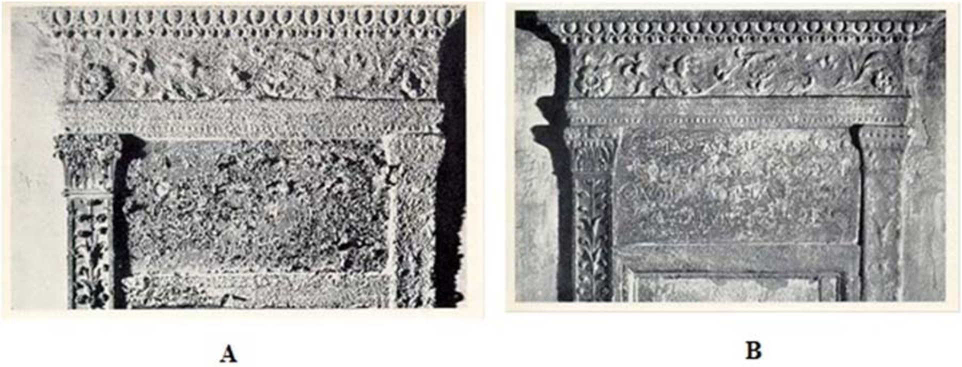


Figure 15. Detail of the tomb of J. Brand (15th century) St. Domenico Cloister, Bologna: Grey sandstone with a hard thin surface layer which appears broken into small plaques. A) Before restoration, B) After restoration and Consolidation with Paraloid B72 and Dry Film. [20]

Figure 16. St Petronio Basilica, Bologna. Sandstone treated with Paraloid B72 and Dry Film. [[21]] (by courtesy of Sailko: http://it.wikipedia.org/wiki/Basilica_di_San_Petronio (03.13.2013).

The acrylic resins in the course of the ageing lose hydrophobicity, connected with the loss of solubility and yellowing, as a function of their exposure to atmospheric agents (Figure 17). In order to obtain protective having a high thermal-and photo-stability, a great variety of acrylic homopolymers and acrylic/methacrylic copolymers has been extensively investigated. [22] Acrylic polymers give rise to cross-linking reactions, while methacrylic ones are subjected to depolymerisation. As an example, the C-H bond of the tertiary carbon in PMA can be easily broken generating a radical; this radical can react with another radical, giving a new C-C bond, that is a cross-linking between two different molecules. The result of this reaction is an increase of the molecular weight of the polymer with loss of its solubility, flexibility and so on. These changes may cause fracture on the film protecting the surface and lack of reversibility.

In the case of PMMA there are no tertiary carbon atoms present in the molecule, but the $-CH_3$ group linked to the main chain may be broken, generating a C=C double bond. This process may be followed by depolymerisation, decreasing the molecular weight and a partial loss of the polymer from the protected surface.

Alternatively, if conjugated double bonds are formed, they may give origin to chromophoric groups that are responsible of film yellowing.

If the polymers are employed as protective coatings for the conservation of monuments or ancient buildings, the limited environmental stability of acrylic polymers makes them inadequate to satisfactorily fulfil, in the long term, the requirements of water repellence, water vapour permeability, reversibility and negligible influence on the colour of substrates.

New applications of polyacrylates are reported. These products are blended with nanoparticles, mainly of anatase (TiO_2) in consideration of its photocatalytic activity [23] in the oxidation of organic contaminants and bacteria. However some problems must be solved because these nanoparticles are highly hydrophilic while polyacrylates are hydrophobic and these polymers may be oxidized by the catalytic activity of anatase. Also a blending of Paraloid B72 and nanoparticles of calcium hydroxide [$Ca(OH)_2$] has been suggested for the protection of stones or plasters. [24]

Silicon Resins

In the Sixties, a very wide class of products appeared in conservation field: silicon resins. [25] These compounds show a high stability of the Si-O bond (more stable than C-C, C-O and Si-Si bonds).

Inorganic silicates, such as Na_2SiO_3 and K_2SiO_3, where firstly used as stone consolidants, but some products of reaction may be dangerous for the stone itself:

$$Na_2SiO_3 + H_2O \longrightarrow SiO_2 + 2\,NaOH$$

In the case of organic silicon compounds (siloxane), silicon may form 2 bonds with oxygen atoms, while remains the possibility to form other 2 bonds with different groups (Figure 18).

The groups linked to silicon deeply affect the properties (and hence the performances) of the siloxanes. As an example, large substituents bring to rigid chains (high T_g), while silicon with small groups show a low T_g.

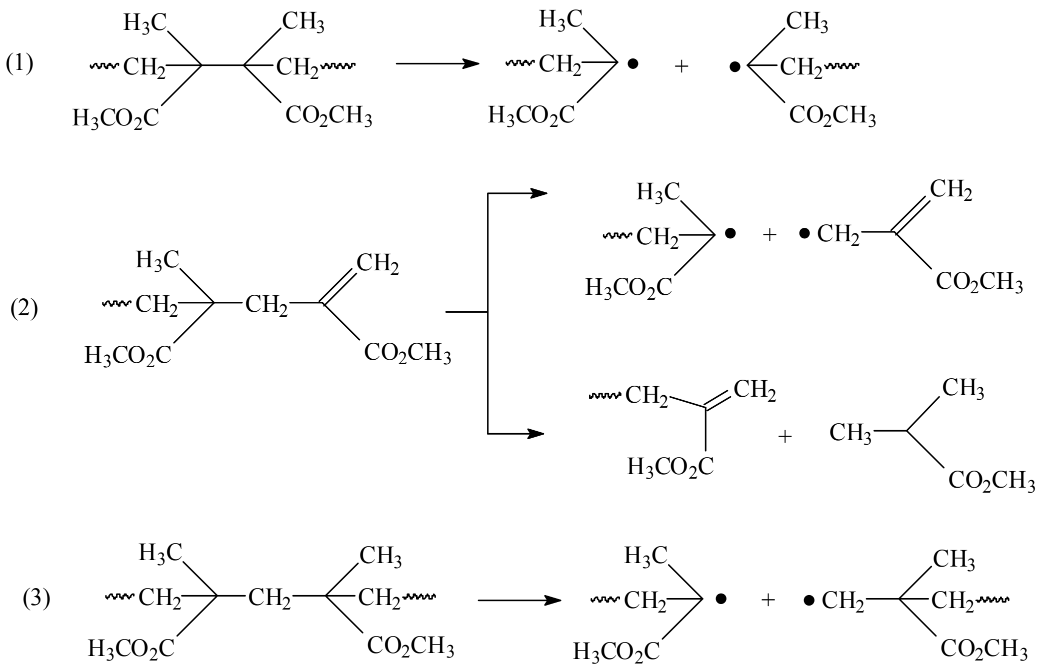


Figure 17. Thermal degradation of acrylic polymers

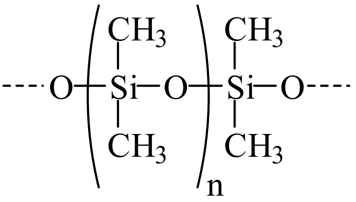


Figure 18. Poly(dimetyl siloxane).

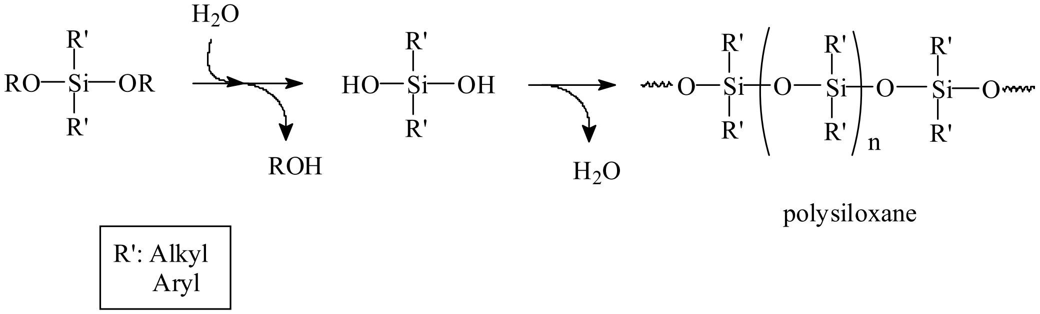


Figure 19. Synthesis of polysiloxane from alkyl alkoxy silane.

The length of the chain is another parameter affecting the properties of the resins. As a general rule, siloxanes with less than 10 silicon groups are liquid at room temperature, otherwise they are waxy stiffness.

In all silicon monomers or prepolymers, the Si-O-C moieties undergo to an easy hydrolysis when exposed to water, and then the -Si-OH groups covalently bind to superficial O-H groups present on the stone as well as they polymerise, giving rise to linear or branched structures, depending on the number of the O-H groups present on a silicon atom.

The rate of hydrolysis and subsequent polymerization of siloxane is strongly affected by the relative humidity of the environment and hence from atmospheric conditions.

The alkyl alkoxy silanes have general formula $R_nSi(OR')_m$ (n = 1, 2, m = 2, 3), the silicon atom is linked to alkyl and alkoxy groups. They are mainly used as monomer, in order to obtain an "in situ" polymerization. In fact the alkoxy groups are hydrolized giving hydroxyl groups that reacts as reported in Figure 19.

The alkyl alkoxy silanes used show a low molecular weight and they can deeply penetrate even in materials having a low porosity. On the other hand monomers are quite volatile, so they can be removed from the substrate by evaporation or washed away, before polymerization. The rate of polymerization depends on the humidity present in the stone and in the atmosphere so the process is not easily reproducible. Furthermore the molecular weight distribution is high and hardly reproducible.

Alkyl alkoxy silanes prepolymers can be also employed: Si-O-C bonds present may hydrolyze, when the product is penetrated inside the stone and gives further polymerization. Their volatility is low avoiding the loss of product by evaporation or washing before the complete polymerization. Both monomers and oligomers have good hydrorepellent characteristics, because the Si-C bond is not hydrolysable. Furthermore, they have good capacity of penetration and interaction with substrate. The polymers formed aren't reversible because they are not soluble in common solvents, so they are very hardly removed.

In polysiloxanes, silicon forms two bonds with two alkyl (or aryl) groups. These groups may be the same, or different. As an example, we show in Figure 18 the repeating unity of poly(dimethyl siloxane). The polysiloxanes used have high molecular weights and their structures can be linear, branched or cross-linked, containing alkyl and/or aryl groups giving flexibility and hydrophobicity. They maintain the initial solubility when applied, but their penetration in a porous substrate is low as usually happens for all polymers due to their high molecular weight.

These products seem to have a good protective efficacy towards pollutant agents like SO_2 and NO_x. Moreover, they have a good hydrorepellency, so they give a good protection even to freeze/thaw phenomena (Figure 20, Figure 21).

Figure 20. Marino Palace, Milan. Ceppo Gentile sandstone before restoration (A) and after restoration with Rhodorsil RC70 and Silirain 50 (1989), two polysiloxanes (B). (By curtesy of Friedrichstrasse http://it.wikipedia.org/wiki/File:Milano_pal_Marino_piazza_Scala.jpg (03.06.2013)).

Figure 21. Fastigium of the S. Marco Cathedral, Venice. Greek marble, restored using Rhodosil 991 and Silirain 50 (1975), two polysiloxanes. (By curtesy of Andreas Volkmerhttp://it.wikipedia.org/wiki/ File:Venedig_Basilika.jpg (03.06.2013)).

Regarding to their permeability to water vapour and their stability to UV radiation, the results reported in literature are controversial. [26]

Silanols containing at least two alcoholic groups linked to silicon may be employed and, after the application of the product, hydroxyl groups react with the same groups of other molecules, giving rise to a Si-O bond. The other bonds of silicon may be engaged by alkyl or aryl groups (Figure 22).

Lastly, the alkoxysilanes are considered on the borderline between inorganic and organic products,because silicon is linked to four alkoxy groups.

The most widespread alkoxysilane is tetraethyl orthosilicate (TEOS), that is a low molecular weight product having a low density.

The reaction mechanism is close to that one of alkyl alkoxy silanes, with hydrolysis and condensation that brings it to a tridimensional silicate polymer. The absence of alkyl groups in the structure gives no protective properties to the product, but it has good performances as consolidant.

In recent years a new class of composite silicon material is offered. It is based on organic polymers and inorganic layered reinforcement consisting of organo modified silicates whose layers have a thick of few nanometers. [27] These systems show a large interfacial area in the range between nanosheets and polymer, with higher properties if compared to unmodified resins. In particular they exhibit higher chemical, thermal and mechanical resistance and reduced gas and vapour permeability, without spoiling the optical properties of the polymeric matrix.

The addition of silica nanoparticles substantially enhances the protective efficiency of silicon compounds and the treated stone surface is super-hydrophobic and self-cleaning. [28] In other way the addition of nanolime, that is nanoparticles of calcium hydroxide (nanorestore), improves the consolidating performances of this blending. [29]

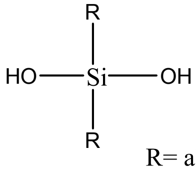
Polysiloxane and fluorine containing siloxane polymers have been developed and used in the protection of construction materials. [30] The inclusion of fluorinated molecules reduces the already low surface energy of alkyl siloxanes. Thanks to the greater mobility of the siloxane chain, fluorocarbon groups can be aligned more effectively on the surface of the polymer. In addition the water and oil repellence is increased by the presence of fluorine that enhances also the chemical, thermal and photo-chemical stability.

Epoxy Resins

Epoxy resins are low molecular weight linear polymers obtained from monomers or short chain polymers containing epoxy groups at both ends of the chain. One of the most common epoxy pre-polymer is obtained from the reaction between epichlorohydrin and bis-phenol-A (Figure 23), as the main component. Similar prepolymer may be obtained by substitution one or the two chemicals employed.

A further reaction of the prepolymer with a cross-linking agent, usually a diamine, gives the epoxy resin (Figure 24).

One of the commercial epoxy resin is obtained from the diglycidyl ether of bisphenol A (DGEBA). It is a viscous oligomer that may be applied together with a catalyst to form the final polymer. Epoxy resins are highly resistant to acids, bases and organic solvents but present serious problems of colour stability: usually these resins become yellow even when stored in the absence of light.



R= alkyl or aryl groups

Figure 22. Di-alkyl/aryl silanol.

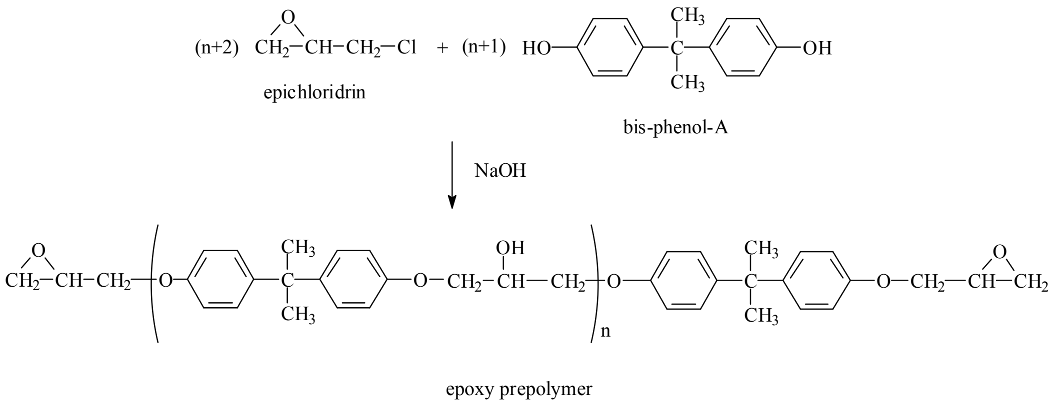


Figure 23. Synthesis of an epoxy prepolymer.

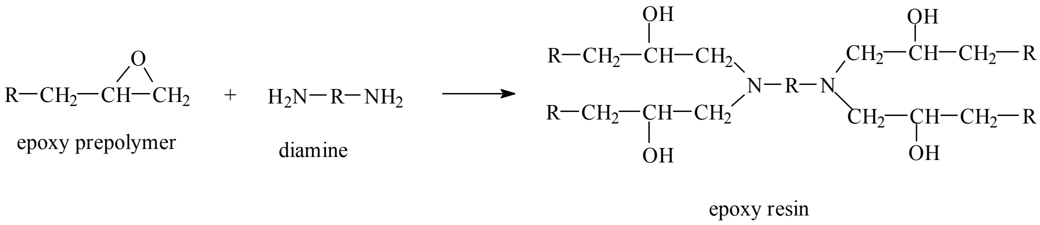


Figure 24. Formation of an epoxy resin.

Epoxy resins have been widely used and tested as adhesives for sticking glass object that will be stored in the museum environment.

Due to the high strength and gap-filling ability, epoxy resins were used for the consolidation and restoration of stone, even if they show a quite important absorption of SO_2 (Figure 25, Figure 26). On the contrary, they are not utilized as protective materials, since they don't contain hydrophobic groups.

Figure 25. Milano dome (Italy) Restored in 1972 using epoxy resins mainly, for sealing purposes, together with acrylic resins [32] (By courtesy of MarcusMark http://it.wikipedia.org/wiki/File:876 MilanoDuomo.JPG (03.06.2013)).

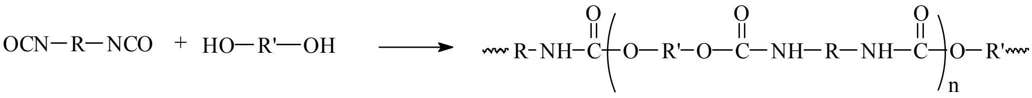
Polyurethane Resins

Polyurethanes are synthesized by reacting a molecule containing at least two isocyanate functional groups with a molecule containing at least two hydroxyl groups (Figure 27) [31]

We can find polyurethanes in every room of our house and practically everywhere we go: they are largely used in daily home furniture, cars and thermal isolation.

In conservation field, polyurethane are mainly employed to seal surfaces of different materials such as wood, metal, and paintings or protect them from rot, corrosion, or fading. As an example, Xylamon LX Hardening N (Desowag) has been extensively used since 1950s for the consolidation of fragile wood [34]. Commercial polyurethanes have been used for the conservation of leather, both as adhesives [35] and consolidants [36]. Rigid polyurethane foams using an appropriate isolating varnish have been used for temporary facing supports in the course of a painting restoration. [37] As adhesives, polyurethanes resist to moisture and heat, so their use is ideal in the case of objects exposed, particularly to sun and salted waters (Figure 28).

Figure 26. Stibbert Museum- Florence (Italy). Epoxy resins have been employed mainly as consolidating agents (1997). [33] (by courtesy of Stibbert Museum-Florence (Italy)).



$$\mathrm{OCN{-}R{-}NCO} + \mathrm{HO{-}R'{-}OH} \longrightarrow \sim\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}}\left(\mathrm{O{-}R'{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}}\right)_n\mathrm{O{-}R'}\sim$$

Figure 27. Polyurethane synthesis.

Nevertheless, polyurethane resins are not extensively used in conservation, because all isocyanate monomers are highly toxic. Furthermore, polyurethane polymers are sensitive to thermal and photooxidative degradation. [38] Expecially polyurethane foam can turn yellow and disintegrate, so it is widely used in the lifting and temporary support of archaeological objects, but when a long life is required, polyurethane foams are substituted by polyether foams.

Polyurethane polymeric structures with fluorinated segments in their chains provide a higher stone protection than neutral perfluoropolyetheres (see also the following paragraph). In fact C-F bond makes the polymer hydrorepellent and chemically stable and, on the other side, the polarity of urethane bond should physically link the film on the stone substrate reducing the stone decay. A further advantage claimed for these products is the possibility to perform the synthesis using a water emulsion.

Fluorinated and Perfluorinated Polymers

In order to improve the properties of polymers used in conservation of stone materials, as they are summarized in a previous paragraph, since the end of Seventies, Piacenti's group proposed the use of perfluoropolyethers. These polymers were promising protective from different points of view: excellent hydrophobicity, high resistance to UV radiation, inertia towards the substrate and most of the pollutants present in the atmosphere.

Figure 28. Freedom monument, Riga (Lettonia) Restored using polyurethane resins mainly, for sealing purposes. [39] (by courtesy of Latvian Tourism Development Agency).

Fluorinated organic molecules are indeed chemically and thermally very stable, due to the high energy of the C-F bond and to the deactivation induced by the electronegative fluorine atoms towards the C-C bonds.

Fluorinated elastomers have a good capacity of adhesion and cohesion, and they are used mainly as adhesives and binders in fillers, but some of them have protective properties too: an example is the commercial product known as NH. Elastomers have however large molecular dimensions, so they are not able to deeply penetrate inside stone materials, and they have good performances mainly on lithotypes having a high porosity.

Perfluoropolyethers on the contrary have medium or low molecular weights, usually between 5000 and 7000 uma, and have a good penetration capacity.

They are obtained from the photo-polymerization of hexafluoropropene or tetrafluoroethene and they were tested and then suggested as water repellents in the field of stone conservation of monumental buildings. [40]

In consideration of their water- and dirt-repellent properties, fluorinated products have been used primarily to develop waterproof coatings, but some researches has been also reported on their anti-graffiti properties. [41]

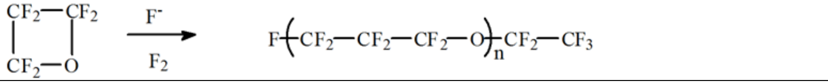
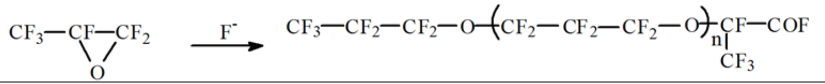
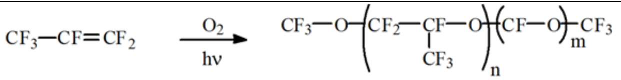
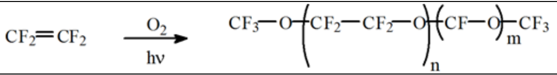
Perfluoropolyethers are extremely stable, colourless, permeable to oxygen, insoluble in water and most of the organic solvents. Moreover, they are liquid and therefore easily applicable on a solid surface. At last they are non toxic, have a low superficial tension and a refractive index very close to that one of water. Akeogard PF and Fomblin Y MET were commercial products largely diffused in the past years.

Unfortunately the good preliminary remarks were followed by some negative features: colour changes and reduction of protective efficacy in relatively short times when applied on some lithotypes.

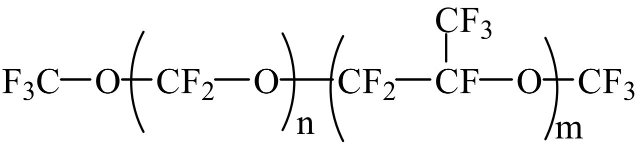
Regarding the first of these two drawbacks, it was noticed that this behaviour is not due to a degradation of the product but to the inclusion of dust particulate on the surface, leading to a darkening of the surface itself, especially on white stones.

Concerning the second drawback, instead, the lone pair of electrons on the oxygen atoms, are deactivated by the fluorine atoms present in the molecule, so they are not available for the interaction between this polymer and the stone surface. Due to the very weak interaction the perfluopolyethers with the surface slowly tend to migrate inside the stone that is they are absorbed by the porous structure. The mobility of the product inside the stone leads to a gradual loss of the protective present on the surface in the course of time, reducing the protective action. On some lithotypes, for example sandstones, this inward diffusion is sufficiently slow due to the texture of calcium carbonate and the presence of clay layers assuring a protective efficacy for a long time, while in many other cases (for example marble or tiles) this phenomenon causes a rapid decrease of the surface protection and requires, in the course of time, further treatments. The protective efficiency in the course of time of Fomblin YR (Figure 29), a perfluoropolyether obtained by photopolymerization of hexafluoropropene is reported in Figure 30. The product was applied on Carrara Marble (porosity lower than 1%) (Figure 31) and Serena Stone (~ 5% porosity), a sandstone with a clay matrix (Figure 32).

Table 3. Some important families of perfluoropolyethers with relatives reactants and commercial names

Demnum	
Krytox	
Fomblin Y	
Fomblin Z	

In order to reduce the mobility of perfluoropolyethers, some new products containing functionalized groups able to form chemical or physical interactions with the substrate were prepared. Perfluoropolyetheric carboxylic acids, esters and amides were very interesting products due to the possibility to transform their functional group in compounds having the possibility to interact with the stone support. [42, 40 [f], 34 [i]]



$$F_3C{-}O{-}\left(CF_2{-}O\right)_n{-}\left(CF_2{-}\overset{CF_3}{\overset{|}{CF}}{-}O\right)_m{-}CF_3$$

Figure 29. The perfluoropolyether Fomblin YR.

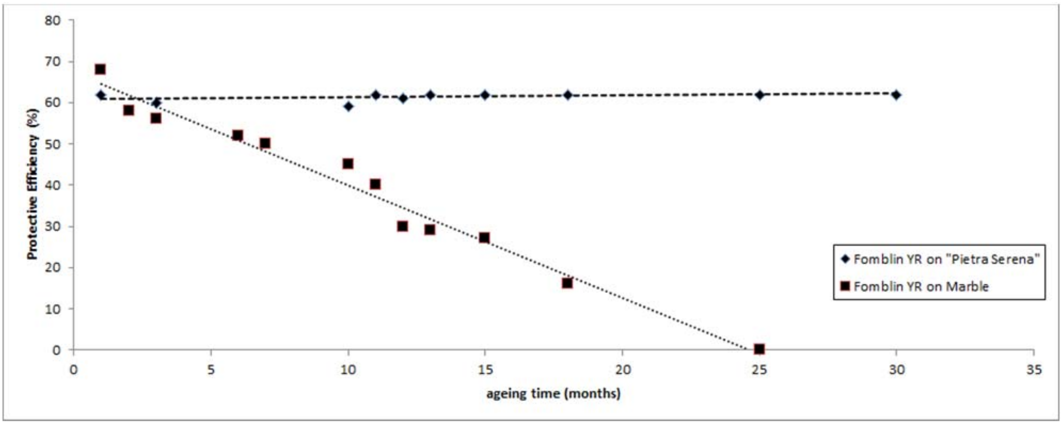


Figure 30. Protective efficiency of Fomblin YR after various time intervals.

Figure 31. The Cathedral of St Martin (*Duomo di Lucca*) and its bell tower in Lucca, Tuscany, Italy, S Giuliano Marble, red nodular ammonitic limestone from Alta Garfagnana, deep green serpentine from Prato, restored with Fomblin Met (1982). [42f] (by courtesy of Diocesi Lucca- Italy)

As an example, perfluoropolyetheric amides were obtained as viscous liquid having high chemical stability. Their properties made them eligible as protective agents for stone objects of relevant historical and artistic importance, in particular for those exposed to an aggressive environment. In Table 4 and Figure 33 are reported the structures of some functionalized perfluoropolyethers (esters and amides).

The use of these functionalized perfluoropolyethers gave very good results in the protection of marble and other stones having low or medium porosity and quite good results were also obtained with high porosity materials (Figure 34, Figure 35, Figure 36).

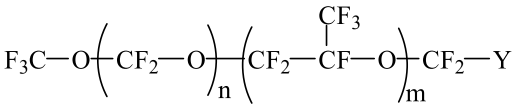
In Figure 37 are reported the performance offered by two of these functionalized perfluoropolyethers (chemical formula in Figure 33) on a Marble and a Sandstone. On Marble, there is a considerable improvement in the retention of the efficiency of protective treatment when applying IBE (ester) or IBA (ammide) instead of the original perfluoropolyether.

Figure 32. Pitti Palace, Florence. Some parts of Pietra Forte restored with Fomblin YR (1982-87) [17 [1]].

Table 4. Some important functionalized perfluoropolyethers with their commercial names

Product code	Chemical formula
IBE	$Rf\text{-}CF_2\text{-}CO\text{-}O\text{-}CH_2CH(CH_3)_2$
IBA	$Rf\text{-}CF_2\text{-}CO\text{-}NH\text{-}CH_2CH(CH_3)_2$
DC2A	$Rf\text{-}CF_2\text{-}CO\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}CO\text{-}CF_2\text{-}Rf$
DC6A	$Rf\text{-}CF_2\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}CF_2\text{-}Rf$
TC2A	$Rf\text{-}CF_2\text{-}CO\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}CO\text{-}Rfz\text{-}CO\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}CO\text{-} CF_2\text{-}Rf$
TC6A	$Rf\text{-}CF_2\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}Rfz\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-} CF_2\text{-}Rf$

$Rf = CF_3\text{-}O\text{-}[\text{-}CF_2\text{-}CF(CF_3)\text{-}O\text{-}]_m\text{-}(\text{-}CF_2\text{-}O\text{-})_n$; $Rfz = \text{-}CF_2\text{-}(O\text{-}CF_2\text{-}CF_2\text{-})_p\text{-}(O\text{-}CF_2\text{-})_q\text{-}OCF_2$



$$F_3C-O\left(CF_2-O\right)_n\left(CF_2-\overset{CF_3}{\overset{|}{C}}F-O\right)_m CF_2-Y$$

YR $Y = F$

IBE $Y = COOCHCH_2CH(CH_3)_2$

IBA $Y = CONHCH_2CH(CH_3)_2$

Figure 33. Perfluoropolyether derivatives of Fomblin YR.

Unfortunately, the application of these compounds on the substrate required the use of chlorofluorocarbons as solvents. In the Nineties, the Montreal international protocol declared the CFC very dangerous for the environment because attributed the ozone hole to the presence of this product in the atmosphere. The use of these solvents was gradually banned, making the application of perfluoropolyethers very hard.

Figure 34. Loggia dei Lanzi, Florence. Protected using Akeogard BA, cealings with Akeogard CO (1988 -90).

Figure 35. St Trinita Church, Florence. Pietra Forte restored with IBA and a fluoroelastomer (1990-92).

In literature is proposed to bypass this problem using aqueous micro-emulsion of perfluoropolyether derivatives [44] but this application is hardly performed. It is also known the use of dispersion or aqueous emulsions of fluorinated polyurethanes for treating marble stones, bricks and similar materials used in buildings and historical monuments [45]. They were obtained by polymerization of perfluoropolyethers having hydroxyl terminal groups, with di-isocyanates.

Many other groups studied different fluorine containing polymers (Figure 38), keeping in mind that the introduction of fluorine atoms improve the chemical, thermal and photo-chemical stability, together with their hydrophobicity as a consequence of the lower surface energies brought by fluorinated groups.

Among these protective, partially fluorinated acrylic and methacrylic polymers, were prepared considering their suitable glass transition temperature, solubility in many organic solvents, water repellence, adhesive and cohesive properties, with the aim to obtain good consolidants for porous decayed materials such as stone or wood artefacts. These polymers may be subdivided into polymers containing fluorine in the ester group or polymers containing fluorine in the main chain. Usually, acrylic and methacylic monomers containing fluorine atoms in ester group are commercially available, while monomers for the syntheses of polymers containing fluorine atoms in the main chain must be synthesised in laboratory through complex procedures (Table 5).

Acrylates containing fluorine atoms in the ester moiety are obtained by partial or total replacement of the methacrylate units in Paraloid B72 (EMA/MA) with fluorinated methacrylates. The expected improvement of the coating properties was not reached: although side chain fluorination of acrylic copolymers has always improved the hydrophobicity of the polymer, the photostability is only slightly improved. Presumably the fluorine atoms are too far from the weak tertiary C–H bonds to provide a significant stabilisation effect. Furthermore in the course of ageing the ester moiety containing fluorine atoms are rapidly lost.

Figure 36. St. Michele and Gaetano Church, Florence. Pietra Forte restored usin an acrylsiliconic resin, Akeogard CO and Akeogard BA (1991-96). [43]

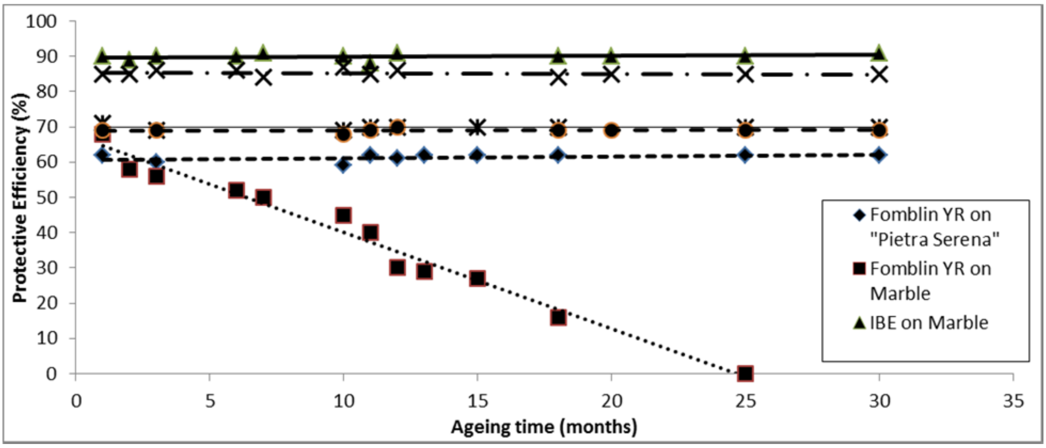
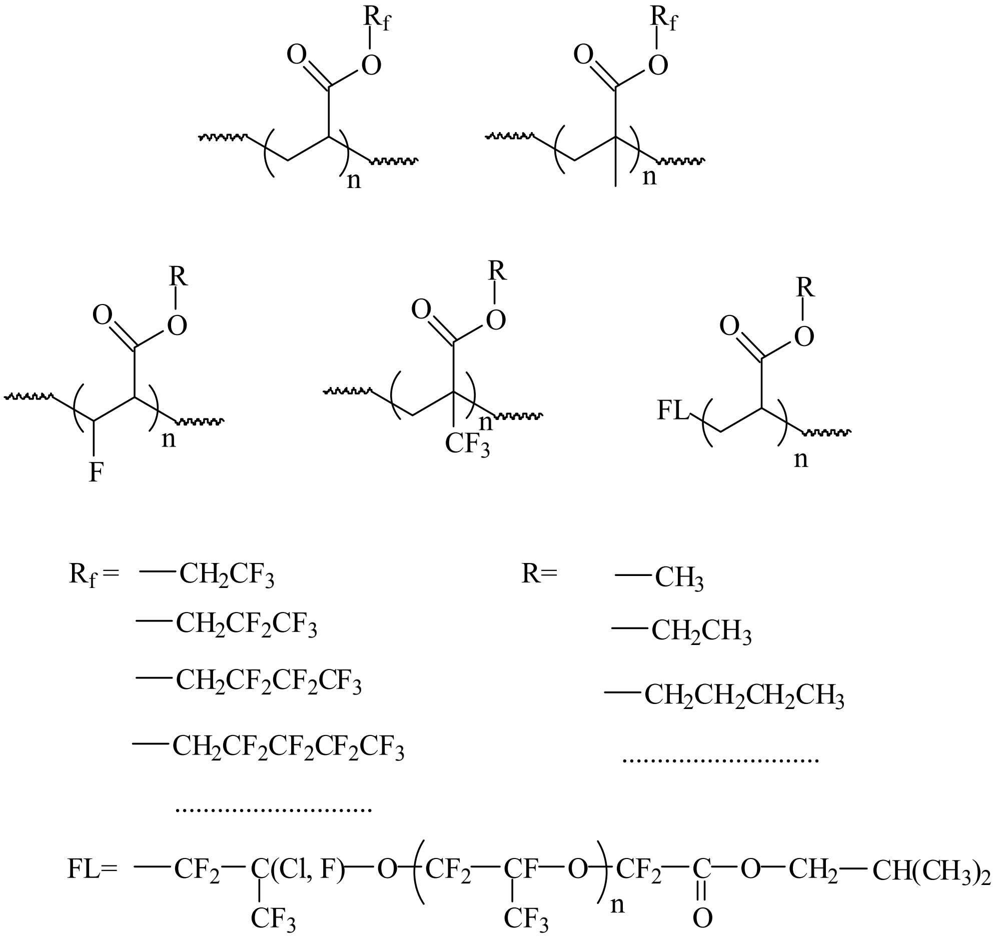


Figure 37. Protection efficiency of different protective treatments during ageing. YR= Perfluoropolyether; IBE= corresp. iso-butylester; IBA= corresp. iso-butyl amide.



$R_f =$ —CH_2CF_3
—$CH_2CF_2CF_3$
—$CH_2CF_2CF_2CF_3$
—$CH_2CF_2CF_2CF_2CF_3$
....

R= —CH_3
—CH_2CH_3
—$CH_2CH_2CH_2CH_3$
....

$$FL= -CF_2-\underset{CF_3}{C}(Cl,F)-O-\left(CF_2-\underset{CF_3}{CF}-O\right)_n CF_2-\overset{}{\underset{O}{\overset{\|}{C}}}-O-CH_2-CH(CH_3)_2$$

Figure 38. Fluorine containing polyacrylate or methacrylate.

Table 5. Chemical formula of commercial or synthesized acrylic and methacrylic monomers

Commercial monomers	Synthesised monomers
CH_2=CH-COO-R_f	CH_2=CF-COO -R
CH_2=C(CH_3)-COO-R_f	CH_2=C(CF_3)-COO-R
R_f= $CH_2(CF_2)_xCF_3$, x=1-2	R = CH_3, C_2H_5

Polyacrylates containing fluorine atoms in the main chain, such as poly(ethyl 2-fluoroacrylate) (PE2FA), showed a stabilising influence of the fluorine atom on the rate of oxidation [46]. Among the different partially fluorinated acrylic and methacrylic polymers, the PE2FA showed the highest chemical stability and it was proposed as protective agents for stone [47]. Copolymers between a methacrylic ester and a modified perfluoropolyether has been obtained by insertion of a perfluoropolyetheric moiety in the course of the polymerization. This process must be performed by Atom Transfer Radical Polymerization (ATRP), [48] using a functionalized perfluoropolyether as radical initiator of the reaction (PFE-X in Figure 39). [49]

Polyesters from Natural Resources

During the last years, a new class of polymers has been growing its importance as protective material for stones because these products may be obtained from a natural, renewable resources. For instance poly(lactic acid) PLA have been synthesized from lactic acid, that is a natural product, easy affordable from many natural sources (corn, sugar beet, or other sugar containing materials), by a fermentation process [50]. PLA can reach a maximum value of T_g = 60°C, and T_f = 180°C, it is biodegradable, it is not harmful for man and environment and it is approved by Federal Drug Administration.

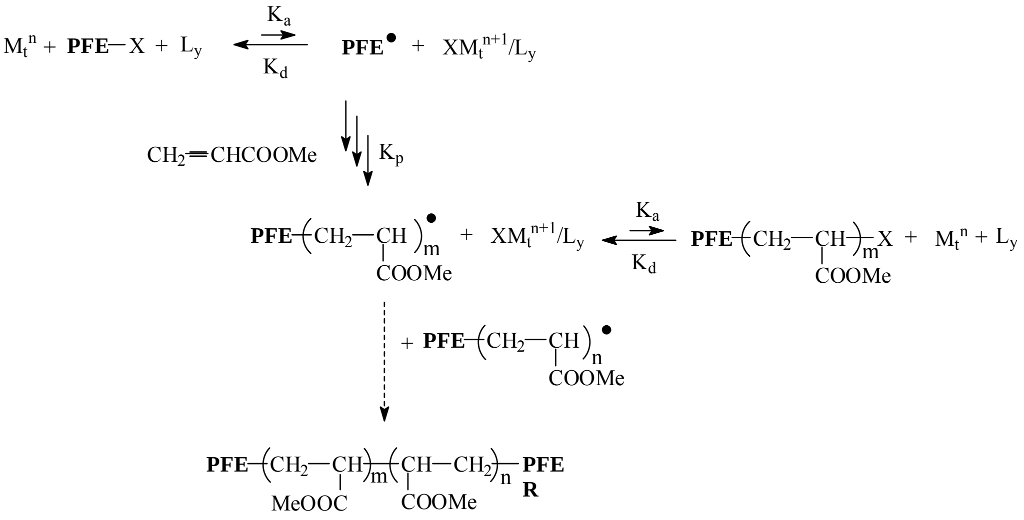
It can be obtained by three different polymerization processes (Figure 40) and its molecular weight depends on the procedure adopted. [51]

PLA are used for different applications like packaging or biomedical applications. [52] In addition to these ascertained applications, PLAs obtained by azeotropic condensation of lactic acid and by Ring Opening Polymerization (ROP) has been evaluated as protectives for stone materials.

The polymers prepared by azeotropic condensation were synthesized using Tin(II) octoate [Sn(Oct)$_2$] as catalyst and L, D or the racemic mixture of L/D-lactic acid as the starting monomers, under different conditions (like monomer/catalyst ratio, temperature, time) [53]. They are soluble in common organic solvents (like ethanol, acetone, THF, chloroform, etc.).

In order to obtain high molecular weight polymers containing low quantities of lactic acid impurities, ROP catalyzed by Tin(II) Octoate [Sn(Oct)$_2$]/ROH has been used for PLAs syntheses (Figure 41). [54]

Lactide monomers used for ROP are generally obtained by high temperature depolymerisation of lactic acid oligomers produced by polycondensation.



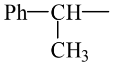
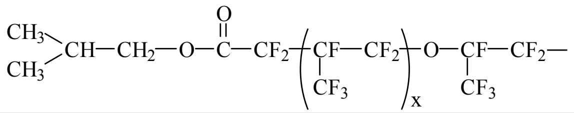
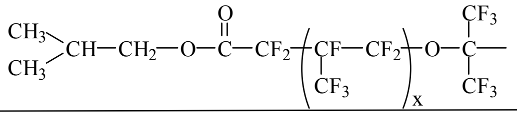
Polymer	PFE	L	X
PMA(n)	 $Ph-CH(CH_3)-$	BPY or TMEDA	Br
PMA-F(1)	 $(CH_3)_2CH-CH_2-O-C(=O)-CF_2-[CF(CF_3)-CF_2]_x-O-CF(CF_3)-CF_2-$	BPY	Cl
PMA-F(2)	 $(CH_3)_2CH-CH_2-O-C(=O)-CF_2-[CF(CF_3)-CF_2]_x-O-C(CF_3)_2-$	TMEDA	Cl

Figure 39. ATRP reaction scheme. Mt: CuCl, BPY: bipyridine, TMEDA: Tetramethylendiamine.

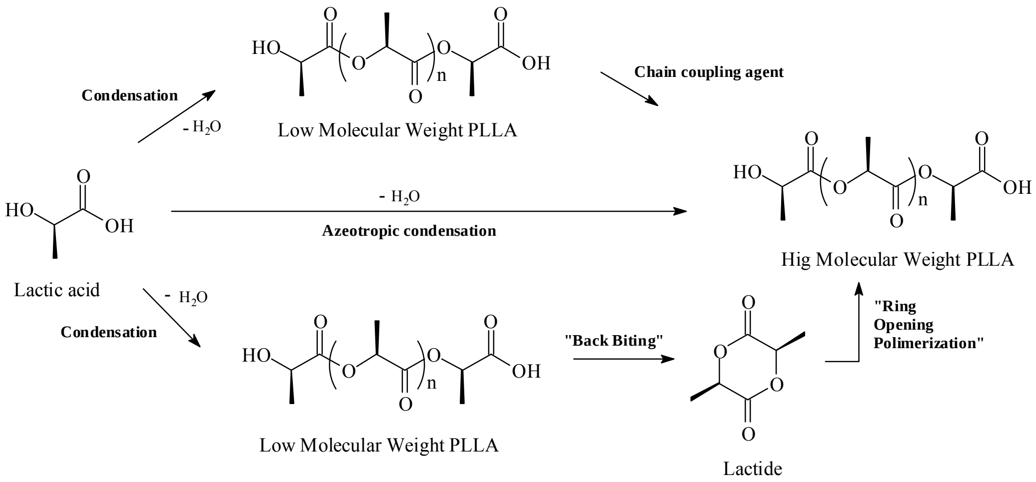


Figure 40. Processes for PLLA synthesis.

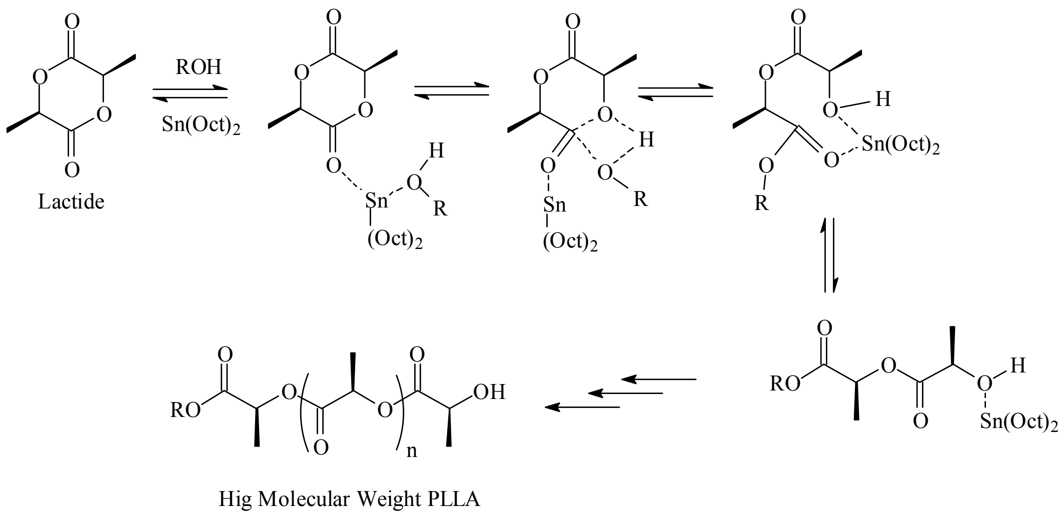


Figure 41. Mechanism of the PLLA synthesis via ROP process.

The stereochemistry of polymers can be easily modified by the choice of an appropriate mixture of L, D isomers of lactic acid or using a different catalytic system obtaining both crystalline or amorphous materials. [55] The modification led to a change in the performance of the polymers especially for what concerns their physical properties.

As an example some selected properties of poly-L-lactide (PLLA), synthesized from L-lactide, and poly-DL-lactide (PLDA, derived from rac-lactide, the racemic mixture of L-and D-isomers) are reported in Table 6.

Table 6. Selected properties of PLA

Physical properties	L-PLA	DL-PLA
Tensile strength (Mpa)	59	44
Elongation at break (%)	7.0	5.4
Modulus of elasticity (Mpa)	3750	3900
Yield strength (Mpa)	70	53
Flexural strength (Mpa)	106	88
Unnotched izod impact (J/m) Notched izod impact (J/m)	195 26	150 18
Rockwell hardness	88	76
Heat deflection temperature	55	50
Vicat penetration (°C)	59	52

PLLA and PLDA obtained by ROP showed molecular weight among 11800 and 83000 g/mol. They were tested on some lithotypes (Sivec Marble, Gioia Marble, Lecce Stone, Neapolitan Yellow Tuff and Serena Sandstone) and showed an interesting photo -stability under (artificial) UV irradiation (Solar Box). In fact, after 1000 hours ageing (500 W/m^2) the polymers maintained their solubility in chloroform, suggesting a good reversibility. [56].

Porous materials (Lecce Stone and Yellow Tuff) treated with PLLA and PLDA showed high water repellence (up to 90%), moreover, this is directly connected to a not negligible colour change. Less porous stones (Marbles and Sandstone) showed a lower hydrorepellency (P.E.% up to 50%), due to a smaller amount of product penetrated inside the stone.

Since in some cases PLA showed a lower protective efficacy than commercial products usually employed as stone protective materials, like PB72, in order to improve the hydrorepellency of PLA polymers, a perfloropolyether was employed as a transfer agent for the ROP of PLA synthesizing block copolymers (PLA-FLK-PLA). Fluorolink D-10H (FLK) was the perfluoropolyether employed: a commercial product characterized by the presence of two hydroxy-telechelic functionalities (Figure 42). [57]

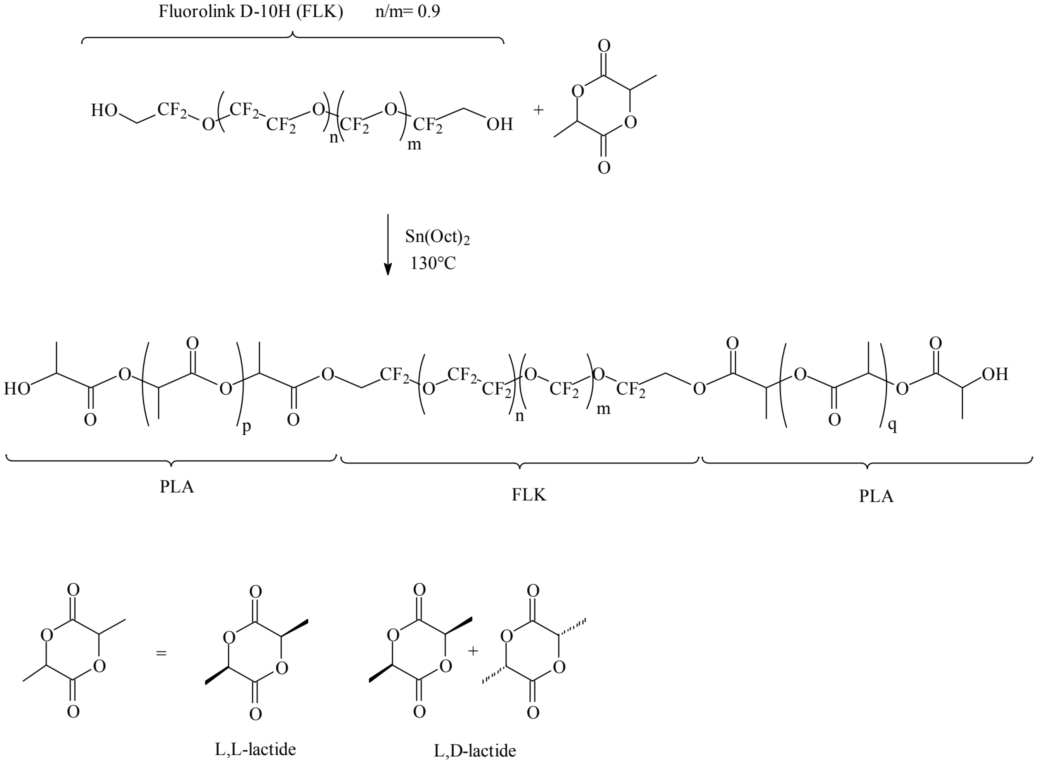


Figure 42. Copolymers PLA-FLK-PLA synthesised from Fluorolink D-10H and lactide.

These new polymers show a good solubility in common solvents and good resistance to UV radiation and seem to be very promising as stone consolidant and/or protective.

Some PLA-FLK-PLA copolymers were applied on several stone materials (Sivec Marble, Gioia Marble, Lecce Stone, Neapolitan Yellow Tuff and Serena Sandstone). The treated samples, as confirmed by colorimetric analysis, showed negligible colour variation, and as forecasted, the presence of a perfluoropolyether block led to an enhancement of water repellence with respect to the PLA homopolymers (~ 75% on Sandstone and ~ 90% on Marble).

PLA-FLK-PLA were also natural and artificial aged. In addition to UV irradiation in a Solar Box, treated samples were submitted to an artificial ageing through thermo-hygrometric cycles in a climatic chamber and to an outdoor natural ageing. UV irradiation and thermo-hygrometric ageing did not cause any relevant variations in polymers performances.

Otherwise, outdoor ageing led to a partial loss of water repellence, probably due to some migration of the polymer inside the stone material especially for the more porous stones (Lecce Stone, whose dry weight didn't change after ageing), or dilavation for the less porous stones (in particular Gioia Marble, whose dry weight decreased after ageing, coming back near to the not treated one).

Nevertheless, the high photo-chemical and thermal stability, the negligible short- and long-term colour changes and an important enhancement of water repellence with respect to PLA homopolymer suggest further study on these very promising polymers.

In order to reduce the fluorine content present in the PLA-FLK-PLA other series of PLA copolymers were prepared with undeniable advantages of higher eco-compatibility, higher solubility in common organic solvents and lower cost. These new series of fluorine-functionalized PLA (Figure 43) were synthesized using two commercial fluorinated alcohols (3,3,4,4,5,5,6,6,7,7,8,8-tridecafluoro-1-octanol and 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) benzyl alcohol as co-initiators in the ROP of L-lactide and rac-lactide with different amount of the two reagents. The polymers were characterized and tested as protective materials on Sivec Marble. [58]

The new polymers proved an interesting photoageing behaviour, close to that one of PLA-FLK-PLA, colour variation in a quite large range (ΔE from 2 to 8) and a protective efficacy among that one of not fluorinated PLAs and PLA-FLK-PLAs copolymers

Further study are in progress on these new polymers.

An interesting development in the synthesis of polyester as protective materials comes from the employment of mandelic monomers in the ROP process. A series of mandelic acid containing copolymers were recently synthetized [59] by copolymerization of L-lactide with mandelide, the cyclic dimer of mandelic acid, using Tin(II) octoate as catalyst in the melt phase (PLA-PMD). The aim was to increase the UV-barrier properties with the introduction of phenyl moieties as lateral groups in the polyester chain, as well as to obtain controlled thermal and mechanical properties (T_f, T_g, crystallinity, etc). Another mandelic/lactic copolyesters was obtained through the ROP of (3S)6-methyl-3-phenyl-1,4-dioxan-2,5-dione (Figure 44) obtaining a random A-B amorphous copolymer. Copolymers containing a perfluoroalkyl moiety were also synthetized in the presence of 3,3,4,4,5,5,6,6,7,7,8,8-tridecafluoro-1-octanol (PLA-PMD-PFO). The copolymers PLA-PMD showed a great enhancement of UV absorption (about ten times higher than PLA in the range 300-350 nm) and an increasing T_g with higher mandelide content (up to 72 °C) even if polymers show a low molecular weight. A decrease of crystallinity was also observed with increasing mandelide content, till no more T_f or T_c was present and the materials were completely amorphous.

Some copolymers were applied on selected Carrara marble samples. The treatment increased the hydrophobicity of the surfaces (P.E. up to 67%) but a loss of protective efficacy and significant color variations were observed after UV ageing. The copolymers PLA-PMD-PFO showed much better water repellence (P.E. = 90%) and stability to photodegradation with negligible color changes. Futher studies are in progress on these new polymers.

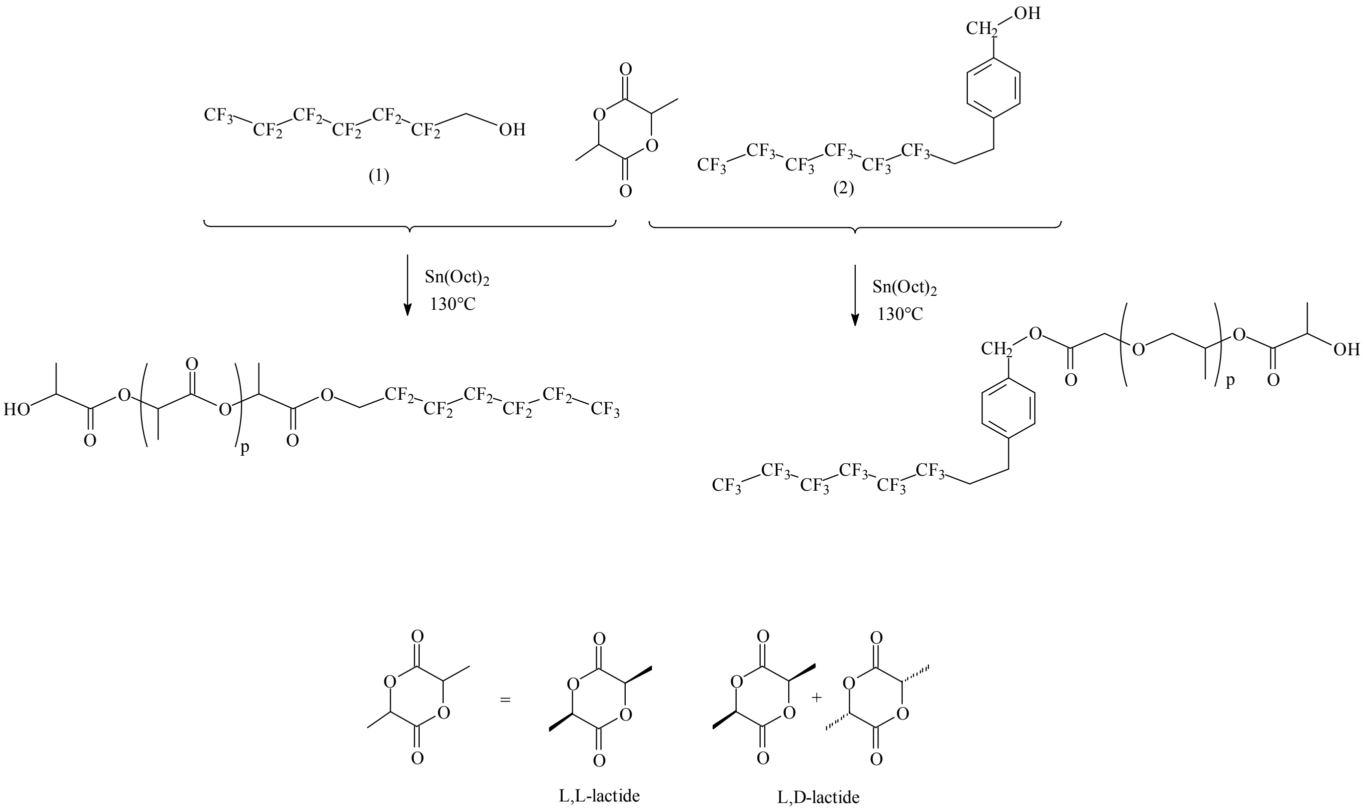


Figure 43. Copolymers PLA-FA synthesised from fluoroalcohol (1) or (2) and L- or *rac*-lactide.

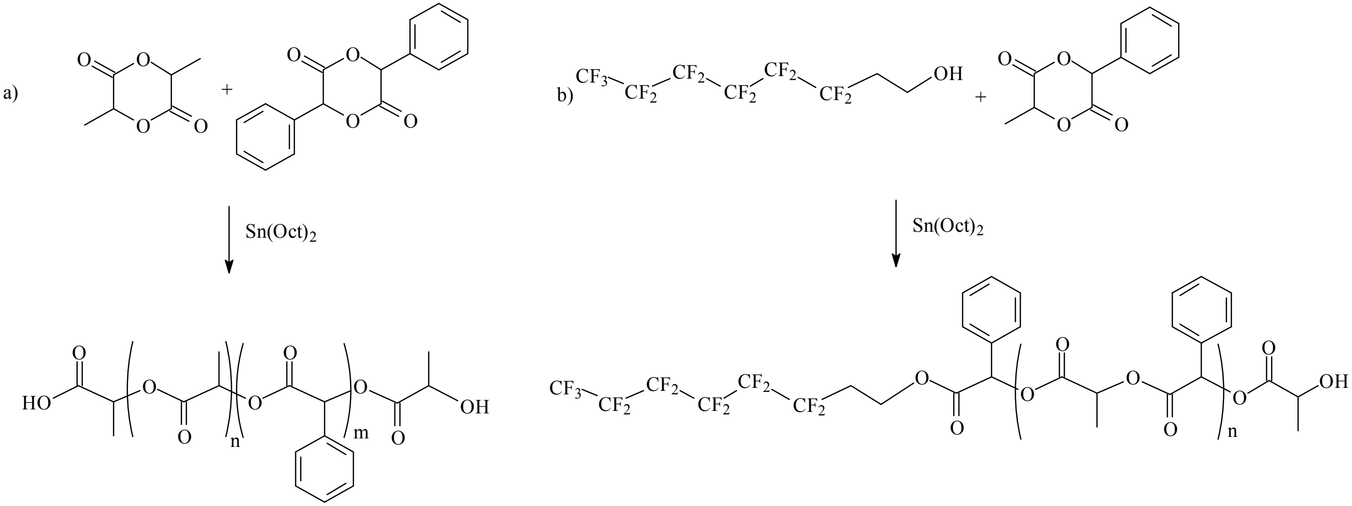


Figure 44. PLA-PMD copolymers synthesized (a) from lactide/mandelide copolymerization and (b) through polymerization (3S)-6-methyl-3-phenyl-1,4 -dioxan-2,5 -dione in the presence of a fluoroalcohol.

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Chapter 4

UV CURED METHACRYLIC-SILOXANE-BASED NANOCOMPOSITES AS POTENTIAL COATING FOR CULTURAL HERITAGE PROTECTION

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ABSTRACT

Novel nanocomposite UV - cured coatings, based on photopolymerizable siloxane-modified acrylic formulations with the addition of organo-modified Boehmite (OMB), are proposed as potential protective coatings for porous stones and wood elements. The OMB nanofiller has been dispersed into an optimized acrylic-based formulation in the presence of a proper photoinitiator for UV-curing. This represents the first example of the use of Boehmite-based UV-cured nanocomposite in the field of Cultural Heritage.

The advantages offered by UV-cured coatings with respect to traditional heat-cured ones mainly reside in the attainment of superior performance achievable in less time. The use of a nanocomposite protective coating will guarantee better surface properties and durability characteristics.

In this chapter, the characterization of the innovative liquid photopolymerizable siloxane-modified acrylic formulations, both in presence or absence of OMB nanoparticles, is presented in order to assess the suitability of the proposed products for the specific applications. A wide experimental characterization of the solid coatings, applied on different substrate and photo-cured by using a medium pressure Hg UV lamp, is illustrated, in order to assess the attainment of the expected superior properties in terms of transparency, hydrophobicity, surface resistance, glass transition temperature, among the most important. An accelerated weathering procedure is proposed as a means to evaluate the weathering resistance of the coatings.

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INTRODUCTION

Degradation and deterioration of stone-based monuments or wood artworks is caused by many factors, among which the presence of water is of predominant importance. Rain water can cause stone and wood degradation by multiple and, possibly, synergistic actions comprising stone disintegration by freeze-thaw cycling inside the stone pores or mineral dissolution, especially by environmentally acidified water. This agent can also be a carrier of pollutants which have their own detrimental contribution to the whole phenomenon.

The protection of stone-based monuments and wood artworks from natural weathering and/or environmentally-induced accelerated disintegration can be achieved with the application of water-repellent polymeric films on the substrate surface. Over the past decades, many different organic compounds have been used as protective coatings for cultural heritage building materials, such as epoxy, acrylic and methacrylic, siloxane, perfluoropolyethers and polyurethane resins.

Polymers based on acrylic and methacrylic resins are widely used in the field of protection and conservation of monuments and other artworks, due to their ability to form water repellent, well adhering and optically clear films. These applications also require durability features for the long-term efficiency of the conservation treatment, especially for outdoor applications. This is the case, for instance, of the stone facades of churches or ancient buildings located in urban areas, where the synergic effects of sunlight, temperature variations, moisture and pollution agents are severe. However, acrylic polymer in most cases can only provide short-term water repellence of the coated surface: they are intrinsically unstable in the photooxidative conditions typical of outdoor exposure of thin protective films. In order to avoid the mentioned limits of acrylic polymers, in the last years water-borne silane-acrylic hybrid polymers and new partially fluorinated acrylic copolymers, or perfluoropolyether polymers belonging to a larger family of analogous materials expressly tailored and synthesized for the protection of stone, have been experimented as protectives for porous stone surfaces. Perfluoropolyether polymer, for instance, is a very stable liquid, being resistant to oxidation and hydrolysis: it is, however, soluble only in fluorinated solvents, which are toxic for atmosphere and operator.

Nowadays there is an increasing interest in the development of new products, especially based on nanostructured systems, possibly environmental friendly, able to overcome most of the deficiencies of the commercial protective coatings, particularly in terms of hydrophobicity, surface mechanical properties, transparency, chemical resistance and barrier properties. On this issue, a new class of surface treatments based on polymeric nanocomposites is recently becoming the subject of many industrial and academic investigations, due to the potential benefits that they could offer. It is well known, in fact, that these organic–inorganic materials, in particular polymer/nanoclay or polymer/graphene systems, are characterized by enhanced mechanical and barrier properties, thermal stability, fire retarding ability, wear resistance compared to the neat resin, even at low loadings of the nanofiller (<6 wt%) [1-13]. However, to the best of our knowledge, experimental papers about the potential applications of nanocomposite-based coating treatments in building constructions and in conservation and restoration fields are scarce and the acquired knowledge is very far from being systematized [14-20]. As an example, Incarnato et al. [17] improved the protective action of two different commercial polymeric resins (i.e. Fluoline CP supplied by CTS S.r.l and Antipluviol S supplied by MAPEI S.p.A.) by dispersing in them, on a nano-scale, small amounts (2, 4 and 6 wt%) of an organomodified sodium montmorillonite without any detectable detrimental effect on the chromatic appearance of the treated substrates. Manoudis et al. [14] obtained the increase of the surface roughness of mineral substrates as a consequence of the application of protective polymer coatings, possessing a nano-scale binary composition composed by silica nanoparticles and appropriate polymer (i.e. functionalized perfluorinated polyether). The increase of the surface roughness allowed a substantial increase of water contact angle of the mineral substrate and, correspondingly, made the surface super-hydrophobic. However, even if the nano-structured systems proposed in literature are able to greatly improve the final performance of the protective coatings in terms of hydrophobicity, they are all thermally cured at room temperature ("cold curing systems"). As a consequence, they display severe deficiencies for the specific applications, such as very long curing time and scarce final thermal and mechanical performances (i.e. low glass transition temperature, pencil and surface hardness). This problem could be overcome by using "photo-reactive polymers", able to react in relatively shorter times under UV/visible light exposure still at room temperature. An additional advantage of photo-reactive systems based on acrylic, methacrylic and epoxy resins is the possibility to activate the polymerization reaction "on demand". The reactive system is, in fact, stable for long times (high shelf and pot life) and its setting is activated only by the exposure to UV (and in some cases visible) light. These reactive systems possess a broad range of properties, from those characteristic of elastomers to glassy polymers, from transparent resins to pigmented ones.

The number of monomers commercially available that can be used in the photo-polymerization process is very high. In particular, acrylate-based photo-polymers are characterized by high reactivity also at room temperature. Free radical photo-polymerization of acrylate monomers, in fact, takes only few minutes to complete the reaction, as a function of the sample thickness. On the other hand, thermal polymerization activated at higher temperatures can take some hours to complete the reaction, or even months when carried out at room temperature.

Other important advantages offered by free radical photo-polymerization reside in the possibility to achieve the final performances of the polymer in a very short time. Moreover, if the radicals are generated by UV/visible radiation, the reaction needs a low energetic consumption.

The photo-polymerization also allows us to solve the environmental problems related with the use of polymers in solution, since it drastically reduces volatile solvents emission. Furthermore, this process leads to protective film with higher final performances in terms of durability as compared to protectives based on the same resin but formed from the evaporation of the solvent.

Protective films obtained by in situ photo-polymerization of monomers are, finally, characterized by higher glass transition temperatures than those obtained starting from the same polymer polymerized at room temperature or by using the solvent method. The typical glass transition temperature of the latter kind of commercial protectives is, in fact, around 40°C, which is somehow low for the mentioned applications.

In this chapter, a review of the recent experimental research carried out by the authors on novel photo-polymerizable nano-structured products, specifically developed as protective coatings for the preservation and protection of materials in Cultural Heritage, is reported. A wide extended description of all experimental works carried out on this topic can be found on recent international publications [21-25].

POLYMER NANO-COMPOSITES

Polymer nano-composites (PN) are defined as polymer composites reinforced with inorganic fillers of dimensions in the nano-meter range. They combine synergistic properties derived from the two organic and inorganic components and they have, consequently, attracted a great interest of academic and industry researchers. The most studied PN are composed of thermoplastic or thermosetting matrix and organically modified montmorillonite (OMMT) [26-29], modified Boehmite [30-32], carbon nano-tubes (CNTs) [33-35] or graphene [13].

Polymer/clay nano-composites are characterized by improved thermal, mechanical, barrier, fire retardant and optical properties compared to either the matrix or the conventional composites, known as “particulate microcomposites”. This is attributed to their unique phase morphology deriving by layer intercalation or exfoliation that maximizes interfacial contact between the organic and inorganic phases and enhances the bulk properties [36, 37].

Since the discovery of carbon nano-tubes (CNTs) in 1991 by Iijima [38], CNTs have been extensively studied by researchers in various fields such as chemistry, physics, materials science, and electrical engineering. Carbon nano-tubes possess high flexibility, low mass density and large aspect ratio, defined as the ratio between the in-plane average dimension and the thickness of the reinforcement, (typically about 300-1000). They have a unique combination of mechanical, electrical and thermal properties that make them excellent candidates to substitute or complement the conventional nano-fillers in the fabrication of multifunctional polymer nano-composites [33]. As an example, the glass transition temperature (T_g) of CNTs dispersed in an epoxy matrix was find to highly increase compared to the neat epoxy in presence of single-walled carbon nano-tubes (SWNTs) and multi-walled carbon nano-tubes (MWNTs) [39]. Several groups have also reported improved thermal stability in nano-tube/polymer composites compared to same neat polymers [40-42]. Specifically, the onset decomposition temperature, T_{onset}, and the temperature of maximum weight loss rate, T_{peak}, measured by using thermogravimetric analysis (TGA), are much higher in the nanocomposites if compared to the neat matrix resins.

The results of a recent research reported in the two relevant reviews [43, 44] indicate that also the introduction of layered silicates into polyethyleneterephthalate (PET) polymer matrix can produce an increase in thermal stability. Furthermore, the presence of layered silicates can increase the barrier and mechanical properties of polymers, as shown by Greco et al. [45, 12]. The introduction of an impervious inorganic phase that increases the tortuosity of the path of a low molecular weight penetrant permeating through the nanocomposite is, in fact, responsible for a reduction in water vapour permeability and a significant increase in the flexural elastic modulus of the neat PET [12]. An increase in flexural mechanical properties and Tg of an epoxy resin was also obtained by adding a small quantity of graphene stacks, obtained by thermal expansion of commercial expandable graphite, at 700 °C for two minutes [13].

PHOTO-POLYMERIZATION TECHNOLOGY

The use of photo-initiated polymerization is continuously growing in industry as reflected by the large number of applications in conventional areas, such as coatings, inks and adhesives as well as in high-tech domains, optoelectronics, laser imaging, stereo-lithography and nano-technology. In contrast to thermally based applications, usually requiring elevated temperatures, photo-polymerization can be performed at room temperature or even below. This is a striking advantage for both classical polymerization of mono-functional monomers and modern curing processes. In photo-polymerization of mono-functional monomers, fewer side reactions occur, such as chain transfer. In the thermal polymerization, on the other hand, the probability of chain transfer commonly is high, which brings about a significant amount of branched macromolecules. Thus, low-energy stereospecific polymeric species, namely of syndiotactic configuration, which are difficult to synthesize by thermal polymerization, may be more easily obtained by photopolymerization.

Another important advantage is the possibility to process, by means of photo-polymerization at low temperatures, monomers with low ceiling temperature: they can only be polymerized at low temperatures; otherwise, depolymerization dominates over polymerization. Also biochemical applications, such as immobilization of enzymes by polymerization, as well as Cultural Heritage applications, such as the preservations of stone or wood artworks, require low processing temperatures. There are also other applications in which thermal curing is difficult to perform, when large areas or fine structures are to be treated, or even unacceptable, such as in the case of dental fillings. In all these cases, photo-polymerization represents the only acceptable and cost-effective alternative.

Photo-initiated polymerization, reported in Figure 1, is usually applied to a chain process that is initiated by light; both the initiating species and the growing chain ends are radicals or cations or, in some cases, anions or weak bases [46].

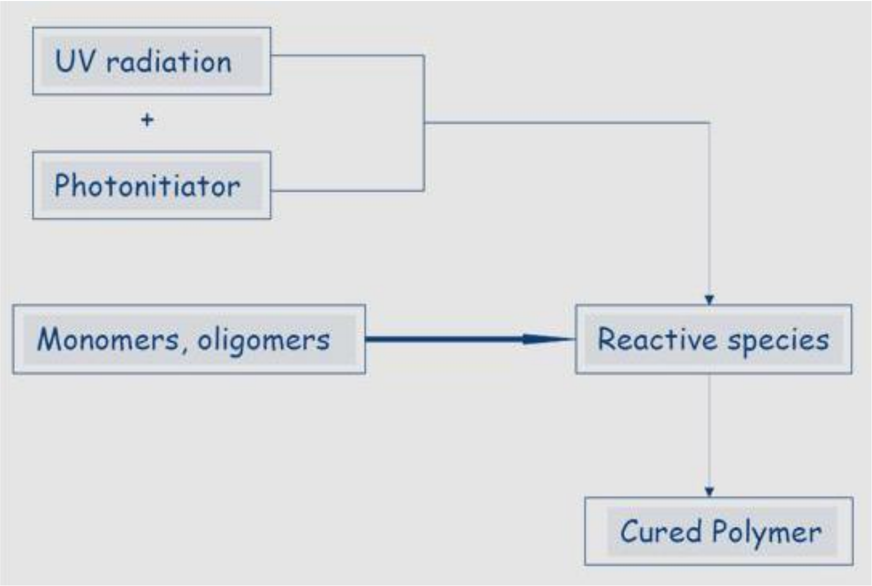


Figure 1. Sketch of photo-polymerization process.

Generally speaking, the reaction mechanism of free radical photopolymerization can be represented with three subsequent steps: initiation, propagation and termination. The initiation reactions can be schematically described by the following equations:

$$I + h\nu \xrightarrow{k_d} R^* \tag{1}$$

$$R^* + M \xrightarrow{k_i} M_1{}^* \tag{2}$$

In the first step, equation (1) represents the photolysis of initiator, *I*, to give two primary radicals, R^*, while equation (2) is the chain initiation process. In the latter reaction, a primary radical reacts with monomer, *M*, to form the first repeat unit of the growing polymer chain, $M_1{}^*$. The rate of both reactions is controlled by the kinetic constants for photolysis of the initiator, k_d, and the chain initiation, k_i, respectively. The propagation reaction is represented by a single reaction (equation 3), with a kinetic constant for propagation k_p:

$$M + M_n{}^* \xrightarrow{k_p} M_{n+1}{}^* \tag{3}$$

Chain termination occurs through two different mechanisms. Bimolecular termination (equations 4a and 4b) occurs when two growing radical chains come together and react to form dead polymer; this reaction can either occur by combination (forming one polymer chain) or disproportionation (forming two chains):

$$M_m{}^* + M_n{}^* \xrightarrow{k_t} \{M_m{}^*\} + \{M_n{}^*\} \tag{4a}$$

$$M_m{}^* + M_n{}^* \xrightarrow{k_t} M_m + M_n \tag{4b}$$

While the mode of termination significantly affects the molecular weight in linear polymer-forming systems, the polymerization kinetics in cross-linked systems, which are predominant in commercial photopolymer applications, are not influenced significantly by the termination mode. Thus, the bimolecular termination reaction will be lumped into a single reaction having kinetic constant k_t. The second termination mechanism is primary radical termination (equation 5), in which a primary radical reacts with a growing polymer chain to form dead polymer:

$$M_n{}^* + R^* \xrightarrow{k_{tp}} P^*{}_n \tag{5}$$

The kinetic constant for this process, k_{tp}, will in general be different from the bimolecular k_t, as the two reactions have different chemistry and different species mobilities are involved in the termination process.

The only disadvantage characterizing the radical photo-polymerization for a possible use in the Cultural Heritage applications could be the detrimental effect of the oxygen towards the kinetic of free radical photo-polymerization reaction. It is, in fact, well known that oxygen inhibition of free radical photo-polymerization causes numerous deleterious effects on free-radically cured products, including slow polymerization rates, long induction periods, low conversion, short polymeric chain length and tacky surface properties [47, 48]. The reaction of inhibition of oxygen occurs after the initiation reaction (2) as follows:

$$R^{\bullet} + O_2 \xrightarrow{k_0} RO_2^{\bullet} \tag{6}$$

where k_0 is the rate constant of the radical scavenging by O_2 molecules. In the case of acrylate monomers, it is reported for k_0 a value of 10^8 L mol^{-1} s^{-1} [48].

In a well-aerated medium, where the concentration of dissolved oxygen is of the order of 10^{-3} mol L^{-1}**,** the photo-polymerization cannot develop because $k_0[O_2] >> k_p[M]$: all the initiator radicals formed are, therefore, reacting with the oxygen dissolved in the monomer [48]. As a consequence of the scavenging reaction, O_2 is progressively consumed and its concentration in the irradiated monomer drops steadily during the inhibition period. The polymerization process will only start once the monomer molecules are able to compete successfully with O_2 for the scavenging of the initiator radicals, i.e., when $k_0[O_2] \sim k_p[M]$. In open systems, a stationary concentration of dissolved oxygen is achieved where O_2 consumption is just compensated by O_2 diffusion from the atmosphere through the surface of the film [48]. By scavenging the initiator radicals, O_2 not only reduces the rate of the polymerization, thus requiring longer exposure times, but also leads to a partial loss of the optical and surface properties of air-cured coatings. As the UV-curing of the acrylate coatings is generally carried out in the presence of air, oxygen inhibition must be always taken into account. Overcoming this undesired slowing of the reaction represents a major challenge in order to use the UV photo-polymerizable acrylate formulations as stone or wood protectives. The effects of oxygen on the UV-curing of coatings have thoroughly been investigated. Hoyle et al. [49, 50] reported a number of possible chemical species and additives for reducing oxygen inhibition including amines, thiols, and N-vinylamides. One interesting aspect that has yet to be explored in quite detail is the effect of the kind of monomer employed on oxygen inhibition of free-radical polymerizations. If specific chemical structures in the monomer itself reduce oxygen inhibition and faster rates, then lower photo-initiator concentrations, and better overall properties, should result. One particular example of this approach has been reported in literature in which (meth)acrylates demonstrate reduced oxygen inhibition during free-radical polymerization in air [51]. A possible solution to limit the inhibition effect of oxygen was proposed by the authors in a previous paper [48]: it consists in the addition of a proper thiol to the methacrylic based mixtures. The addition of the mercaptopropyltriethoxysilane in the mixtures allowed us to obtain a good rate of reaction and a higher conversion, even in the air.

NOVEL UV CURED METHACRYLIC-SILOXANE BASED NANOCOMPOSITES

Starting from a promising experience in the realization of UV-curable coatings, based on siloxane-modified acrylic formulations, able to react at reasonably rates at room temperature and in presence of oxygen and displaying good surface and hydrophobic characteristics, the same research group realized a nanocomposite by adding to the same resin mixture an organo-modified Boehmite and verified its potentiality as protective coating for different substrates.

The methacrylic resin, which is the main component of the coating, is Trimethylolpropane trimethacrylate (TMPTMA, supplied by Cray Valley), possessing a high reactivity and adequate viscosity for the selected applications. An organically modified Boehmite (OMB, supplied by Sasol with the trade name Disperal-MEMO) was selected as nanofiller for the methacrylic resin. The organic stabilizer for OMB nanoparticles, i.e. trimethoxypropyl silane methacrylate (MEMO, supplied by Dow Corning as Z6030), was also used as a coupling agent to enhance the dispersion of the nanofiller into the organic coatings. (The chemical formula of the above and below listed components, as well as the projection of the crystalline structure of unmodified Boehmite (UB), is reported in Scheme 1).

The target application of the experimental product suggested the addition of vinyl terminated polydimethylsiloxane (VT PDMS, supplied by Aldrich) to the methacrylic mixture to enhance the water repellence of the coating. In addition, 3-Mercaptopropyltriethoxysilane (MPTS, supplied by Aldrich) was added to the siloxane-modified methacrylic resin in order to reduce the effect of inhibition of oxygen toward radical photopolymerization, as previously illustrated. The functionalization of VT PDMS with MPTS was performed by mixing the two components at 100°C in 1:1 molar ratio in presence of 1% wt. of Diethylamine (DTA, supplied by Aldrich).

Irgacure 819 (purchased from Ciba) was selected as photoinitiator being able to start the reaction of the methacrylic resin under the UV radiation.

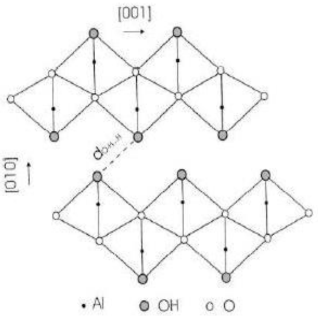
In Table 1, the compositions of some of the mixtures produced are listed. For all systems, a simple mixing procedure was employed: OMB was dispersed in MEMO, because of its high compatibility with modified Boehmite, and subsequently added to TMPTMA resin and VT PDMS, the latter functionalized with MPTS (in the following named as $PDMS_m$). The mixing procedure was carried out at room temperature.

The selection of the more suitable system to propose as protective coating for wood or stone artworks started from a deep analysis and a wide characterization of all the formulations produced, both in liquid and in solid state. The reactivity of the mixtures was first studied by isothermal photo-calorimetric analysis (p-DSC): it was found that all the UV-cured formulations are able to photo-polymerize very quickly, both in air and in nitrogen atmosphere. The time in correspondence of the maximum reactivity was found to be always lower than 40 seconds, even in absence of the nanofiller. The presence of nanoparticles in the photo-polymerizable liquid mixtures brings about an appreciable increase in conversion of reactive species, in absence of the MPTS functionalization. The latter modification is able to further increase the reactivity of the methacrylic resin and to reduce drastically the reaction time.

The second characteristic measured on all the liquid mixtures was their viscosity, since it represents a key parameter in the applicability of the formulations on different substrates possessing a variable porosity. It was found that, even thought the viscosity values of all the liquid methacrylic-based formulations increase in presence of OMB nanofiller, they remain still suitable for the described applications [21].

Table 1. Composition of the formulations produced

Sample	Weight Composition
67 T-30 M-3 PDMS_{819}	67% TMPTMA, 30% MEMO, 3% PDMS, 1 pph Irgacure
67 T-30 M-3 PDMS-3 OMB_{819}	67% TMPTMA, 30% MEMO, 3% PDMS, 1 pph Irgacure, 3% wt. OMB
77 T-20 M-3 PDMS_{819}	77% TMPTMA, 20% MEMO, 3% PDMS, 1 pph Irgacure
77 T-20 M-3 PDMS-3 OMB_{819}	77% TMPTMA, 20% MEMO, 3% PDMS, 1 pph Irgacure3% wt. OMB
85 T-10 M-5 PDMS_{m819}	85% TMPTMA, 10% MEMO, 5% PDMSm, 1 pph Irgacure 819
85 T-10 M-5 PDMS_{m}-3 OMB_{819}	85% TMPTMA, 10% MEMO, 5% PDMSm, 1 pph Irgacure, 3% wt. OMB



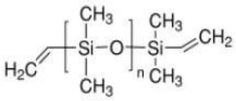
UB

$[H_2C{=}C(CH_3)CO_2CH_2]_3CC_2H_5$

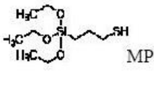
TMPTMA

$CH_2{=}C(CH_3)\text{-}COO\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$

MEMO



VT PDMS



MPTS

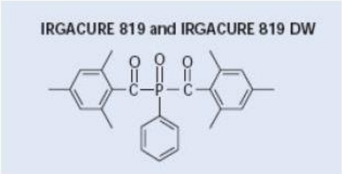


Figure 2. Chemical formula of all the materials employed.

The results indicated that the formulation containing 3% wt. of OMB (85T-10M-5PDMS$_m$-3OMB$_{819}$) can be considered the more suitable in terms of reactivity and viscosity: it was, therefore, applied on different substrates (glass, wood, stone). For comparison purposes, the “control” formulation 85T-10M-5 PDMS$_{m819}$, i.e. that possessing the same composition but not containing OMB nanoparticles, was applied on the same substrates. Both filled and unfilled liquid mixtures were applied on an untreated glass, a porous stone (calcarenitic type “Leccese stone”) and a walnut wood specimen and UV-cured for 12 hours using a UV lamp with an irradiation intensity of 9.6 µWatt/mm^2. In Figure 3, some images of the UV-polymerization process of the coatings applied on glass (Figure 3A), on wood (Figure 3B) and on stone (Figure 3C) substrates, are shown.

Several surface properties (transparency, glass transition temperature, scratch and Shore D hardness’s, contact angle and colour change) were measured on both coatings applied on glass substrate and UV-cured as described. It was found that the presence of Boehmite nanoparticles in the photo-cured films, revealed by SEM observations and EDX analysis, allows to appreciably increase the surface properties and the hydrophobicity of the film, without affecting the transparency of the coating itself [24].

In particular, the nanofilled system possesses a glass transition temperature only slightly higher (about 3°C) than that of the organic system, but a pencil hardness and a shore D surface hardness much higher than those measured for un-filled coatings. The light transmittance of the nanofilled coating was found to be about 99% in the visible range of wavelength. As an example of the high transparency of both coatings, a photograph of the filled and unfilled coatings is reported in Figure 4, where the transparency of the nanofilled UV-cured system (on the right) is compared with that of the unfilled coating (named control, on the left).

Figure 3. Images of some of the preparation/application steps performed.

Figure 4. Comparison of transparencies of unfilled (on the right) and nanofilled (on the left) UV-cured coatings.

The same surface properties were measured after a QUV treatment (i.e. Accelerated Weathering Tester) performed on the coatings, in order to verify their durability towards natural weathering [24]. After a first QUV accelerated weathering cycle of 100 hours, the surface properties of the coatings were not reduced. On the contrary, they increase, achieving plateau values that remained unchanged after a second UV cycle of the same duration. This occurrence was explained in terms of completion of UV-curing reactions of the methacrylic-based coatings in the QUV weathering chamber. On the other hand, the presence of OMB nanoparticles in the siloxane-modified methacrylate film is not able to limit the yellowing effect due to long UV-exposure time, as clearly shown in Figure 5 reporting the nanofilled coating after two QUV cycles.

The contact angle value of the nanofilled coating remains very high (about 110°) even after the second QUV cycle, as shown in Figure 6.

As an example of the good final properties of the OMB-filled coating, in terms of hydrophobicity and colour change, some of the results obtained on the coating applied on walnut wood specimens are briefly summarized. In Figure 7, a comparison between the inner part of walnut wood specimens treated with unfilled (Figure 7A) and filled (Figure 7B) coating, is reported.

The presence of the unfilled polymeric treatment on the walnut wood surface causes a clear darkening of the wood substrate (Figure 7A). On the other hand, the nanofilled coating applied on the same kind of wood determines only a slight yellowing of the natural wood coloration (Figure 5B). The presence of small white particles in the pores of the wood (as indicated by the arrows) suggests that nano-filler is partially penetrated into the pores but it has not completely filled them. The change of the color of the walnut wood as a consequence of the treatment was measured by means of a Konica Minolta CR-410 in total reflectance and double channel mode, using a Xenon-lamp light source. The results confirmed that the nano-filled coating applied on walnut wood specimens determines a limited yellowing of natural wood coloration.

Figure 5. OMB filled coating subjected to two cycles in the QUV weathering chamber.

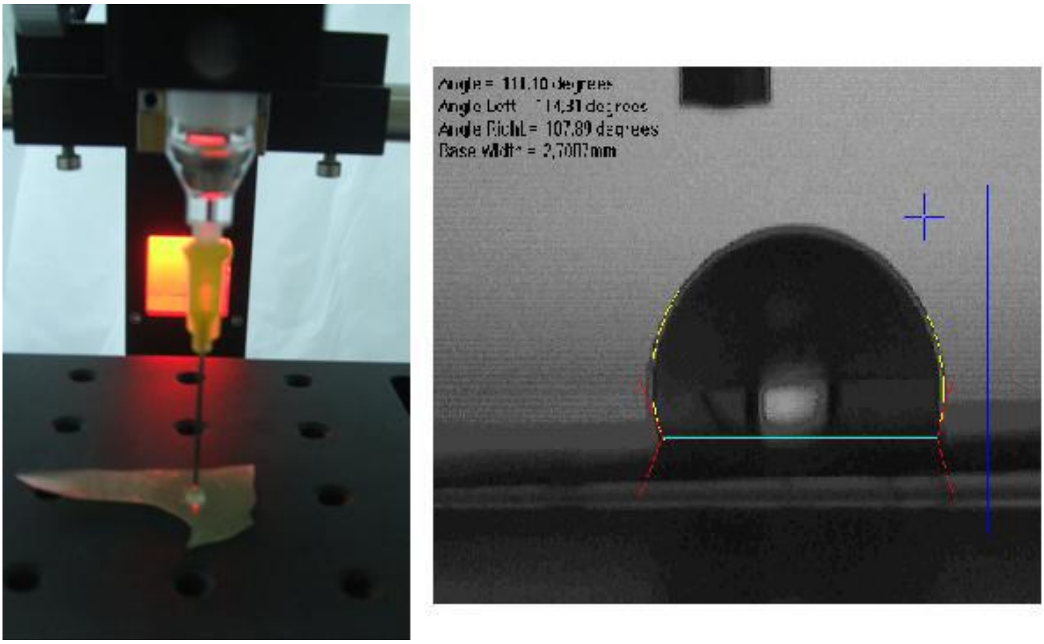


Figure 6. Contact angle measurement performed on the nanofilled coating after two cycles in the QUV weathering chamber.

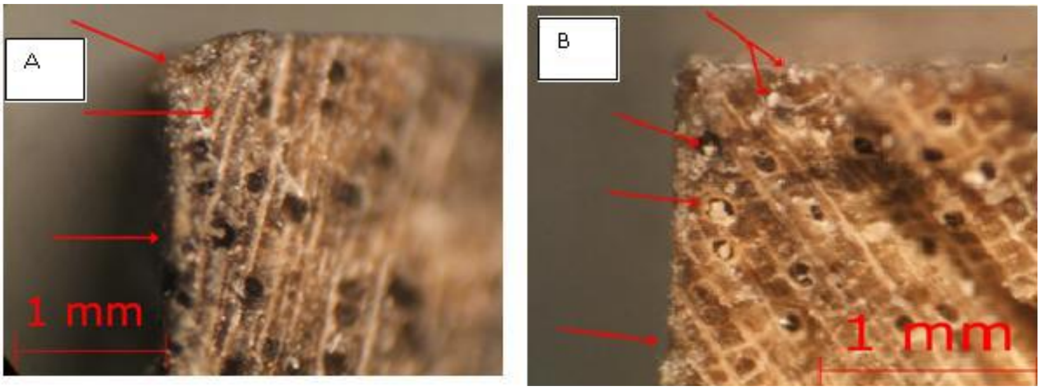


Figure 7. Optical microscope photographs performed on walnut wood specimens coated with unfilled (Figure 7A) and filled (Figure 7B) systems.

The hydrophobicity of both treatments on walnut wood was measured by dynamic contact angle measurements. It was found an increase of about 20% in the contact angle of the nanofilled coating (about 130°) with respect to the unfilled one. Furthermore, the water absorption capacity of the walnut wood samples coated with nanofilled system was appreciably reduced with respect to uncoated ones. As shown in Figure 8, the samples coated with nanocomposite coating absorb much less water than the uncoated wood specimens, especially in the first immersion period (up to 21 days), confirming the great potentiality of the novel methacrylic-based nanocomposite realized.

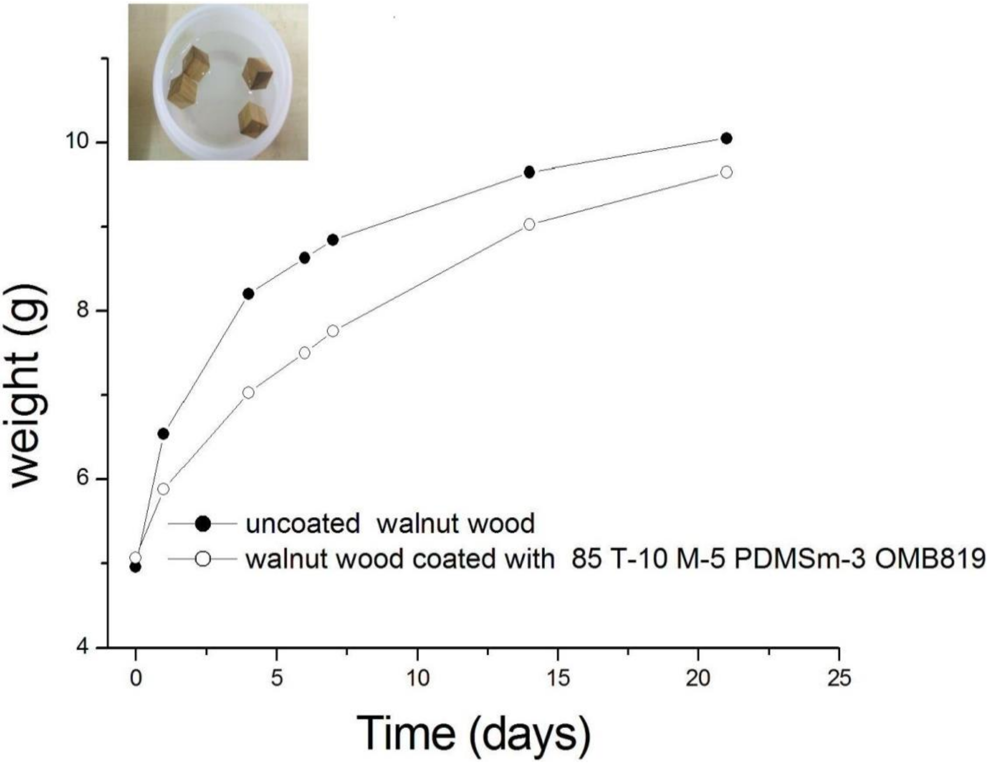


Figure 8. Water absorption behavior of walnut wood samples coated with the nanofilled system compared to uncoated specimens.

CONCLUSIONS AND ONGOING WORKS

The results found in the described research devoted to nanocomposites based on modified methacrylic resins are particularly interesting for applications in Cultural Heritage materials preservation. By employing a small amount (3% wt.) of Boehmite nanoparticles it is in fact possible to obtain good hardness values of the coating, which can also be very transparent. An appreciable increase of the hydrophobicity of the coated substrates, measured by contact angle tests, was also obtained. Finally, a large reduction of the water absorbed by coated wood specimens is achievable with the new nanocomposite products. The reactivity and viscosity characteristics of the liquid mixtures containing the nanoparticles are absolutely suitable for the described applications.

The possibility to activate the photo-polymerization reactions under visible light has been currently investigated, by selecting a different proper photoinitiator. The possibility to avoid the use of the UV-lamp for the photo-polymerization of the nanocomposite coatings could be, in fact, an important advantage for the specific applications, extending the possible use of these novel nanostructured systems to the preservation of large areas of stone or wood structures or artworks, even outdoor placed.

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Chapter 5

ORGANIC-INORGANIC EPOXY-BASED HYBRIDS AS POTENTIAL ADHESIVES FOR CULTURAL HERITAGE CONSOLIDATION

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ABSTRACT

In the last years there has been a considerable interest in a new class of materials, known as organic–inorganic (O-I) hybrids, which present unique characteristics arising from the combination of organic and inorganic components.

Recently, epoxy-based O-I hybrids, consisting of epoxy resins with interpenetrating silica domains, have been optimized by the authors. The methodology for their production is based on the sol-gel technology, involving the hydrolysis and condensation of metal alkoxides in aqueous solution, which is able to bind chemically, at nanometric scale, the organic phase with the inorganic one. These novel hybrid systems present superior properties then those of the parent resins. The presence of nanostructured co-continuous organic and inorganic domains, in fact, allows higher glass transition temperatures, greater mechanical properties and enhanced adhesion to different substrates than those experienced by epoxy resins to be achieved.

Thanks to their peculiarities, these epoxy-based hybrid systems have been investigated by the authors as potential “cold-cured” adhesives, i.e. to be cured at ambient temperature and to be used in Cultural Heritage for restoration of artefacts and consolidation of masonry structures. The main interest in cold-cured epoxy-silica hybrids lies, in fact, in the possibility of overcoming the main limitations of conventional cold-cured epoxy resins, currently used as adhesives and matrices for FRP (Fiber Reinforced Plastics) in the restoration and repair of ancient masonry structures. They require, in fact, long curing times, while, due to the incomplete cure, the glass transition temperature (Tg) of the final products can only achieve values about 10-20°C higher than the temperature used for the curing process. Moreover, the Tg of cold-cured epoxies can decrease to even lower values through the absorption of water, due to plasticization phenomena caused by strong association of OH of water with NH groups of the epoxy.

The aim of this chapter is to analyse the properties of the organic–inorganic epoxy-based hybrid systems, highlighting their potential as efficient, structural and non-structural, adhesives for Cultural Heritage

INTRODUCTION

Among polymer adhesives, epoxy resins are widely used in the repair and restoration of monuments and artworks thanks to their non-common characteristics: excellent adhesion to most materials, curing at room temperature with a minimum shrinkage and without development of secondary products, excellent mechanical properties, limited water sensitivity, good chemical resistance to acids, bases and organic solvents, easiness of application along with economic advantages, possibility to tailor the viscosity of the adhesive by means of suitable functionalized solvents.

Epoxy adhesives undergo a chemical reaction, called "curing" or "cross-linking", upon mixing with a proper hardener or "curing agent", which can be an amine or an anhydride. The amount and the type of hardener employed control the rate of cross-linking and, consequently, the final properties of the adhesive. The epoxy adhesives used in Cultural Heritage repairing and restoration are "cold curing" resins, that is, they are based on bisphenolic epoxy resins that, for practical and economical reasons, are cured at ambient temperatures [1,2]. Aliphatic amines are usually used as curing agents for this purpose, since they are able to react with epoxies also at low temperatures. Furthermore, in the restoration and repair of ancient masonry structures, epoxy adhesives cure at ambient temperature in conditions which are very often uncontrolled.

Among the consequences of a curing process carried out at ambient temperatures, the cold-cured epoxy systems typically display a glass transition temperature never greater than 65–70°C [3-6]. The glass transition temperature, known as Tg, is the mean value of the temperature range below which the cured adhesive behaves like a solid, able to effectively bond two different materials, and above which it behaves in a manner similar to a rubber. When the range of the glass transition temperature is approached, a dramatic decrease (up to 70%) in stiffness and strength is shown, along with a drastic reduction in its adhesion strength [7-8].

Long curing times (in the order of weeks) are necessary to achieve sufficient mechanical properties when the curing process is carried out at low (ambient) temperatures: the lower the curing temperature, the longer will be the curing time [9]. In addition, the cross-linking reactions taking place in epoxy resins at ambient temperatures are often not completed due to kinetic restraints; they can, therefore, eventually start again. There are, in fact, residual reactive groups which can potentially continue the curing process if they gain enough molecular mobility, as the following will explain [10-11].

During the outdoor exposure of cold-cured epoxy resins three concurrent events, namely water plasticization, further cross-linking within the network and "physical aging", can occur. The plasticization of the network, caused by the absorption of water, leads to a decrease in the Tg of the resin with a consequent enhanced mobility of un-reacted species. The residual reactive groups can, therefore, undergo further cross-linking reactions during environmental aging. The resulting additional restrictions on the molecular relaxations within the network counteracts the plasticization effect of the "bound" water, and may bring about an overall, albeit small, increase in the Tg of the cured system. Finally, as the Tg of cold-cured systems is not much higher than ambient temperature, physical aging may take place both during curing and the subsequent environmental aging [3, 12]. Physical aging of glassy polymers causes itself as a densification process, resulting from further molecular packing in addition to that imposed by the increase in cross-linking density caused by chemical reactions. In conclusions, the cold-cured epoxies are in an unstable thermodynamic state during their service life.

Recently, epoxy-based organic-inorganic hybrids, consisting of epoxy resins with interpenetrating silica domains produced by sol-gel method, have been optimized by the authors. Their superior performances and durability compared to those of unmodified epoxy resins and their ability to be cured at ambient temperature, which makes them potential "cold-cured" adhesives to be used in Cultural Heritage for restoration of artefacts and consolidation of masonry structures.

In this chapter, a review of the recent experimental research carried out by the authors will be used to illustrate the properties achievable with organic–inorganic hybrids and their potential applications in Cultural Heritage.

DURABILITY OF EPOXY ADHESIVES FOR CULTURAL HERITAGE APPLICATIONS

The durability of polymeric adhesives depend on the chemical nature of the base materials, on the conditions in which the resins set and harden, and, mainly, on the environmental conditions in which they "operate" [13]. Generally speaking, even thought widely employed in the rehabilitation of cultural heritage, the durability of cold-cured epoxy adhesives exposed to natural environment is still a highly debated issue.

The excellent properties of epoxy adhesives may be modified by the environment which often acts as a degrading agent. Of particular relevance is the humidity of the atmosphere that, in actual service conditions, has serious detrimental effects on the epoxies, leading to property changes as a consequence of physical and/or chemical transformations. Actually, epoxy adhesives exposed to a wet environment absorb water because they possess polar groups linking water molecules. Once inside, water may alter the properties of the polymer both in a reversible manner, through plasticization, and in an irreversible manner, if hydrolysis, cracking or crazing occur [2].

The lowering of the Tg due to water ingress into epoxy resins (for example, as atmospheric moisture or rain) can be particularly harmful for cold-curing epoxies whose typical Tg, as already underlined, is not much higher than the service temperature [14-15]. Therefore, if this last temperature approaches the Tg of the system, a lowering of the mechanical properties of the adhesive is likely to take place [2]. The detrimental effects of moderate service temperatures on the performance of a resin are reflected also in its behavior as adhesive. A service temperature close to its Tg is able to reduce appreciably the adhesion strength and the fatigue resistance of the adhesive [8, 16]. For this reason, the environmental temperature under working conditions for cold-curing adhesives should be at least 20°C below the glass transition temperature [17].

The presence of water can be particularly dangerous when the adhesive is used to join two dissimilar adherents. Water may easily penetrate through a permeable adherent like the stone and it can diffuse or be transferred along the interfaces through capillary action. Water in contact with the joint, may cause deterioration of the bond by reducing mechanical properties and adhesive displacement at the interface. The displacement is even augmented by pre-existing micro-cracks or not linked areas originated from poor wetting by the adhesives [18]. Several authors reported that substantial decreases in bond strength over aging time (up to 40-50% loss in some cases) are experienced under wet and moist environments [4, 19-26]. Summarizing, the typical features displayed by cold-cured adhesives produce heavy concerns about the efficiency and durability of such materials especially for their typical outdoor applications.

EPOXY-SILICA ADHESIVES FOR CULTURAL HERITAGE APPLICATIONS

In the last years, hybrid organic-inorganic epoxy resins have been synthesized by in-situ formation of an inorganic structure within an organic polymer matrix. Sol-gel process is usually employed to form nanometric silica domains chemically linked to the organic chains [27-29]. The presence of inorganic co-continuous domains in epoxy-silica hybrids is expected to enhance the Tg and the load-bearing properties of the adhesives, their adhesion strength to different surfaces and, eventually, their durability. These new class of organic-inorganic hybrids have been also called bicontinuous nanocomposites.

The possibility of varying the structure of formed particles with regard to the conditions of the process of synthesis is one of the special features of the sol–gel method of synthesis of organic–inorganic materials. The process of sol formation is influenced by many factors: the pH of the medium, the nature of the solvent, the presence of a compatibilizer, the water content used for hydrolysis of alkoxy compounds and the order of addition of components. Understanding the morphology of synthesized hybrid materials makes the interpretation of the “composition–structure–properties” dependences much easier and can even have a predictive character [30].

The most successful approach for producing bicontinuous nanocomposites based on thermoset matrices is aimed at obtaining an organic phase-separated macromolecular network, which is chemically bound to the surrounding inorganic domains [27]. In the case of epoxy-silica hybrids, this can be achieved by i) one-step polymerization, in which the formation of the resin/hardener network proceeds simultaneously with the sol-gel polymerization of TEOS; ii) two-step polymerization, in which TEOS is pre-hydrolyzed and then mixed with the epoxy/hardener mixture to start the “simultaneous” formation of both organic and inorganic phases.

Whenever the polymerization method, the in-situ generated silica is produced in all cases by sol-gel reaction, involving hydrolysis and condensation steps, as reported in Figure 1 [27-28, 31].

Recently, an optimized formulation of epoxy-silica hybrid, able to cure at ambient temperatures, has been developed by the authors’ research group [32-33]. It is based on silane-functionalized epoxy resins containing highly hydroxylated silica co-continuous domains. Its peculiarities make it an attractive alternative to the traditional cold-cured epoxies for Cultural Heritage, structural and non-structural, applications.

VISCOELASTIC AND MECHANICAL PROPERTIES

The peculiar structure of the developed hybrid system is responsible of a significant increase in the mechanical and viscoelastic properties compared to those of the corresponding unmodified adhesives. As can be clearly observed in the dynamic-mechanical spectra reported in Figure 2, the epoxy-silica hybrid presents much higher values of storage modulus, both at room temperature and in the rubbery plateau region, where, in particular, the increase is of about an order of magnitude. This evidences an enhanced elastic response and confirms the improved performances at high temperature of the hybrid system provided by an increased glass transition temperature. The Tg value of hybrid system, in fact, calculated from the peak of the loss modulus (G'' curve in Figure 2), is 12°C higher than that of the parent epoxy resin. This considerable increase in the Tg of the cold-cured hybrid has been also confirmed by differential scanning calorimetric (DSC) analysis [31].

The loss modulus curves of epoxy resins are almost symmetrical according to the prediction of the viscoelasticity theory. Unlike the curves relative to epoxies, the loss modulus curve of hybrid is asymmetrical and highly skewed at the upper side of the Tg. Moreover, the amplitude of the G'' peak is less than one third that of the corresponding curve of the epoxy resin. This indicates that the high level of molecular relaxations, experienced in epoxy resins above the glass transition temperature, is drastically reduced when the silica is present as nanostructured co-continuous phases as observed by Mascia and co-workers [34-35]. The silica domains, chemically connected with the polymer network, significantly hinder the segmental motion of the polymer chains by reducing their effective volume that contributes to the relaxation processes [36-38]. These relaxations occurs in the epoxy network and not within the siloxane domains, in agreement with Matejka et al. [39], who concluded that the siloxane domains, with a glass transition in the region of 340°C, are in the glassy state over the temperature range of the polymer glass transition.

Therefore, the increase in Tg and mechanical properties and the depression of G'' peak is a clear indication of the formation of a co-continuous system through the presence of molecularly dispersed silica domains, likely of nanometric size, as demonstrated by SEM micrographs, reported in Figure 3. The fracture surface of the neat epoxy (Figure 3a) shows distinct fracture lines, characteristics of brittle resins. The cracks are mainly oriented in one direction, i.e. the direction of the applied load. The SEM micrograph of the hybrid sample (Figure 3b) is completely different from the other. It displays the typical features of organic-inorganic hybrids, which consists of diffuse silica domains very well dispersed within an organic matrix without fracture lines. EDS analysis confirms a widespread and continuous presence of SiO_2.

The presence of silica domains at nanometric scale within the epoxy matrix is also responsible of the higher transparency of the organic-inorganic epoxy-silica hybrid. It has been found that the light transmittance is more than 40% higher than that of the parent epoxy resin, where some fluctuations in density can be present [31]. This property can be very important for Cultural Heritage applications.

Hydrolysis reactions

a) Si(OEt)4 + n H2O → (HO)nSi(OEt)4-n + n EtOH

b) Organic*units[-Si(OMe)3]x + m H2O → Organic*units-[(HO)m Si(OMe)3-m]x+ m MeOH

Condensation reactions

i) ≡SiOEt + HOSiO≡ → ≡Si-O-Si≡ + HOEt (***silica***)

ii) Organic*units[-Si(OMe)3]x+ y HOSiO≡ → Organic*units[-Si(OMe)(3-y)]x-O-Si ≡ + y MeOH

iii) Statistical co-reactions from steps i) and ii) → (***siloxane***)

*Chain in the silane functionalized epoxy resin and organic segments of silane coupling agent

Figure 1. Hydrolysis and condensation reactions during the sol-gel process.

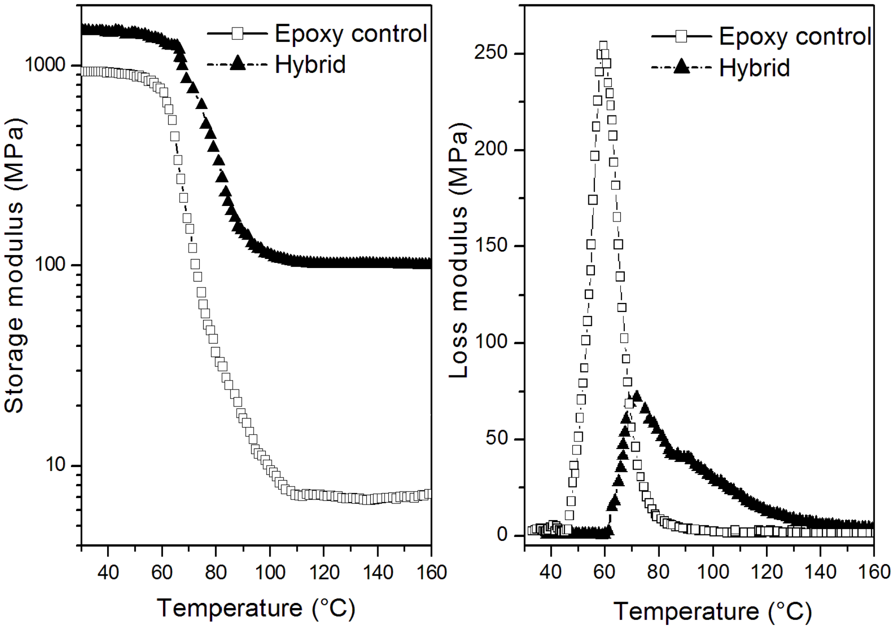
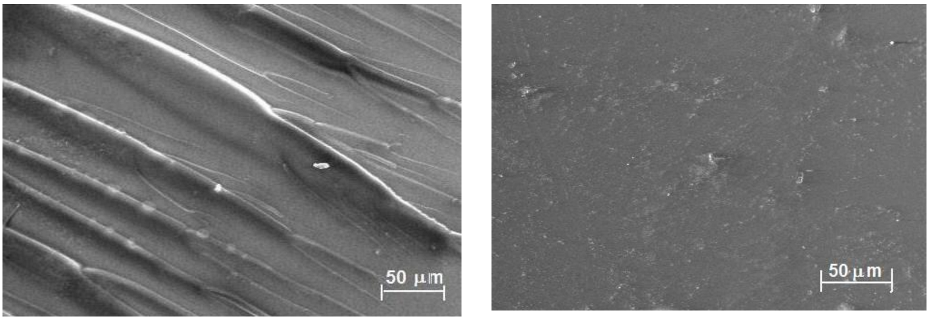


Figure 2. DMTA spectra obtained on the epoxy-control and epoxy-silica hybrid systems.



(a) (b)

Figure 3. SEM micrographs of the fracture surface of a) Epoxy-control; b) Hybrid.

The flexural mechanical data, shown in Figure 4, illustrate the significant enhancement in mechanical properties of the hybrid adhesive, provided by the efficient reinforcement of the siloxane domains. Compared to unmodified epoxy adhesive, the epoxy-silica hybrid presents a doubled strength and a modulus increased of about 60%. In addition, the mechanical tests have been performed at 50°C, which can be an achievable temperature in Cultural Heritage applications, for instance when a surface is exposed to direct sun radiation for a prolonged time. At 50°C a decrease in flexural characteristics is expected, since the glass transition region of the adhesive is approached. However, this decrease is somehow limited in the case of the hybrid system (about 40%) compared to the control (about 60%). It should be underlined that the strength and the stiffness measured at 50°C in the hybrid specimens are much higher than the same properties measured at room temperature on the control resin, representative of a commercial epoxy-based structural adhesive [31].

Thermogravimetric studies confirm a greater thermal stability of the hybrid and the presence of volatile products due to the condensation reaction during the sol-gel production of silica [31]. A two-step degradation profile has been observed. The observed improvement in the thermal stability of hybrid system is related both to the degree of the interaction between the polymer matrix and the inorganic phase and to the inherently good thermal stability of the inorganic component [36].

DURABILITY UNDER AGEING IN DIFFERENT ENVIRONMENTAL CONDITIONS

A deep study of the aging at room temperature of the developed system has been carried out by means of calorimetric analysis, as reported in Figures 4 and 5. In this case, the cured system has been left to age at room temperature for a period up to 6 months. As the cure proceeds, the Tg of the system increases and, at some time, it will exceed the cure temperature, i.e. the vitrification process occurs. At this stage, the mobility of the reactive groups is significantly reduced, the curing reactions are diffusion controlled, i.e. they appreciably slow and finally stop; consequently, the value of the Tg tends to level off. As can be seen from Figure 5, the Tg increases more rapidly for the unmodified resin, as also observed by Lionetto et al. [31] from gel time measurements. After 4 days of cure at room temperature, on the other hand, the Tg of the epoxy-silica hybrid increases more rapidly (see inset in Figure 5) as also observed by Afzal and Siddiqi [40], reaching a considerably higher value than that of the corresponding reference system. This can be considered as an indication of the phase interlinking of matrix-silica components.

The Tg of the epoxy-control system is continuously increasing during the investigated aging time while the residual heat of reaction achieves, after about one-month, an almost constant value of about 50 J/g (as shown in Figure 6). For longer ageing times, the heat of reaction very slowly decreased, down to about 40 J/g. The existence of a residual heat of reaction after a very long aging time confirms that in the epoxy system cured at ambient temperature the complete conversion of the reactive species is not achieved. The maximum Tg achievable by the epoxy cured at ambient temperature, i.e. about 60°C, is attained after 6 months of aging at ambient temperature. This value is quite typical for an epoxy cured at ambient temperature, as already underlined. On the other hand, the hybrid system is able to achieve higher Tg, about 72°C, after a shorter ageing period (5 months) at ambient temperature. In addition, the reaction is roughly complete in this case (ΔHr ≈ 15 J/g).

The experimental epoxy-silica hybrids show superior properties compared to those of unmodified epoxy resins even during environmental aging under high humidity conditions. The siloxane domains enclosed in the epoxy-silica hybrids, in fact, undergo additional sol-gel reactions, which bring about a further increase in Tg and substantial increases in Young's modulus and flexural strength. Furthermore, the moisture in the atmosphere has been found to assist the extraction of the residual ethanol in the specimens. The observed effects are more pronounced when the siloxane component is modified with small amounts of ammonium molybdate in the formulation [32]. The reason of these enhanced performances is the continuation of the cross-linking reactions that, during aging, occur more predominantly within the siloxane domains and the interphase regions, which can hinder the long-range molecular relaxations responsible for the glass transition. This offsets the plasticization effect of the network resulting from the absorption of water [4, 32].

The behaviour of epoxy-silica hybrid systems is very different from that of conventional cold-cured epoxy resins insofar as the latter have generally been found to exhibit a reduction in Tg and a deterioration in mechanical properties when aged under high humidity conditions [4, 41]. Although further cross-linking reactions can also take place in conventional epoxy systems, due to the presence of residual unreacted groups in the resin and hardener, in this latter case the plasticization effect of the absorbed water predominates over the rigidifying effect of an increase in network density [12].

The enhanced performance of the novel epoxy-silica hybrids may open the possibility of overcoming some of the deficiencies of conventional epoxy resins in masonry repairing and structure strengthening applications.

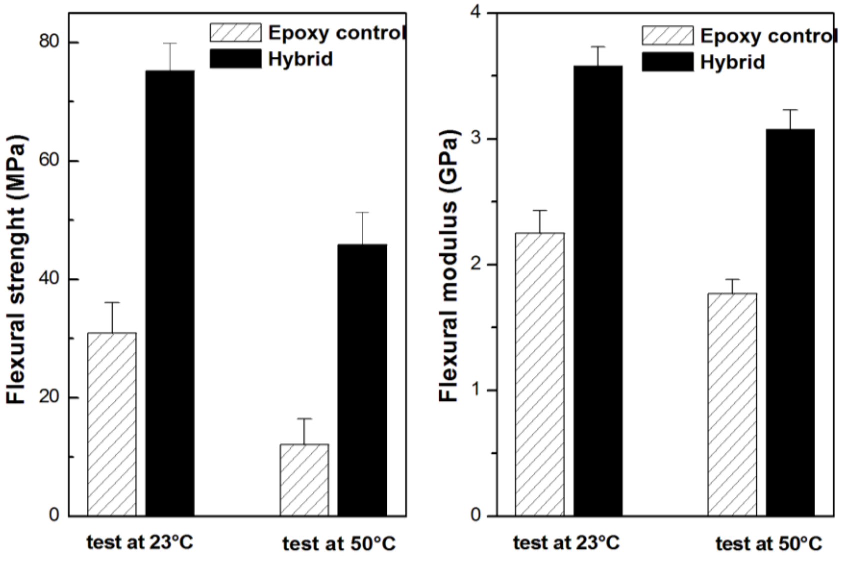


Figure 4. Flexural properties (strength and modulus) calculated for the epoxy-control and epoxy-silica hybrid systems.

Currently, experiments are on going aimed at verifying the effectiveness of the optimised hybrid system as an adhesive for stone, wood and other substrates frequently encountered in Cultural Heritage applications. Mechanical tests have been carried out on adhesive joints composed of cylindrical masonry blocks of Calcarenitic *Leccese* stone, cut at a 30° angle from vertical and bonded together by a 3 mm layer of adhesive (Figure 7).

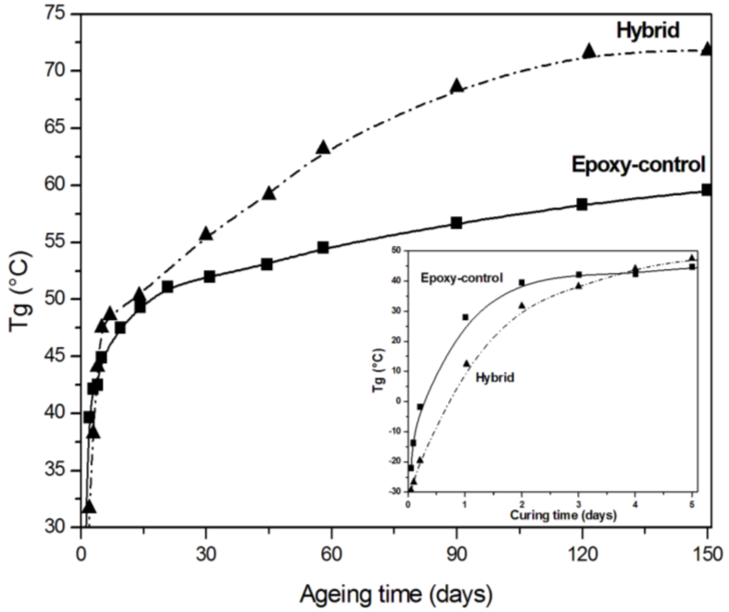


Figure 5. Tg values vs. ageing time at ambient temperature for the epoxy-control and epoxy-silica hybrid systems. In the inset, the evolution of Tg in the first 5 days of curing is evidenced.

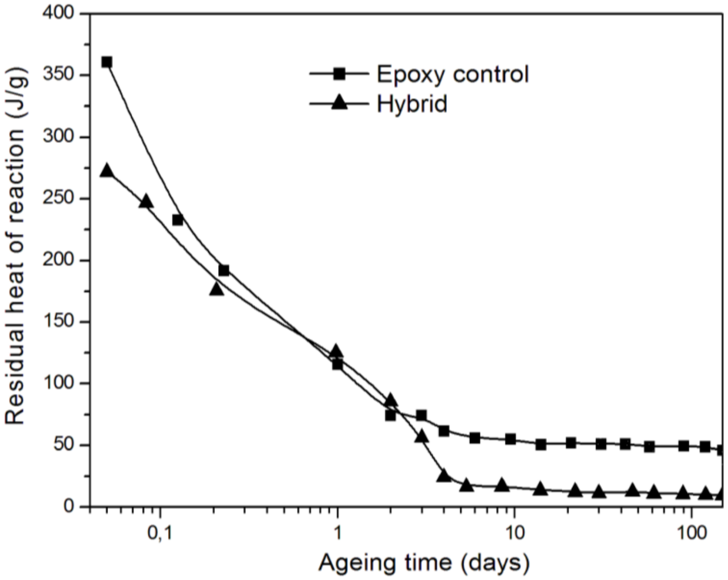


Figure 6. Residual heat of reaction vs. ageing time at ambient temperature for the epoxy-control and epoxy-silica hybrid systems. (For sake of clarity the time scale is logarithmic.)

Figure 7. Adhesive joints composed of cylindrical masonry blocks bonded by an epoxy-hybrid adhesive.

The adhesion strength between adhesive and the masonry has being studied in accordance with the ASTM C 882-91 standard. Preliminary results are very satisfactory even after exposure to different environmental conditions [42]. The optimized hybrid adhesive displays greater adhesion strength with masonry also at moderate temperatures and in presence of water. Further studies are in progress to assess the performance of the hybrid adhesive after a prolonged outdoor exposure.

CONCLUSION

In this chapter, the physic-mechanical, morphological and durability properties of organic-inorganic epoxy hybrids have been reviewed. These novel systems, based on silane-functionalized epoxy resins containing interpenetrating silica domains, have been recently optimized by this research group and proposed as a cold-cured adhesive for structural applications.

It has been found that the presence of inorganic co-continuous domains in epoxy-silica hybrids is responsible of: i) the enhancement of their load-bearing properties; ii) the increased glass transition temperatures, substantially higher than the cure temperature; iii) the increase of the mechanical properties, even at moderate temperatures; iv) the enhanced light transmittance, v) the reduced relaxations within the epoxy network. Moreover, the rigidity of the siloxane domains mitigates against the plasticization effects of the absorbed water in the organic network, alleviating the deterioration in load-bearing properties when the adhesive is exposed to severe environmental conditions.

The enhanced performance and the possibility to be cold-cured open the possibility of overcoming some of the deficiencies of conventional epoxy resins in masonry repairing, structure strengthening and artefact restoration by extending the use of these novel nanostructured materials in Cultural Heritage applications.

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Chapter 6

AN INTRODUCTION TO ARCHAEOLOGY AND PROTECTION OF MARITIME CULTURAL HERITAGE IN GHANA

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ABSTRACT

Although Ghana is home to several World Heritage sites and is no stranger to the complexities of national and international protection and development of cultural heritage, currently it has no provisions for the protection of the equally significant maritime heritage. Maritime activities over the past 500 years played an indelible role in international trade and relations along the coast, and archaeological materials provide testament to the many facets of history played out in the maritime arena. Ongoing maritime archaeological investigations along the Ghanaian coast necessarily highlight the question of what is or can be done to protect and preserve these non-renewable national and international heritage resources. A brief overview of archaeological research serves to illustrate both the fascinating maritime past of this region, and the precarious situation of submerged cultural heritage.

INTRODUCTION

Amidst a plethora of problems that threaten economic as well as cultural values in Africa, one researcher [1] notes that archaeology offers a means of deepening cultural connections to roots, values, and dignity. While there is a great deal of hope in this statement, it is not made without recognition of the reality of the times. Rapidly changing patterns the world over, from development to environment, and unprecedented demands to compromise on giving up the valuable spaces and places that heritage takes up to make way for development mean that

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efforts to preserve heritage and the stories of the past are now more critical than ever [2]. Unfortunately, however, it is also true that the ‘‘future of African archaeology, as it’s past, is inextricably bound to politics: disciplinary, national, regional, continental, and international’’ [1]. Until the values of the past are fully recognized and actively pursued by those in the heritage management and political realms, efforts to balance the investigation, conservation, protection, and preservation of the past with the present will continue to be overshadowed by those with louder pocketbooks.

This chapter is a brief introduction to some of these challenges as they apply to maritime heritage and archaeological research in coastal Ghana, West Africa. A short case study of submerged heritage near Elmina Castle, a UNESCO World Heritage Site, will serve to highlight both the research that has been done on the submerged heritage in the region, as well as imminent and potential threats to this nonrenewable global heritage and the lack of legislation in place to protect it. In doing so, it draws attention to the stage that is set for the next step; whether that will be towards the protection of submerged heritage, or towards its irrevocable destruction, however, has not yet been determined.

SUBMERGED CULTURAL HERITAGE IN GHANA

Virtually none of the vast coast of West Africa, including its islands, has been systematically surveyed by maritime archaeologists to date, and few formal protections are in place for either natural or cultural resources in them [3]. Of coastal West Africa, the majority of this limited maritime archaeological research has been conducted in Ghana, where traces of the maritime past of Ghanaian coastal societies as well as of the Atlantic trade spanning the last 500 years lie in its waters. This dearth of maritime archaeological research in a region that was and is arguably vitally important in terms of understanding historical Atlantic and global trade is clearly problematic, as is briefly illustrated here. At the same time, research to date has made significant strides toward the goal of understanding Africa’s international maritime past. In fact, while maritime archaeological research in Ghana is unique in virtually all of sub-Saharan West Africa, and maritime research there has a relatively short history, it has already provided fascinating insights into the maritime aspects of the Atlantic trade period. While all underwater work associated with this research has been conducted with the permission and overview of the Ghana Museums and Monuments Board (GMMB), the GMMB has little investment in the research and a generally limited understanding of it. This fact, along with limits of funding, training, and logistical infrastructure, means that the only documentation and mitigation of submerged sites in Ghana has been completed under the auspices of the Central Region Project, the umbrella project under which maritime archaeological work has to date been conducted [4,-7].

As with the majority of sub-Saharan West African states (Benin, The Democratic Republic of Congo, Gabon, and Nigeria being the exceptions), Ghana has not ratified the UNESCO convention on underwater heritage. Nevertheless, the presence of submerged cultural heritage in Ghanaian waters places responsibility for its protection, preservation, and even investigation directly into the realm of Ghanaian government responsibility or concern [8] The work of research is further complicated by the fact that underwater cultural heritage does not fit in the traditionally accepted Ghanaian government model for the management of monuments [i.e. 9], heritage, and historical sites, and is not readily understood or protected. Although in the continuum of cultural resource management plans and actions Ghana ranks above many other West African nations [10, -12],standards are still low. For example, it has no explicit legislation addressing submerged cultural heritage. Until the last decade, this has not really been an issue, as no submerged sites had been located or studied and there were relatively few direct threats to submerged cultural heritage. With the discovery of a mid-seventeenth century European shipwreck off the coast of Elmina in 2003, and the subsequent discoveries of additional submerged sites, along with increased development, fishing and oil-related traffic, however, circumstances are now unalterably changed.

Cultural Heritage Protection in Ghana

The identification and documentation of archaeological and cultural heritage is essential for its management, protection, and preservation, whether on land or underwater. Comparable to many nations' legislation for research and preservation, Ghana has numerous legislative mandates for the protection of cultural heritage. A thorough discussion of cultural heritage legislation and protection in Ghana has been provided by Kankpeyeng and DeCorse [13], but it is useful here to review a few key points in order to highlight the limited protection that exists for submerged heritage sites and the framework within which protection and legislation may be developed.

The managing institution for cultural heritage is the Ghana Museums and Monuments Board (GMMB), which is under the supervision of the National Commission on Culture (NCC). The GMMB was established formally under Ordinance 20 in 1957 as part of a desire to develop a national identity for the newly emerging state [13]; its duties were formally outlined by the National Liberation Council Decree (NLCD) 387 of1969, now known as Act 387 of 1969, and further strengthened by the Executive Instrument (E.I.) 29 of 1973 [14]. Although lacking in any mention of submerged cultural heritage, legal definitions of cultural heritage in Ghana are fairly comprehensive and may clearly apply to all cultural heritage located on the seabed in Ghanaian territorial waters (up to 12 miles offshore [15]) in the same way as for cultural material located on land. The lack of substantive action to protect and preserve cultural heritage stemming from these definitions and legislation is increasingly problematic, however, as opposing concerns for development and heritage protection arise, particularly as development accelerates [13].

In addition to a lack of proactive preservation, bureaucratic red tape and inefficiencies, unclear jurisdiction of regions, natural resources and cultural heritage, inadequate or insufficient legislation, inadequate funding and training, and blatant mismanagement of resources [13,16] have resulted in inadequate investigations and protection of cultural heritage in Ghana. A recent (2010) performance audit of the GMMB by Ghana's Auditor General found that since its inception in 1969, the GMMB has achieved "good initiatives and efforts," but on the whole has failed in its objectives of protecting and preserving Ghana's cultural past, stating that castles and forts in particular are "not well maintained; not well marketed; [and] the management of human resources is ineffective" [17]. This inefficient and ineffective enforcement of legislation and cultural heritage management clearly shows both a lack of understanding of the importance of cultural heritage, as well as a lack of foresight in terms of the future. In addition, problematic practices within the agency also by extension affect those who work under its mandates, for instance, and researchers. By way of illustration of the latter, a recent granting of a permit by the GMMB for maritime archaeological work in Ghana was accompanied by wishes for success in finding “gold and diamonds,” illustrating the fundamental lack of understanding, even at the level of individuals in the oversight department, of the goals and aims of archaeological research.

As there is at present no specific legislation in place to oversee and protect submerged cultural heritage in Ghana, and current heritage legislation is ineffective in terms of supporting research and protecting heritage, those sites located in the marine environment are particularly vulnerable, especially considering their generally isolated physical contexts. Even in cases where sites are known, such as the Elmina Wreck site (discussed below), the GMMB has essentially no resources for continuing investigations and enforcing protection, and has shown little initiative towards this end. As Kankpeyeng and DeCorse [13,13] observe, ultimately Ghana is responsible for the protection of heritage sites, but if they are to be effectively managed, the Ghanaian government must also seek partnerships with other non-governmental organizations and academic institutions and avoid hindering them, such as with excessively high fees for foreign research permits. Crucial for the protection of the essentially invisible submerged cultural heritage will also be partnerships with other nations, and particularly those that share in Ghana’s international heritage. Several of these partnerships are noted below, but it is important to first look at some particular challenges internal to Ghana, and how they are or are not currently being addressed.

Challenges to Submerged Heritage Protection

Challenges of cultural heritage management in Ghana include many of the issues affiicting heritage management the world over, including lack of funding, training, personnel, effective oversight and fundamental misunderstandings about how to preserve and protect sites, but also a range of issues including concerns about who owns the shared cultural heritage (i.e. 18,19]. Specific concerns are particularly sensitive for designated World Heritage Sites such as Elmina Castle. These include concerns over who is responsible for its upkeep [20, 21]. Pragmatically, in an economy where the majority of people live on a day-to-day basis and have an understandably limited concern with heritage in general [3, 6], the government must also balance and appropriately use available resources for other national interests [i.e. 22, 23], complicating the already difficult task of preserving heritage.

In addition to this, there appears to be a general lack of understanding of the intrinsic nature of both natural resources and cultural heritage in the marine environment in Ghana, and as a result, there is a lack of a coherent plan for the investigation, protection, and preservation of maritime resources. The general dearth of funds accompanied by an awareness of the finite nature of archaeological heritage in much of Ghana has not gone unnoticed by the international community [13], but solutions to the problems must first and foremost come from Ghana. In order for that to happen, a great deal of concerted effort is required from those who realize the threat and are in positions to act on it. Threats to submerged cultural heritage in Ghana fall under two general categories: development and unintentional risk, typically stemming from activities of the general population. Two primary and interconnected factors may be considered under the ‘‘development’’ category: technology/development and tourism. Unintended risks from the day-to-day lives of the general population may have as significant an impact as those from planned developments and tourism, although this has not yet been studied in detail.

The second category, tourism, and its attendant economic development, poses a significant threat to cultural heritage in Ghana [13, 24]. While tourism is growing in coastal Ghana, and particularly at Elmina as it is a World Heritage Site, infrastructure and other developments related to the tourism industry do not generally include provisions for the protection of the marine environment, although they may mention related shorelines or beaches [i.e 25]. In addition, an emphasis on developing tourism as a sustainable national income based on conservation of historic heritage and natural resources [23] is a part of legislation and recent discourse in Ghana [24, 26], but there is little to no discussion of the impacts of tourism on submerged cultural remains. The importance of protecting cultural heritage in its own right, as well as developing cultural tourism as a sustainable means of both protecting the sites and providing revenue for the country [i.e. 27, 13] has long been known in Ghana; the problem, as with so many other African nations, is effective enforcement. In addition, recent discussions with several GMMB personnel suggest that there is less of an understanding of the potential and importance of preservation of submerged sites than there is for other heritage. The concept and importance of world heritage, which is common to all humanity [28] and significant in terms of the history of central coastal Ghana, does mean a collective responsibility for the use of resources, including those related to tourism and the sea, but the primary responsibility must lie with Ghana to protect and preserve their natural and cultural heritage [i.e. 29, 30]. If these concerns are not addressed in the near future, the very source of income that is driving development will be at risk along with terrestrial and submerged heritage.

ELMINA AND ITS PLACE IN GHANA'S MARITIME HISTORY

The sea was the connection between disparate places of the Atlantic world, including the west coast of Africa and all those who came to trade there, and the seascape was the theatre in which historical maritime interactions took place. The ship was the instrument that blurred continental boundaries [31]. But ships and the sea could not sustain trade alone – it was its connection to the shore, with its attendant peoples, trade facilities, and resources that made it so important for the intersection of vastly different worlds and that provided transition points between the sea and land for both people and goods. It is impossible to understand international maritime interactions, cultures, and the archaeology of such, apart from the marine environment, seascape, or cultural maritime landscape in which they existed and exist today [32, -40], and this is especially true in the maritime Atlantic trade in Africa [41].

The rich heritage of the Ghanaian coastal seascape, consisting of local and international interactions along the shore, littoral, and on the sea, leaves little room for doubt that there is a multifaceted record of these activities hidden below the waves. In 1986 Merrick Posnansky and Christopher DeCorse [42] noted the potential for underwater archaeological investigations in West Africa, but this potential was not confirmed in regard to most of sub-Saharan West Africa until the discovery of a European shipwreck off the coast of Elmina, Ghana, in 2003 confirmed the presence of submerged historical remains [42](see [43, -45] for the only published exceptions to this). Investigating culture contact and West African trade and interactions [46], Greg Cook’s pioneering maritime archaeological survey and shipwreck discovery has opened the door for both fascinating historical exploration, and for the difficulties associated with investigating, protecting, and preserving cultural heritage in a country filled with potential yet rife with challenges.

Maritime history in Ghana (historically known as the Gold Coast) is both indigenous and international, including the complex events and affairs of the Atlantic trade era. Although traditional West African interactions with the sea rarely included the offshore zone, there is a long history of living near the sea and utilizing it (the nature and shape of the interactions historically is, however, debated, i.e. [47, -51]). Over the past centuries Ghanaian interactions within the seascape (for purposes here considered to be the area encompassing the coastal zone, shore, near-shore, and off-shore zones where ships sailed and anchored) have continued, but have adapted, changed, and developed. Foundational to these transformations was the Atlantic trade and its attendant relations with Europe and the Americas. These relationships served to provide the impetus and technology that created changes in the use of the coastal West African environment, including the connection of different parts of the coast that had previously not been in contact with each other [51]. In addition, it was through the Atlantic trade that the Ghanaian seascape became a part of European and American history, and in turn, their histories have become part of Ghana’s. This global cultural heritage [28] or international identity [52], common to so many different nations and a central issue in much of maritime archaeology (i.e. [53, 54]), provides the justification for the ‘‘examination, preservation and designation of archaeological and cultural monuments’’ and sites related to this shared heritage [52]. This also presents significant challenges, as is illustrated in maritime archaeology in Elmina. While the remains of castles/trading posts and merchant shipwrecks tend to leave the most visible mark, international interactions, the seascape and all it contains, are integral parts of the overall heritage landscape that must be incorporated to our understanding of a maritime past.

Sites relating to the Atlantic trade era, including Elmina, have been extensively studied and documented. The historically important site of Elmina was initially selected for maritime survey primarily because of its dynamic, pre-eminent, and well-documented role in the maritime Atlantic trade between Africans and Europeans on the west coast of Africa [48, 51, 55, -60]. A large number of international vessels traded in this region for over four centuries, contending with both man-made and natural hazards for the right to trade. Originally called São Jorge da Mina, Elmina Castle was established by the Portuguese in1482 and was the first European trading post in sub-Saharan West Africa, built in an effort to protect the Portuguese gold trading interests. In 1637, Elmina Castle was captured by the Dutch and remained in Dutch hands as a trading establishment until it was ceded to the British in 1872 [48; 57; 59].

Elmina Castle was named a UNESCO World Heritage Site in 1979 [62], and currently plays a key role in Ghana’s cultural heritage, including in the growing heritage tourism arena. The first heritage related research conducted at Elmina focused primarily on documenting the architectural history of the Elmina Castle itself and on some of the surrounding area [56, 61 - 63]. In 1985, Christopher DeCorse began a comprehensive archaeological excavation and investigation into the African settlement associated with the historical structure. Beginning in 1993, his work expanded to include surveys of prehistoric and historic occupations in areas around Elmina as a means of situating it in a broader cultural and historical context [48]. As this research continued, the Central Region Project was formed [64], and maritime archaeological survey in Ghana was developed under the auspices of this archaeological research project [42].

MARITIME ARCHAEOLOGY AT ELMINA

In total, four seasons of maritime archaeological research have been conducted in coastal Elmina, including a short survey project in 2003 that led to the discovery of themid-17th century European shipwreck now called the Elmina Wreck [42], mapping of the Elmina Wreck site in 2005 [4], limited excavations and investigation through sediment core micro-sampling of the Elmina Wreck site, and recording of timbers from the Benya Lagoon vessel in 2007 [5, 7, 65], and a regional remote sensing and diver survey in 2009 that provided monitoring of the Elmina Wreck site and lead to the discovery of additional submerged heritage in the region [66]. Underwater research in this environment is inherently dangerous and difficult, as the incredibly dynamic coastline can punish those who venture into its waters; despite this, the potential to learn about such a potent and pivotal period in humanity's history and in culture contacts between African and western worlds cannot be overstated [i.e. 67].

Ghana's submerged heritage is an integral part of global history and its investigation and protection need to have a defined and active place in local, national, and global affairs. National legislation as well as international conventions provide guidelines and regulations for the treatment, conservation, and protection of the terrestrial as well as the underwater cultural heritage, but at present there is no national legislation in Ghana specifically intended for submerged heritage. The turbulent waters of coastal Ghana make working conditions extremely difficult, but as this will be dissuasive to the casual diver and treasure hunter, it is likely one of the best insurances that submerged sites have against intentional disturbance. Two sites that are demonstrative of the documentation and mitigation of submerged cultural heritage in Ghana will help to illustrate problems with heritage management and protection in Ghana in general, and in the underwater realm in particular.

The Elmina Wreck Site

The Elmina Wreck site is located approximately two kilometers southeast of the Elmina peninsula and is clearly located within the historical roadstead (essentially the area in which vessels would anchor while doing business on shore) [6, 7]. Interestingly, this same area is used as the roadstead and shipping zone along the coast today and this presents one of the most serious threats to submerged cultural heritage. While local traffic in small fishing canoes or even in larger fishing vessels may pose some unintentional risk to the site, including fishing net and line entrapment, the use of the roadstead by much larger vessels poses a more serious concern. For example, in 2007 two Asian fishing trawlers were precariously anchored using a single anchor in tandem less than 500 metres west (upcurrent) from the wreck site. As we watched from our vantage point anchored directly above the wreck, the vessels dragged anchor to within 50 metres of the site in line with dragging their anchor directly over it, at which point we were able to convince them to weigh anchor and reposition elsewhere.

Although this is a single example, it is unlikely that it is unique (damage to other submerged sites has been documented), and since most of the waters in coastal Ghana, and indeed, West Africa, have not been surveyed for submerged cultural heritage, it is impossible at this point to measure actual risks to submerged sites apart from noting that they are real and very probable. In situations such as these, enforcement of fishing zone laws, which exclude large (usually foreign) vessels [24], would provide some degree of protection to sites within historical use zones, although a great deal more research is necessary to ascertain the degree of risk and likelihood of protection.

The Benya Lagoon Vessel

The clearest, although most unfortunate, example of the mitigation of submerged cultural heritage in coastal Ghana, as well of the ineffective oversight and management by the GMMB, may be found in the story of the Benya Lagoon vessel. The Benya Lagoon is still used by local fishermen, but as it was silted up and filled with trash, in 2007 the Ghanaian government paid a Belgian company to have it dredged so that the space could be used more effectively. In the process of excavating the lagoon with a large clamshell dredge, four concreted cannon and a number of large timbers were discovered by workers. These were brought to the attention of the Belgian manager, who immediately suspected that they may have been associated with ahistorical vessel. The manager alerted archaeologists from the Central Region Project to the fact, and we were invited to look at the site.

It is interesting to note that the significance of the find was not realized until the cannon were discovered, and if not for them it is unlikely that the site would have been noticed at all [7] All dredging activities were carried out without monitoring or participation of the GMMB, although the lagoon was known to have numerous historical materials in it. This is in contrast to archaeological activities, which are mandated to be monitored, and is illustrative of misplaced priorities, or at least misunderstood impacts of development activities on cultural heritage both in terrestrial and underwater environments. Even when the artifacts were discovered, GMMB made no effort to intercede, despite being mandated to do so if it is deemed necessary for the protection of cultural heritage associated with national monuments [68], for example, with Elmina Castle, near which the discovery was made.

Although not required to, the dredgers were kind enough to allow us access to the site after it was discovered, and even provided logistical assistance. Because of the method of dredging using scoop excavators, the context for the find was essentially destroyed. It is likely that there were elements remaining in the waters of the lagoon, but because of health hazards and time limits, no diving was conducted on the site. Despite this, it was abundantly clear that the materials that did survive the process of excavation, water sieving, and dumping were the remains of a European vessel [7].

By the time archaeologists reached the site, one of the four cannon had already disappeared, likely to be melted down for iron. Upon inspection of the large pile of debris dredged from the bottom of the lagoon, approximately fifteen timbers representing a wide range of structural components were visible. Diagnostic timbers were collected for analysis, while the cannon were investigated at the dredging headquarters near the site. Continued monitoring of the dredge spoil provided no other clearly associated cultural material. Because of the circumstances of discovery, limited time frames, and the nature of the find, the remains of the vessel were investigated as a salvage project, constituting the only investigation into the site or the materials recovered from it. The recovered remains were recorded in their location on the dredge spoil pile, through detailed drawings and photographs of the recovered timbers, and by examination of the cannon [7].Based on an analysis of timbers, cannon, and dendrochronological date of 1700– 1701 for the felling of trees of North German provenience, Pietruszka [7] suggests that the vessel was of Dutch construction, likely ranging between 20 and 36 metres in length. Under ideal circumstances, of course, dredging operations could have been stopped and divers deployed to at least investigate what may have remained of the site and its submerged context, but given the circumstances of this discovery and the extremely fragmented nature of the materials recovered, an impressive amount of information has been gleaned from the extant remains.

The GMMB collected the cannon and hull elements for storage at the Cape Coast Museum, but as there are no facilities there to conserve materials from submerged marine sites, the artifacts are now in poor condition. Lessons learned from this mitigation event highlight the need for legislation to assist in the process and recovery of materials from submerged sites, for the resources in order to process and conserve materials from them, and for the concerted on-going and effective participation of the GMMB and those responsible for protecting cultural heritage.

They also highlight the need for education and awareness of the cultural and historical value of archaeological sites, including those seemingly invisible ones under water, and of the need to be unrelenting in efforts to support the investigation and protection of these invaluable sites.

OTHER THREATS TO SUBMERGED CULTURAL RESOURCES IN GHANA

The preceding case studies illustrate problems with legislation, implementation, development, and a general misunderstanding of the importance of cultural heritage, but there are other threats to heritage as well, including exposing submerged sites to possible threats through the simple act of investigating them. Various aspects of economics play vital roles in destruction and preservation, and it is important to incorporate these factors into an overall discussion of heritage protection and mitigation in Ghana.

Dangers of Opening New Research Areas

As noted, the maritime archaeological work in Elmina is the first such project in Ghana, and one of the first in sub-Saharan West Africa. Implicit in this venture is recognizing the importance and dangers of exposing a previously untouched, and therefore at least somewhat protected region, and concerns for what protection may or may not be in place [4,6]. Assessing this requires an understanding of both the threats/dangers to underwater cultural heritage, and of any national and international mechanisms in place to protect them.

While it is important and necessary to find, document, and study submerged cultural heritage sites, both for their historical import and for management purposes [20], it cannot be overemphasized that risks to these resources are likely to increase in direct cadence with investigative activities. In the case of coastal Ghana, risks include such things as attention to a potential resource that has not yet been tapped (both in terms of submerged heritage and natural marine resources) by entrepreneurs interested in monetary gain and possessing the equipment to access submerged sites, local fishermen who know the seas and seafloor being misled into providing assistance to those who would misuse submerged resources, and misunderstanding of research intentions, including the ever-present assertion that researchers are looking for ‘‘gold and treasure,’’ and its attendant ramifications in terms of acceptance and understanding of submerged cultural heritage by local and leader alike. Potentially compounding these dangers is ineffective legislation and insufficient means to apprehend and prosecute offenders. These issues, combined with other threats to cultural and natural heritage, position Ghana’s submerged cultural heritage in a precarious position at best.

Other Problems – Potential and Real

The effects on submerged cultural heritage related to any of these activities do not appear to be in the present purview nor implementation of the Maritime Authority. The Maritime Authority partners with the Ghanaian Navy, however, because the Navy’s preoccupations are with national security, monitoring and protecting offshore operations, and controlling illegal fishing activities, it has few resources (i.e. boats) for the monitoring and protection implementation of submerged cultural heritage sites. The strongest rhetoric for resource and environmental conservation and protection in Ghana, and therefore potentially the most effective legislation to tie submerged cultural resource protection into, can be found in the recently-developed legislation relating to the offshore oil industry [i.e. 69]. The monumental challenge of regulating a wily industry with its own agenda [i.e. 70] will tax the country’s resolve and have consequences reaching much further than whatever income is generated, including ramifications for cultural heritage. Numerous examples of international legislation and programs to assist African and specifically West African nations in the development of sustainable practices concerning the coastal zone have been established [i.e. 71, 24], providing vital information and frameworks for implementation. This is the most crucial time for Ghana to either firmly embrace its maritime heritage, or essentially write it off forever.

GHANA’S CULTURAL HERITAGE

While oil clearly has economic implications for Ghana [71, 72], tourism plays a greater role in cultural economics, and tourism is perhaps the greatest benefit for, as well as the greatest threat to, cultural resources in Ghana. Drawing from Throsby’s [73] discussion of cultural economics, it may be important to address attitudes towards the research, monitoring, and protection of cultural heritage, versus the purely economic possibilities it offers. While tourism certainly provides an economic advantage in Ghana, it is vitally important that sustainable practices of managing and protecting cultural heritage are implemented in order to maintain and protect that valuable income stream, as well as the national and international cultural value of heritage. According to Throsby [73], something can be broadly said to be of cultural value if it contributes to shared elements of human experience. Distinct from economic value, cultural value can have both tangible and intangible elements and effects that may or may not be empirically measured. If understood and used appropriately, cultural capital can be an asset both to cultural value and economic value. Refining understanding of these values seems a crucial part to the protection of cultural heritage, including underwater cultural heritage, in Ghana.

Although there is recognition of the ‘‘tremendous cultural, historic, economic and political potential of the material record of the past’’ [13, p 92; see also 33], challenges for those tasked with cultural heritage protection in Ghana are clearly extensive. In seeking ways of management and protection, some initiatives, primarily through international collaborations, are working towards identifying and defining cultural heritage, towards creating plans and legislation to protect it, and towards active conservation [i.e. 74; 30]. These collaborations include plans for the Ghanaian people to control and maintain ownership of cultural resources, and to maintain control of the bene fits they generate, both monetary (cultural economy) and cultural (cultural value) [30; see also 75]. Historically there has been some effort to enlist the aid of local peoples in the reconstruction, maintenance, and monitoring of historical and culturally-significant sites in Ghana, but this has had minimal impact on their long-term preservation [16]. It is possible in the future that through education there may be some progress made in terms of local coastal people working towards protection of the marine environment, primarily because it is the lifeline for so many, but progress in this area is slow.

Ghana’s International Cultural Heritage

A number of nations, including The Netherlands, Denmark, and the UK, also have a vested interest in the international cultural heritage in Ghana, primarily as a result of Atlantic trade and colonial engagements there. For example, the Joint Ghana-Netherlands Mutual Cultural Heritage Policy Framework highlights issues of cultural identity and mutual cultural heritage, as well as the joint responsibility of all parties involved for its protection. The overall goal of this policy framework is to structure cooperation on the sustainable preservation and management of the mutual heritage in Ghana and The Netherlands, including in the ‘‘exchange of knowledge, education and support for awareness of both tangible and intangible cultural heritage, promotion of heritage tourism activities, introduction of legislation and technical support’’ [74, p 2–3]. As with Ghanaian national legislation on cultural heritage, however, there is discussion of terrestrial heritage such as forts and castles and archaeological surveys and protection around them [i.e. 74], but discourse on submerged heritage and the maritime environment tends to be lacking or non-existent.

Management of Submerged Heritage

Unfortunately, even Elmina’s status as a World Heritage Site does not afford explicit protection for submerged sites associated with it. Not until the waters around and between Elmina and Cape Coast Castle (10 kilometres east) are designated also as protected under World Heritage agreements, for instance, as a World Heritage Maritime Seascape, will there be some form of effective protection in place. The very nature of submerged heritage sites as not inherently visible entities presents a challenge to archaeologists and those who would protect such sites. The problem with this is the all-too-often true adage ‘‘out of sight, out of mind,’’ meaning that if people cannot see the heritage, they are generally less interested in protecting it. Ironically, the lack of awareness of submerged sites in Ghana is currently the lone force protecting them from purely opportunistic destruction by treasure hunters and looters of all descriptions. Since the poor diving conditions and lack of diving infrastructure in most of West Africa mean that Ghana is extremely unlikely to ever be a tourism diving destination, sites are presently safe. That being said, however, in the future this is not guaranteed, particularly as oil brings in more people with the skills and equipment, and more money into the general populace, which has the potential to create interest and demand for diving in Ghana, and therefore to allow access to submerged sites. If protection is not in place before this happens, the submerged cultural heritage of coastal Ghana faces a potentially dismal future.

DISCUSSION AND CONCLUSIONS

Management of submerged cultural heritage is complicated by the fact that this heritage is largely ‘‘invisible,’’ and therefore rendered intangible. It is also complicated by its inherent position intertwined with the natural resources in the sea. For much of the world, management is also made more difficult by the many stakeholders in the marine environment and what it holds [76 39]; while there are many stakeholders in the natural resources of the sea in Ghana, at present there are few interested in its cultural heritage, but this is likely a short-term scenario. As aptly predicted by Joe Flatman [2, p 5.]:The growth regions for twenty-first century maritime archaeology—the seas and coasts of Asia, Latin America, Africa, the Arctic and Antarctic—are all those areas most likely to be fought over in the future as nations, corporations and individuals alike compete over increasingly scarce resources. It seems inevitable that maritime archaeology will become embroiled in the conflict over such resources. Already a part of this with the relatively recent discovery of oil, Ghana has not yet taken definitive steps in the vital realm of protecting submerged cultural heritage in its waters. As has been demonstrated so many times in the past in both terrestrial and maritime contexts, this failure to protect means that the government will be continually vulnerable to the lure of quick profits from developers and treasure hunters, to the detriment and likely demise of the non-renewable and irreplaceable history in its waters [77], in addition to the loss of real and potential educational, cultural, and economic benefits [20]. Because of its rich national and international history, the cultural heritage of coastal Ghana, particularly those sites related to the historic Atlantic trade, are in many ways a global responsibility [9, 77, 78, 79]. Unfortunately for submerged cultural resources in Ghana, it is likely to be primarily through international efforts that these sites are preserved, unless there is a concerted national effort in the near future to fully acknowledge and protect both the sea and the sites it contains.

Misunderstanding or misconceptions of the past at all levels are common in Ghana, but are far less acceptable at the level of educator and government than for those, such as local fishermen in Elmina, who struggle daily to make a living. While not condonable, it is easy to understand how, upon seeing an opportunity, someone would take a historical cannon for its iron without regard to its historical value, or would temporarily abandon fishing to participate in the looting or obtaining of gold found washing out of a bank of the Benya Lagoon [80; 81]. It is precisely a well-defined concept of cultural capital and its value (such as preserving these historically important materials) at the local, national, and international levels that is needed in order to sharpen the policy articulation process in terms of cultural heritage, and to provide it the legitimacy and power to actually protect sites [73] so that benefits are obvious at all levels.

The question that must be asked, then, is: can mitigation be preventative as opposed to reactionary? In the case of Ghana, I propose that it can be, and indeed it must be, if there is going to be any hope of preserving the local and international cultural heritage entombed in its waters [82]. The examples of the Elmina Wreck site and the Benya Lagoon vessel highlight both the invaluable information that can be learned from submerged sites in Ghana, as well as the lack of oversight, funding, and control of submerged cultural heritage there; one of these sites is already completely destroyed, the other is being naturally preserved for the time-being, but this is not a long-term solution. In order to make these and other sites relevant and relatable from the level of the fishermen through national and international government, it will require making the invisible heritage visible and accessible, and encouraging interest in submerged cultural heritage to foster a sense of ownership of collective history. Because a tourism diving industry based on submerged sites is not likely in Ghana, the primary means of accomplishing this will be through museums, education, and public awareness programs [i.e. 83; 84] that encourage participation at local, national, and international levels. Museums serve as the link between history, researchers, and the people of today [i.e. 85; 86], and could lead the way in championing legislation with teeth that provides firm guidance, oversight, and control, as well as effective management, of both terrestrial and submerged cultural heritage. The importance of the Ghanaian seascape as an integral part of the national and international ‘‘heritage-scape’’ [9] cannot be overstated, but until its inherent value is embraced by Ghana itself, submerged cultural heritage remains at risk.

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Chapter 7

EVALUATING THE STATE OF PRESERVATION OF WATERLOGGED ARCHAEOLOGICAL WOOD PRIOR TO CONSERVATION

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ABSTRACT

In the past, wood used to be largely utilized owing to its good mechanical and physical properties, to the easiness of its use and workability, as well as to its considerable availability and cheapness. Therefore, wood artefacts are an important issue to be taken into consideration in the modern approach to conservation of Cultural Heritage. Among the wooden objects deserving attention, waterlogged archaeological wood represents a highly interesting case. In fact, this material, being preserved under the water table and thus in conditions of almost complete anoxia, is altered only limitedly and in a manner which does not compromise the exterior integrity of the objects. However, waterlogged wood is attacked internally by microorganisms (bacteria and fungi), as well as environmental factors. These elements appreciably decay the wood tissue by changing both its cellular structure and its chemical and physical properties compared to non-degraded material. In fact, nearly always the altered material needs to be treated before it can be put on display in a museum (it mostly depends on the extent of decay), and the conservation procedure must be based on the correct evaluation of the state of preservation.

This chapter reports on the characteristics of waterlogged archaeological wood decayed at various levels, analyzing a large number of samples of different wood species and burial times, coming from several archaeological excavations in Italy. The chapter also analyses how a correct diagnostic evaluation can be obtained only after an integrated multidisciplinary approach, making use of quantitative and reliable data.

It is possible to carry out detailed evaluations through simple and broadly used techniques, which, however, have to be taken into consideration attentively before the

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state of preservation of the material can be established. For example, microscopy allows both to identify the timber used and to observe the anatomical structure present, thus enabling to recognize the decay agents and the parts of the cell walls degraded. Chemical analyses enable to quantify the depletion of structural polysaccharides caused by the decay process, as well as any other possible changes in the chemical structure of the wooden tissue. Physical characterization enables to evaluate the mass loss after decay and the increase in water content (i.e., porosity) present in the material.

Furthermore, in order to attain consistent evaluations and establish how specific factors (such as the wood species) affect resistance against alteration, the various physical and chemical parameters need to be combined among each other so as to increase the readability and usefulness of the data. The “effective” chemical parameters can thus be used instead of the raw ones (directly coming from chemical measurements), enabling to refer to the presumed original mass of wood (i.e., before burial and therefore before any process of decay) rather than to the mass of degraded, ash-rich, archaeological material. This also allows for a direct comparison of data referring to materials even in highly different states of preservation.

A correct diagnostic evaluation helps to understand the new properties of decayed wood and, in perspective, to classify the material according to its true level of decay. Analogously, a correct classification of the material can enable to tailor the treatment method on the basis of the decay class.

This chapter is mainly oriented toward conservators, and in general toward those who are in charge of following and possibly setting up a conservation process, from retrieval to the phases leading to the actual treatment, in the attempt of giving the right importance to the preliminary diagnostic analysis.

Keywords: Diagnosis, microscopy, maximum water content, basic density, lignin, holocellulose, bacteria, wood decay

INTRODUCTION

Wooden artefacts found during archaeological excavations provide insight into past cultures. Therefore, their declared archaeological value is fundamental as they testify concerning both man’s use of natural resources, and the development of woodworking techniques and artistic endeavour. Wooden artefacts can also testify of ancient climates and trading routes [1].

Wood has always been greatly used with the aim of producing a wide range of artefacts owing to its good mechanical and physical properties, to the easiness of its use and workability, as well as to its considerable availability and cheapness.

However, wood is an organic, biodegradable material and the findings of wooden objects during archaeological excavations occurs less than expected, although wood is the major organic material found in wet archaeological excavations [2].

When carrying out excavations, wooden artefacts can appear in seemingly remarkable good conditions, with very few signs of deterioration. Often, though, the aspect of the artefact does not reflect the state of preservation of the material.

In fact, contrary to fresh wood, waterlogged archaeological wooden artefacts are fragile. Moreover, they can rapidly crack, warp and collapse irreversibly as soon as the moisture content falls.

According to ICOMOS, Charter on the Protection and Management of Underwater Cultural Heritage [3], once the presence of wood has been identified, retrieval must be carried out only when suitable conditions for safeguarding the objects can be ensured in advance, unless retrieval is absolutely necessary.

The fragility of wooden objects requires to verify the actual economic and technical possibilities for carrying out the necessary operations in a given time-frame: characterization of the site where the wood artefacts are found, storage of the findings in suitable and controlled micro-climatic conditions, characterization of the material, restoration, and possible showcasing in temporary exhibitions and/or for museum use.

When resources are deemed insufficient, the possible retrieval must be postponed, simply preparing relevant documentation and undertaking all suitable protection and temporary conservation measures. A sudden and long-lasting interruption of the process at any moment could lead to the complete or partial loss of the artefact.

Hence, wood needs specific care during its retrieval (thus before its conservation). Measures to protect it from direct radiation and high temperatures (for instance through screens, roofs, and constant spraying or wetting) must be adopted, and the level of water, if present, must be regulated (with suction pumps etc.) so as to operate in controlled environmental conditions.

The Italian standard UNI 11206:2007 [4] provides several operational prescriptions, among which it is noteworthy to mention that if wood comes from confined sub-aerial sites or from underground sites characterized by a dry climate, the seemingly unaltered appearance of the artefacts must not lead to underestimate the importance of caution in the retrieval phase. In such cases as well, wooden artefacts must be prevented from being exposed to sudden variations of relative humidity, in order to avoid drastic shrinkage, swelling or collapse which could lead to dramatic deformations and even breakage.

Therefore, the retrieval of waterlogged wood must be carried out avoiding the evaporation of water as much as possible. For instance, it is preferable for small size wood pieces to be placed in hermetic containers, possibly incorporating the sediment and a quantity of water adequate to maintain the waterlogged conditions.

On the contrary, large size wood artefacts (which require more time for retrieval) must be constantly wet so as to avoid irreversible damage.

After retrieval and before the conservation process is started, it is necessary to characterize the material in order to define the level of decay which the wood has undergone both in qualitative and in quantitative terms. This enables to identify the mechanisms and the agents that caused said decay. When possible, non-invasive investigations should take precedence, by carrying out sampling so as to gather significant data with the least removal of material possible.

Before any analyses, samples must be preserved in microbiologically pure water within containers suitably sealed in order to maintain the original moisture content of the wood.

Moreover, samples must be kept in conditions unfavorable to biological growth (e.g. T < 4°C, no light). The size of each sample depends on the type and number of analyses.

The evaluation of the state of preservation of waterlogged archaeological wood has crucial diagnostic value in the preparatory fact-finding stage, in order to set-up a project aiming at making suitable and proper choices for the conservation of the wood.

In fact, conservation of archaeological wood artefacts may be defined as a set of operations carried out through a coherent, coordinated and planned activity of studies, prevention, maintenance, and restoration [5]. Said conservation process is aimed at extending the life of the conserved artefacts as much as possible.

Furthermore, a preliminary and complete diagnostic characterization of the wooden material constituting archaeological artefacts may become a crucial reference to understand the possible evolution of decay (or however a variation in the state of preservation) in treated objects: for instance, because of the lack of compatibility between the product used for the treatment and the compounds present inside the wood preserved in waterlogged conditions for a long time (e.g., iron salts or oxides, sulphur compounds etc.). Without such reference, it is practically impossible (or however, not very reliable) to measure any kind of variation subsequent to conservation. As a practical example, the moisture content at the moment of retrieval (usually called the Maximum Water Content) is routinely used to assess the state of preservation of waterlogged archaeological wood findings. However, the values measured for this parameter are useless once the objects have been treated, because conserved wood is no longer at its maximum imbibition state.

The aim of this chapter is to describe the preliminary phases of the conservation process, that is to set out what needs to be done before the treatment of the objects, so as to evaluate correctly the state of preservation of waterlogged archaeological wood. The diagnostic approach used is analyzed in detail, presenting widespread techniques more easily accessible to conservators (complex techniques, or difficult to interpret, or which do not give quantitative and reliable data were not taken into consideration). Moreover, at the end of the chapter, examples are provided concerning the possible use of the diagnostic results as regards the purposes of conservation.

THE BIOLOGICAL ORIGIN OF DECAY IN WATERLOGGED ARCHAEOLOGICAL WOOD

Waterlogged archaeological wood can be preserved for a very long time, even if a certain degree of deterioration always occurs, producing physical and chemical modifications of the wood substances and changes in the anatomical structure of the material [6]. The knowledge of decay agents and of the effects of their action on wood and material enables to understand the differences between sound wood and waterlogged archaeological wood: this is an essential prerequisite for conservators to correctly approach the conservation process [6, 7].

Wood is a biodegradable material: it can be biologically transformed, in only a few decades, by the most aggressive decay agents, such as rot fungi and insects, up to becoming humic substance. Nevertheless, owing to favorable environmental factors restricting the degrader activity, it is possible to unearth archaeological wooden objects after long periods (even millennia) [7, 8]. In terrestrial environments, wood is primarily degraded by insects and fungi. Insects often spend part of their life cycle inside the wood at larval state. Larvae feed on wood (although polysaccharides are mostly attacked), and can destroy it in a very short time [9]. Analogously, white- and brown-rot fungi mainly attack either holocellulose (that is, cellulose and hemicellulose) or the lignin inside wood. White-rot fungi (taxonomically related to *Basydiomycetes* and certain *Ascomycetes*) are particularly dangerous because they utilize all cell wall components (therefore, both holocellulose and lignin). Some species are even more specific organisms in the degradation of lignin [7]: the common name of this class of fungi is related to the aspect of the wood, which becomes whitish after the removal of lignin. In brown rot, cellulose and hemicellulose are preferentially digested. This type of decay is characterized by a rapid degradation of the S_2 layer, whilst the S_3 layer and the lignin-rich middle lamella remain unaffected in practice [10]: the effect of the carbohydrate component decrease is the transformation of wood into “cubes”, which “finally crumbles into powder” [10]. Brown-rot fungi are very aggressive wood degraders, and they are capable of strongly impairing its physical-mechanical properties [7].

The organisms heretofore described, typical of terrestrial environments, need specific conditions to develop, which are related to the presence of oxygen, as well as to a suitable temperature and moisture content, the latter especially in case of fungi. If the contents of oxygen and moisture are adequate, decay by fungi may occur very quickly, sometimes leading to the complete collapse of the material [11].

In marine environments, where there is enough oxygen and high salinity, marine borers (shipworms and *Limnoria*) and crustaceans usually strongly damage wood [8, 12, 13].

Concerning the waterlogged archaeological wood preserved in terrestrial environments, conditions such as low oxygen level, high humidity, and low temperature ensure that only some organisms can survive, and hence the decay in wood proceeds very slowly. Actually, waterlogged archaeological wood can be attacked only by both soft rot fungi and bacteria, although the artefacts may also show the effects of other previous attacks started during their “service life” (like those related to shipworms in wrecks, or to insects in beams). In fact, while marine borers can act only in oxic conditions (> 3.0 mg/l), soft rot fungi need less oxygen to develop, and they are the main degraders in both dysoxic (0.3 - 3.0 mg/l) and suboxic (0.01 - 0.3 mg/l) environments. Furthermore, bacteria are able to decay wood also in suboxic and even anoxic (< 0.01 mg/l) environments [8]. The presence of elevated quantities of organic materials or sediment layers can prevent the action of marine borers, but this promotes the development of bacterial and fungi decay, unless anoxic conditions are soon developed (in such case the decay process slows down appreciably). The same mechanism of reducing the availability of oxygen and making a physical barrier against shipworms is also utilized in the *in-situ* preservation of waterlogged archaeological wood material, that is, the reburial of remains by adequately thick covering layers (at least 50 cm, as reported in [14]) to create completely (or almost completely) anoxic conditions [12, 14–16].

The action of both soft rot fungi and bacteria within the wood tissue results in different parts of the degraded cell wall attacked and in a different morphology of the decay depending on the type of microorganisms. For this reason, the use of microscopes is fundamental to identify the agents that caused decay, to evaluate the extent of their damage and the extension of the related phenomena.

Soft rot fungi are taxonomically related to *Ascomycetes* and *Deuteromycetes* [13]. The macroscopic effect of their action is the transformation of external layers of wood in a soft material [17]. The chemical effects of soft rot attacks are the preferential depletion of both hemicelluloses and cellulose, and the demethylation of methoxyl groups [10]. This type of organism differs from brown and white rot because its development is due to a hyphal tunneling inside the lignified cell walls [10] (Figure 1). The attack begins from the surface by hyphae penetrating inside the wood. At the beginning, hyphae move through the “natural openings like rays and pits” [18] already present in the structure.

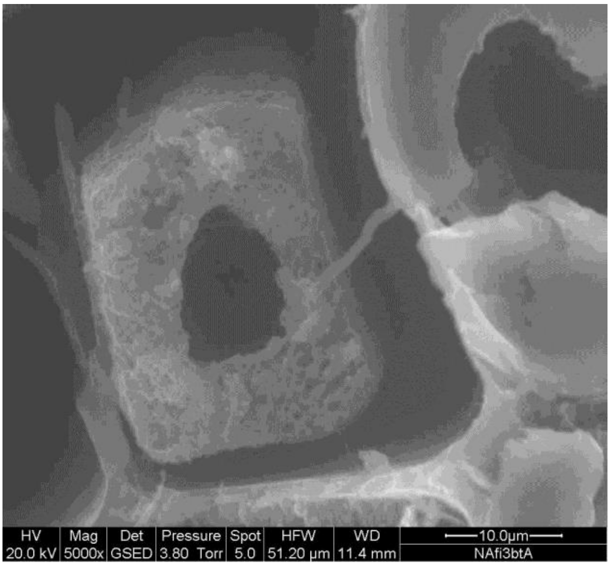
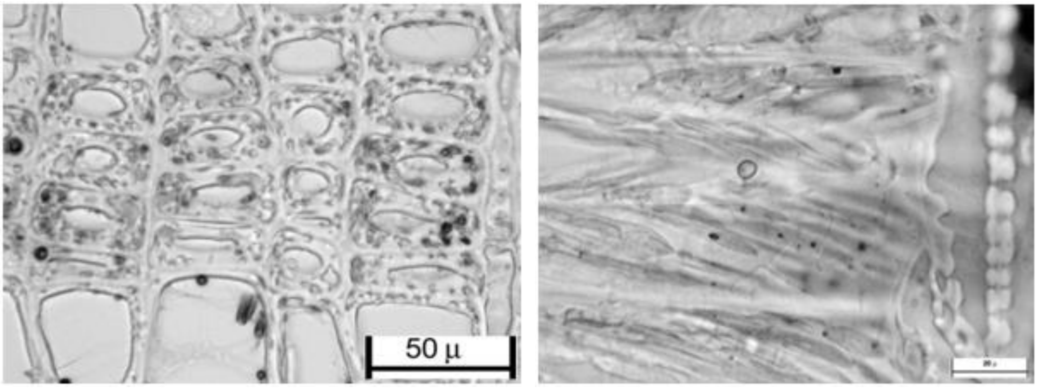


Figure 1. ESEM picture showing a detail of the transverse section of cluster pine: a fungal hypha coming out from the cell lumen is well visible.



a

b

Figure 2. Cross section observed at the light microscope showing the holes produced by soft rot in an advanced level of attack (a). In (b), soft rot cavities in radial section going along the cellulose microfibrils. They have the typical pointed ends.

Hyphae then spread into the secondary wall forming typical cavities with conical ends (Figure 2): they move in the S_2 layer parallel to the orientation of cellulose microfibrils. Owing to the action of enzymes, cavities around hyphae are formed: in a transversal section they look like holes in the secondary wall [14] (Figure 2). In a more advanced stage, when holes join together, the secondary wall may appear completely destroyed.

The bacteria able to decay waterlogged archaeological wood are rod or spherical shaped (Gram-positive and -negative); they are 2 - 8 μm long and 0.5 - 0.9 μm thick [18]. The attack of bacteria begins in the rays against materials stored within, and then the decay of parenchyma cells occurs [19]. All cell types are degraded, except for vessels. This occurrence may be used for their identification: in fact, bacteria are distinguished depending on which part of the wall they attack and on the aspect of the degraded walls.

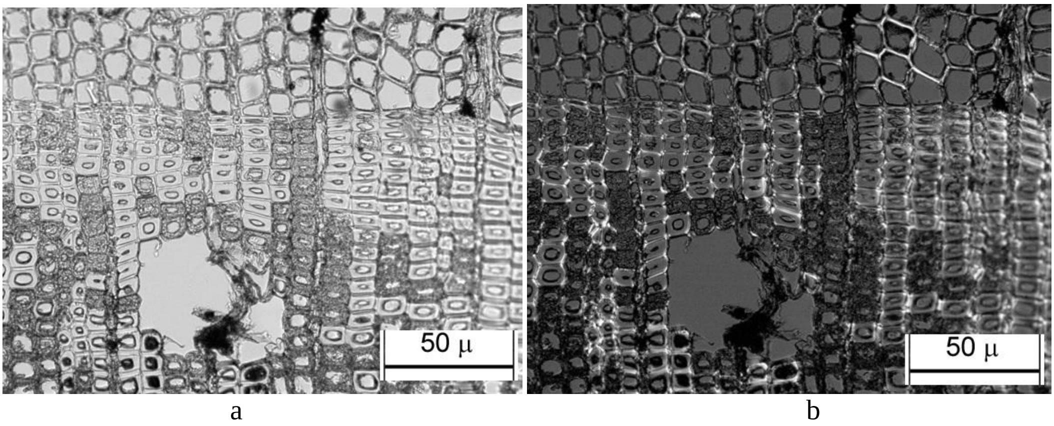


Figure 3. An initial decay by erosion bacteria in cross section: in (a), some degraded cells surrounded by sound cells (light microscope); in (b), the same light microscope-photo with polarized light. The possible absence of crystalline cellulose, due to the biological decay, is apparent in polarized light. In fact, only some cells retain the birefringence while others cells disappear.

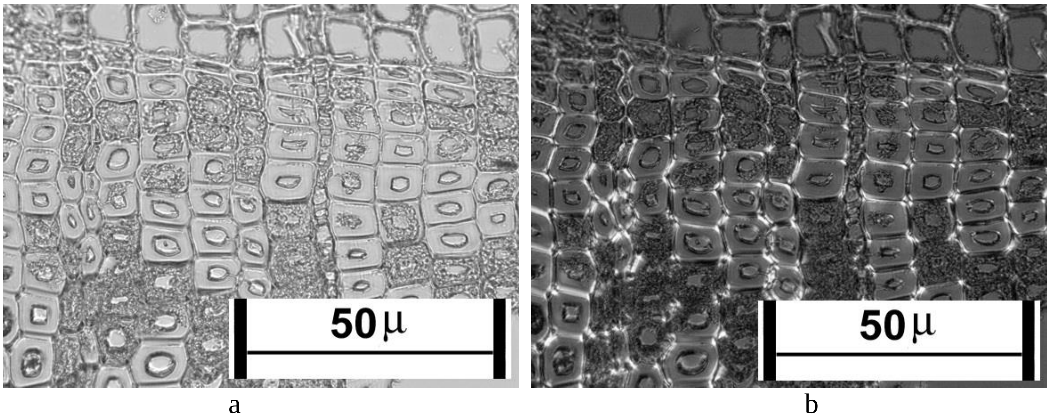


Figure 4. At higher magnification it is more evident how erosion bacteria attack at the cell wall level. In (a) it is visible how the degradation is mainly oriented towards the S_2 layer (light microscope). In (b), the same picture but with polarized light.

Erosion bacteria are the most common among the tunneling bacteria, because tolerant to near anaerobic conditions [18]. Like soft rot fungi, they move into the cell wall along the orientation of cellulose microfibrils. They can digest only cellulose and hemicelluloses, whereas lignin is left intact: for this reason, they are considered less dangerous than the other tunneling bacteria (Figure 3). They degrade the cell wall by erosion starting from the lumen, and then proceed from the S_3 into the S_2 layer (Figure 4) forming a groove in the cell wall with a dimension more or less similar to the bacterium [13]. The erosion is due to an enzymatic activity around each bacterium [20]; moreover extracellular mucilage enables the motility and the adhesion to cell walls [13].

In case of very heavy attacks, holes in the S_2 merge in larger voids, also inducing the disappearance of the whole wall. In a longitudinal section, these bacteria produce “V” notches and groove-like erosions, more or less along the microfibril angle [21].

The tunneling bacteria are Gram-negative, motile but not flagellate, variable in shape, slime producers and able to attack cellulose and, occasionally, the lignin present in the so-called compound middle lamella [13]. They are so called because they produce tunnels in the S_1 and the S_2 layers, thus degrading the wall: inside each tunnel there is only one bacterium at the end. The direction of the tunnels is not along the helical orientation of cellulose, but they can follow every direction, passing through the S_1 layer and the compound middle lamella. For this reason, they are more aggressive than erosion bacteria. Concave cross walls are visible along the tunnels (Figure 5).

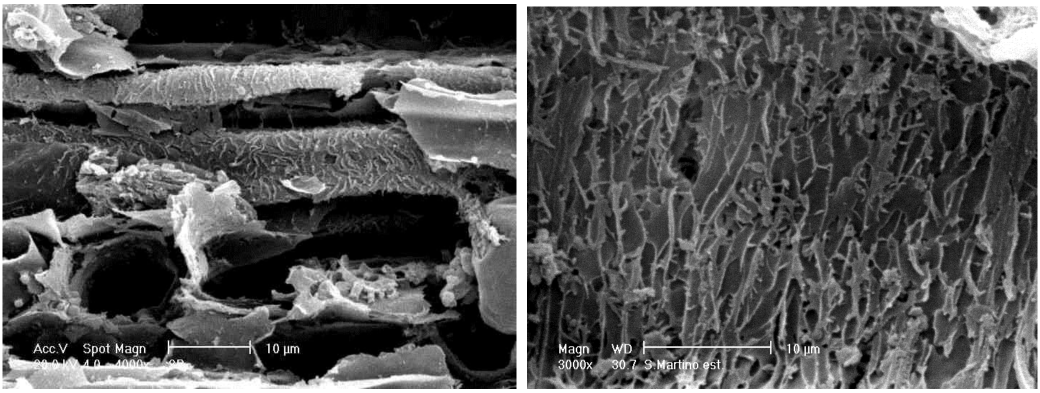
Several hypotheses have been formulated to explain this presence: they could be the result of a process of start-stop-start-stop advancement (the cross walls indicate each position of the bacterium) [13], or these bands are formed by the waste products of bacteria metabolism [12, 22, 23].

MATERIALS AND METHODS

Materials

This study reports on the results obtained on a large number of analyzed wood samples from wet archaeological excavations carried out in Italy. The samples were representative of different waterlogged environments, burial times, wood species, and states of preservation; their main characteristics are briefly described in Table 1. More details about the various samples may be found in other published papers [6, 24–30].

In the majority of cases, small blocks (approximately 4 x 2 x 1 cm^3 edges) were analyzed from the various findings, being careful to remove the material in the center of the objects, in order to limit the inhomogeneity in the extent of the decay which usually characterizes waterlogged wood. Considering that the material was always milled after drying, no specific orientation was chosen.



a b

Figure 5. SEM pictures of longitudinal sections of two different samples (a, b) showing the typical aspect of tunneling bacteria attack: concave cross walls along the tunnels are visible.

Table 1. Number and representativeness of the archaeological wood samples whose results are reported in present chapter. All of them were preserved in waterlogged conditions.

Analysed wood species	Age (min-max)	Burial environment	Total number of samples	Range of MWC (min-median-max)
Alnus sp.p.	XIV-XVIII c. A.D.	lagoon	31	173-423-703
Cupressus sempervirens	I-II c. A.D.	coastal	12	120-240-451
Juglans sp.p.	I-II c. A.D.	coastal	4	462-502-699
Larix decidua	I - XVIII c. A.D.	coastal, lagoon	9	105-142-372
Picea abies	I-II c. A.D.	coastal	7	194-339-625
Pinus sp.p.	VII c. B.C. - II c. A.D.	coastal, river	15	238-368-727
Quercus sp.p.	VII c. B.C. - XVIII c. A.D.	coastal, river, lagoon	45	119-342-822
Ulmus sp.p.	VII c. B.C. - XVIII c. A.D.	coastal, deltaic, river, lagoon	16	134-445-751

The acronym MWC stands for Maximum Water Content

Methods

Micromorphological Characterization

Identifications of wood species and morphological investigations are usually performed by means of light microscope, scanning electron microscope (SEM), and Environmental Scanning Electron Microscope (ESEM). Transmission Electron Microscopy (TEM) can be occasionally used. However, the disadvantage of this technique lies in the fact that the required embedding phase is very long and complex, and it cannot be considered as a routine technique.

The most widely used instrument to carry out micromorphological characterization is light microscope. Observations are usually carried out on thin sections (10 - 20 µm), while 50X and 100X magnifications are used to have an overall view of the sample anatomy. Instead, higher magnifications (200X or higher) enable to carry out in-depth studies of the biological decay, with the consequent identification of the signs of bacteria and fungi attacks. Often the characterization of decay is also evidenced by using polarized light, which is able to highlight the crystalline cellulose’ structure, or its possible loss due to the action of fungi and bacteria. The pictures presented here were obtained on a DM LB 2 (Leica) microscope. Sections cut along the three diagnostic anatomical directions (transversal, longitudinal-radial, and longitudinal-tangential), obtained on frozen specimens (by means of a freezing plate) were observed.

In the case of SEM observations, very small wood samples may be used. However, the most relevant aspect to be considered in SEM analysis is the sample preparation.

Table 2. Series of phases for the dehydration of samples before SEM observations

Acetone 99.5%	Distilled Water	Duration
25	75	30 min
50	50	30 min
75	25	30 min
100	-	30 min
100	-	30 min

In the Table, “Duration” indicates the time of immersion in the different solutions

In this work, the samples observed were cut manually along the three anatomical directions through a razor blade. After the cut, the samples had to dry. Before drying, they were dehydrated with acetone, and then the dehydrated samples were critical-point dried in a Balzers CPD 030 apparatus using liquid CO_2 as the substitution fluid. For the dehydration of the samples it was necessary to prepare distilled water / acetone solutions in different percentages, up to 100% acetone, thus to avoid any possible dramatic effects of drying on the wood structure.

These solutions were prepared as reported in Table 2. Before dehydration, samples were fixed as suggested in [11]. The SEM pictures shown in this chapter were obtained on a Philips XL 20 microscope.

The samples observed by ESEM do not require any preliminary preparation: this occurrence can be very useful in case of highly decayed and very small (and therefore difficult to manage) specimens. However, according to our experience, this technique reveals limits in detailed analysis, in that the quality of the images collected is highly dependent on the degree of dehydration of the wood [29]. The ESEM picture shown herein was obtained on a QUANTA 200 FEI microscope.

It is worth adding that, although microscopic techniques usually give only descriptive-type qualitative results, often influenced by the specific experience and skills of the operator, some Authors propose to grade the state of preservation of waterlogged wood by means of decay classes. Björdal et al. [12] suggested a classification of decay based on light microscope observations: 4 levels of decay were proposed aimed at highlighting the percentage of biological attack within the cells.

Moreover, Klaassen [21] introduced a classification of bacterial degradation for four different wood species aimed at reaching a systematic knowledge of pattern, causes and processes of degradation in wooden foundation piles in the Netherlands. The issue concerning the fact of grading the decay of waterlogged archaeological wood according to micromorphological characterization is highly interesting, because it would enable to gather numerical values, which can be then compared to measurements obtained by means of other widespread used diagnostic analyses (namely, the physical and the chemical ones).

Physical Evaluations

In fresh wood, the physical characterization normally concerns the measurement of density and shrinkage/swelling coefficients within the hygroscopic field (i.e., between nominally 0% and nominally 30% of moisture content), which are the basic characteristics to be determined so as to predict the technological behavior of wood.

However, when wooden objects found in wet archaeological excavations have to be analyzed to determine the extent of decay, different parameters are preferred, which include the measurement of density and of moisture. In such cases, the knowledge of the density of wood assumes new meanings. In fact, if the actual value of density is compared to the presumed value that the same sample should have had when non-decayed, it is possible to estimate the mass loss occurred in the sample.

Density is the ratio between mass and volume, and in wood it is generally expressed as g/cm^3 or kg/m^3 (these units are not numerically equivalent). In sound wood both mass and volume change continuously following the moisture content, thus the density of wood is usually expressed in several ways:

a based on oven-dry weight and oven-dry volume (thus avoiding the issue related to moisture content);
b based on weight and volume at a known moisture content (usually 12% is selected);
c based on oven-dry weight and water saturated volume (thus, again, avoiding the issue related to moisture).

In the case of waterlogged archaeological wood the latter way of measuring density is the most appropriate one, because the decay frequently causes dramatic distortions in samples after drying, imputable to the occurrence of collapses, which make the measurement of volume unreliable [31].

This kind of density is generally called Basic Density (BD). Another advantage of measuring BD in waterlogged wood is that volume can be easily measured by means of the water displacement method [32], which enables measuring any kind of specimen of any irregular shape. This characteristic is important mainly in archaeological wood, considering the limited possibility of sampling on artefacts.

Basic density is thus given by the expression:

$$BD = \frac{M_{ANHYDR}}{V_{WET}}, \ [\mathrm{g/cm^3}] \qquad (1)$$

where V_{WET} is the volume of the waterlogged sample (measured with the water displacement method) and M_{ANHYDR} is its oven-dry mass, i.e., obtained after drying at 103°C until constant weight.

The obtained values can be considered a real evaluation of the decay only when they are compared to the possible original density of the same piece of wood. Of course, this value is unknown; however, it can be estimated by assuming that it is the same as the average value of fresh (non-degraded) wood of the same species.

Then, the Residual Basic Density (RBD) parameter can be evaluated as the percentage ratio between the measured BD value and the average BD of the same wood species in sound conditions, that is:

$$RBD = 100 \cdot \frac{BD_{sample}}{BD_{fresh\,wood}}, [\%] \qquad (2)$$

RBD represents a more direct way to obtain a real measurement of decay. However, wood is characterized by an important scattering of data, and the average value of BD in fresh material cannot be really representative of the original BD of the sample. This implies that it is possible to obtain RBD values very close to 100%, or even higher, for samples whose level of decay is very low, or which were originally denser than usual. Yet, in most cases the observed decay is so high that RDB can be considered as an important reference parameter to be reliably considered.

As mentioned, the other characteristic usually considered in archaeological wood is the water content. In the case of waterlogged material this parameter is usually referred to as Maximum Water Content (MWC), and it is usually calculated according to the following expression:

$$MWC = 100 \cdot \frac{M_{WET} - M_{ANHYDR}}{M_{ANHYDR}}, [\%] \qquad (3)$$

where M_{WET} is the mass of the waterlogged sample. As for BD, MWC is very easy to calculate because only a precision scale and an oven are needed, whereas specimens can have any shape or dimension.

Due to the easiness of measurements, MWC is the most diffused parameter to evaluate the decay in waterlogged archaeological wood. In fact, the attack by bacteria and soft rot fungi causes in cell walls a microporosity increase. In wet environments, the wood substance digested by microorganisms is substituted by water [33, 34], hence the water content in waterlogged wood increases proportionally to its decay (the higher the MWC, the higher the decay). However, this parameter represents the state of preservation of samples only when it is really related to wood at its imbibition state.

Therefore, it is necessary to pay careful attention in the correct handling of samples from their collection to their measurement.

Usually, maintaining samples in water during this period ensures the fully waterlogged condition.

According to the wood species and its natural porosity, in sound wood MWC may vary between 90% - 100% on less porous species, up to 250% – 300% on the most porous timbers [35]. Higher values are usually found in archaeological material, and they indicate an attack by microorganisms.

In the worst cases, measurements as high as 1000% can be obtained [36].

It is worth mentioning that there is a very strict relationship between BD and MWC. This occurrence is imputable to the fact that fully waterlogged wood is constituted just by wood tissue and water (the inorganic substance due to the sediment, and present inside cells, can be often neglected). Such a relationship is given by the simple expression [31, 32]:

$$BD = \frac{100}{MWC + 67}, \text{ [g/cm}^3\text{]} \qquad (4)$$

Figure 6 shows an example of the behavior of MWC vs. BD for 130 archaeological samples. In such a case, the R^2 of the tendency curve is 0.99.

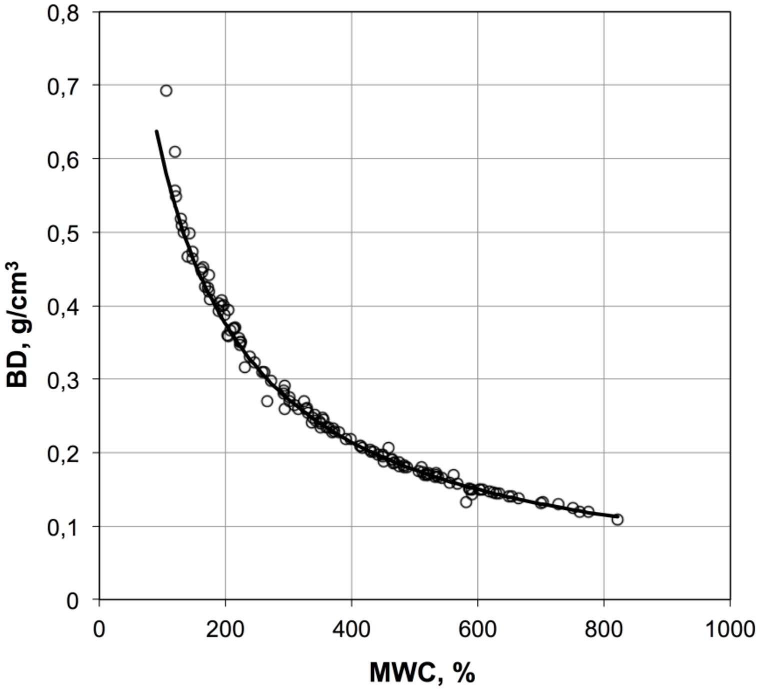


Figure 6. BD vs. MWC for 130 archaeological samples (one open circle per sample). The line represents the estimation of BD basing on Equation 4.

Conventional Chemical Analysis

Conventional chemical analyses so as to establish the chemical composition of archaeological woods, are usually carried out using specific standards, or well-established methodologies. Although these derive from procedures expressly designed for use in the pulp and paper industry, no practical alternatives exist and several authors currently use them in archaeology [6, 24, 33, 37, 38]. All wood samples undergo an initial phase of drying and subsequent milling. Usually, only the 40-60[1] mesh fraction is utilized for the analysis, as it is specified in the adopted standards. Moreover, moisture content at the beginning of analysis is calculated in order to be able to relate all the results to the anhydrous weight of wood. The following parameters are measured in succession:

- moisture content, by keeping the samples in an oven at 103°C for at least 24 hours and/or until a constant weight is reached;
- content of organic extractives (*OE*), according to Tappi T204-cm07 [39]. Often, a mixture of toluene and ethanol is used as extracting solvents instead of the

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[1] Occasionally, owing to the limited quantity of available material, a wider granulometric interval may be used.

recommended standard mixture of benzene and ethanol, due to health and safety reasons;

- content of aqueous extractives (*AE*), carried out on the previously extracted meal by using deionized water. This procedure of extractions in succession is also recommended for the subsequent evaluation of lignin;
- lignin amount (*L*), measured on the extracted meal according to the Klason's (or acid) method, Tappi T222-om02 [40]. Basically, this involves treating the extracted meal with sulphuric acid, firstly in a concentrated solution at room temperature and subsequently in a diluted solution at boiling temperature;
- ash content (*A*), according to Tappi T211-om02 [41], which provides the air calcination of wood samples at 550°C.

The remaining part of the wood meal constitutes the holocellulose [42]. This fraction can be either evaluated arithmetically or measured directly. The arithmetic evaluation is carried out by calculating the difference with the sum of all the other chemical components (considered as 100% in the original amount of wood meal) according to the following equation:

$$H = 100 - (L + OE + AE + A), \text{ (all values in \%)}. \tag{5}$$

In this expression, the generic parameter P (that is: L, OE, AE, A) is given by:

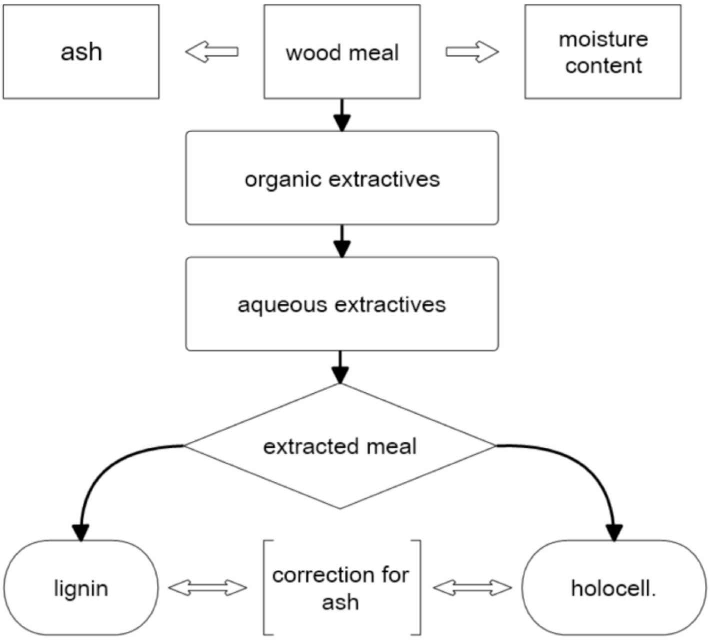
$$P = \frac{M_P}{M_{ANHYDR}}, [\%] \tag{6}$$

where M_P is the mass of the considered parameter and M_{ANHYDR} the mass of the anhydrous wood sample. It is also possible to directly measure the holocellulose amount, for example by using the method of Norman and Jenkins [43]. This method involves subjecting the extracted wood meal to an alternating succession of repeated treatments with acidified sodium hypochlorite and boiling sodium sulphite, until the red color caused by the occurrence of the Mäule reaction disappears. However, it was shown previously that the method underestimates the real quantity of holocellulose [28]. The sequence of analyses making up the whole procedure is shown in Figure 7 for the sake of clarity. In addition to these direct determinations, also some derived parameters are usually considered very helpful in the evaluation of the archaeological wood decay. More specifically, these derived parameters are:

- the H/L ratio, that is the ratio between the values of holocellulose and lignin obtained from direct measurements. This parameter is very helpful, because it gives a direct measurement of the relative decrease of holocellulose compared to lignin. In fact, as already mentioned, decay processes in waterlogged archaeological wood induce the polysaccharide fraction depletion (both hemicelluloses and cellulose), whereas lignin is generally considered unchanged. Therefore, the decrease of H/L indicates an increasing level of decay;

- if the H/L ratio for archaeological sample is compared to the analogous value for fresh wood of the same species, the Holocellulose-to-Lignin-Relative-Ratio (HLRR) can be calculated as follows:

$$HLRR = \frac{\left(\frac{H}{L}\right)_{sample}}{\left(\frac{H}{L}\right)_{fresh\,wood}}, [\%] \quad (7)$$



Adapted from [28].

Figure 7. Scheme of the sequence of analyses used in the assessment of the chemical composition of waterlogged wood samples. Samples are milled dry.

In this evaluation, the chemical composition of recent wood must be evaluated with the same procedures used for the archaeological samples, in order to improve the reliability and the effective comparison of data.

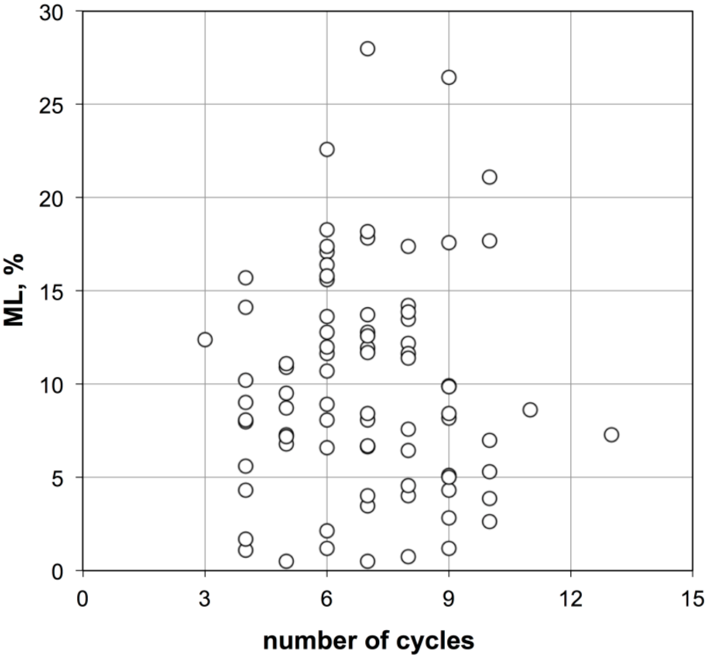
As mentioned, the reported procedures have been set-up for use in the pulp and paper industry, hence it could be questioned that the results obtained using these methods are dependent on the extent of material decay. In fact, the presence in wood cell walls of components that were chemically modified during the decay process could imply a need for use of specifically developed reagents and/or methodologies, because the repeated treatments provided in those procedures could further damage the decayed wooden tissue, hence causing additional loss of material.

On the other hand, if the damage were significant, increased inaccuracy of measurements would be observed as a consequence of the greater number of repetitions needed for the execution of the procedures, that is a direct relationship between the number of treatment cycles and the loss of wood mass should be observed.

However, a validation process carried out previously for use on archaeological material on a large-scale basis showed that this occurrence was not an issue [28]. In fact, if the eventual mass loss is expressed as:

$$ML = 100\% - (\text{total \% weight of the components measured}), [\%] \quad (8)$$

where ML is the difference between the "target value" of 100% and the sum of the other components (all of which were directly measured), the results as reported in Figure 8 are obtained (a lower number of samples compared to those shown in [28] is reported here).



Adapted from [28].

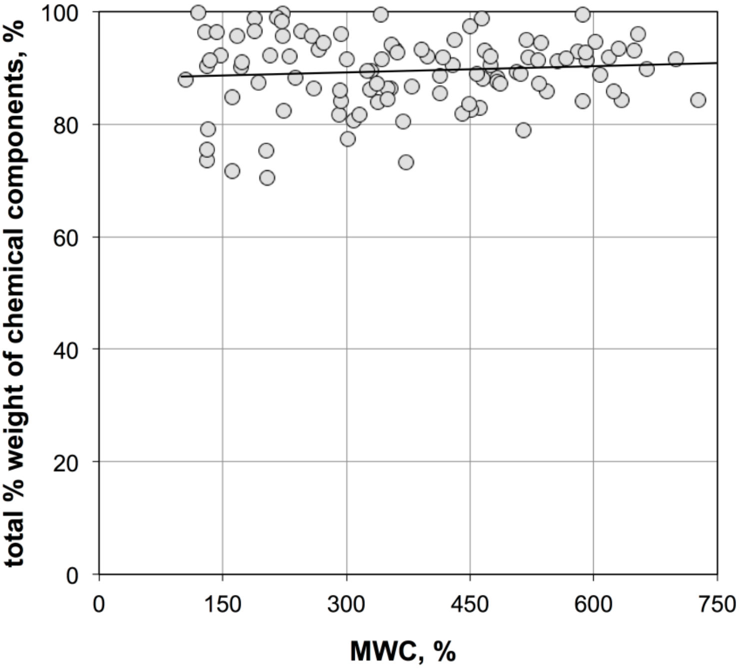
Figure 8. Difference with respect to the total of 100% for the sum of all the chemical components of wood (ML, Equation 8) versus the number of iteration cycles employed during the procedure for the assessment of holocellulose. Each open circle represents a sample.

It is clear that there was no relationship between ML and the number of cycles executed, even when an elevated number of cycles were performed in the assessment of holocellulose. For most of the analyses, the value of ML ranged from 5% to 15%, and about 6-8 cycles were needed to reach the end of the delignification process. Even when an elevated number of cycles was performed, the resulting differences were comparable with those observed following few reiterations.

Moreover, no relationship exists between the total % weight of the chemical wood components (all directly measured) and MWC. In fact, Figure 9 shows that the various experimental points are aligned on a straight line which is roughly parallel to the MWC-axis, thus enabling to conclude that results are not affected by the state of preservation of archaeological findings.

Other Methods of Quantitatively Estimating the Chemical Composition in Archaeological Wood

In addition to conventional chemical analyses, other techniques can be used to evaluate the chemical composition of decayed wood. These include several approaches, such as those making use of FT-IR spectroscopy, Py-GC/MS, GPC, TGA and NMR [44, 45]. However, most of these techniques are very complex both in their use and in the deep comprehension of the results obtained: often their interpretation strongly depends on the specific knowledge and expertise of the analyst. Instead, FT-IR spectroscopy is the most promising technique to be used as a routine method, because it is widespread, easy to manage, and not too difficult to interpret.



Adapted from [28].

Figure 9. Total % weight of chemical components of wood versus the MWC parameter. Each gray-filled circle represents a sample.

Although it is normally used in wood for qualitative analysis [46, 47], it can also be used for quantitative purposes if a preliminary calibration procedure is carried out. Nevertheless, while this procedure has been already executed in non-degraded wood [48, 49], only few attempts have been carried out so far to use FT-IR for quantitative evaluations in case of archaeological material [50, 51]. These attempts were often based on single or few bands used as a reference, by means of simple linear regression analysis. However, such a univariate analysis is quite inadequate to perform consistent evaluations, owing to the following reasons [46, 52]:

a) the high variability in terms of chemical structure of the decayed fossil material;
b) the presence of a considerable amount of inorganic components in the waterlogged material, able to potentially disturb the interpretation of analyses;

c) the overlap of signals attributable to non-structural compounds, such as extractives, with the structural ones (namely lignin and holocellulose).

Instead, statistical multivariate analysis, making use of chemometric methods to ensure the validity of calibration procedures, can be considered an interesting and promising procedure to easily get quantitative and reliable data from FT-IR spectroscopy, both in the mid-IR and the near-IR regions. In non-degraded wood this approach allowed to obtain very good results, mainly if used together with Partial Least Square (PLS) analysis [49, 53, 54]. In this perspective, it is also advantageous to use the integrating sphere in the near-IR, and the Attenuated Total Reflectance (ATR) device in mid-IR spectroscopy, which evidences several advantages in comparison to the more traditional IR analysis making use of KBr pellets [55].

However, although this approach has huge potentiality, further work and investigation are necessary before it may be really helpful in the diagnostic process on waterlogged archaeological wood.

RESULTS AND DISCUSSION

The Importance of an Integrated Approach for the Correct Interpretation of Diagnostic Analyses

In the majority of cases the various diagnostic approaches give results in good agreement among each other. Recently, however, it was shown how, occasionally, some misleading results can be obtained in single diagnostic techniques, thus making it necessary to use an integrated approach in order to obtain a correct evaluation of the sample state of preservation [29]. It is worth reporting some of those examples.

The first concerns the case of one out of three Roman shipwrecks (Ship B) found close to the coast of Naples, during the excavation carried out in 2004 to extend the subway network [6]. The results concerning some of the samples analyzed for that ship are reported in Table 3.

Some noticeable contrasts between the results from the physical evaluations and the H/L ratio values can be noticed: samples NB6 (*Picea abies* Karst.) and NB9 (*Cupressus sempervirens* L.) showed low MWC values (below 200%), while their H/L ratios were among the lowest (0.3 and 0.7, respectively), thus evidencing an opposite trend.

This discrepancy was related to the high amount of ash. In fact, for sample NB9 an ash amount approximately of 70% was measured, and this apparently affected both the MWC and the BD values, which were based on gravimetric measurements. On the contrary, the H/L ratio was virtually unaffected by a high ash content, because both the lignin and the holocellulose were calculated on the basis of the effective wood mass (the amount of ash was excluded from the sample weight).

Table 3. Main physical and chemical results of some selected samples of various excavations.

Sample	**Excavation**	**Wood Species**	**BD ($g \cdot cm^{-3}$)**	**RBD (%)**	**MWC (%)**	**Lignin (%)**	**H/L**	**Ash (%)**
NB6	Naples	*Picea abies*	0.41	107	194	62	0.3	9.7
NB7	Naples	*Cupressus sempervirens*	0.52	100	129	37	1.4	3.4
NB8	Naples	*Cupressus sempervirens*	0.31	60	258	39	1.2	2.9
NB9	Naples	*Cupressus sempervirens*	0.61	117	120	43	0.7	68.9
NB11	Naples	*Cupressus sempervirens*	0.37	70	208	36	1.2	13.7
V-L	Venice	*Alnus sp.p.*	0.17	42.3	519	51	0.6	3.0
V-M	Venice	*Alnus sp.p.*	0.36	90	204	70	0.4	4.0
V-N	Venice	*Alnus sp.p.*	0.15	37.5	603	65	0.4	2.9
V-P	Venice	*Alnus sp.p.*	0.13	33.1	703	54	0.7	5.4
PA-A1	Pisa	*Quercus sp.p.*	0.31	46	261	64	0.1	n.r.
PA-A3	Pisa	*Quercus sp.p.*	0.18	26	506	69	0.1	n.r.
PA-A6	Pisa	*Quercus sp.p.*	0.14	21	633	51	0.1	n.r.

One to three replicates per sample were carried out, depending on the availability of material.

Lignin values and H/L ratio refer to the effective mass of wood (i.e. by excluding ash from the sample weight)

Results have been taken from [29] (‘n.r.’ means not reported).

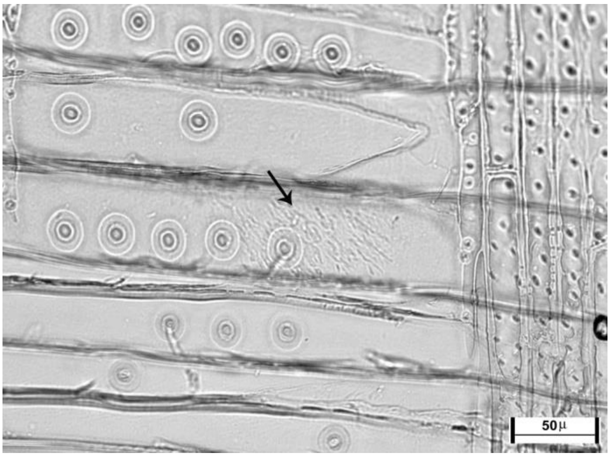


Figure 10. Light microscope image of the radial section of a larch sample taken from one of the analyzed foundation piles in Venice. Groove-like erosion into cell walls, a typical feature of attack by erosion bacteria, was evident (this was indicated by the arrow in the figure).

Another example is related to samples obtained from the foundation piles of some historic buildings (XIV-XVII AD) in Venice [25, 26]. The decay in the wood appeared to be extensive, mainly on the piles made of alder (*Alnus glutinosa* (L.) Gaert.), mostly due to erosion bacteria (Figure 10). The results of chemical and physical analyses on several piles are also shown in Table 3 (they can be compared with the analogous values for non-decayed wood reported in Table 4).

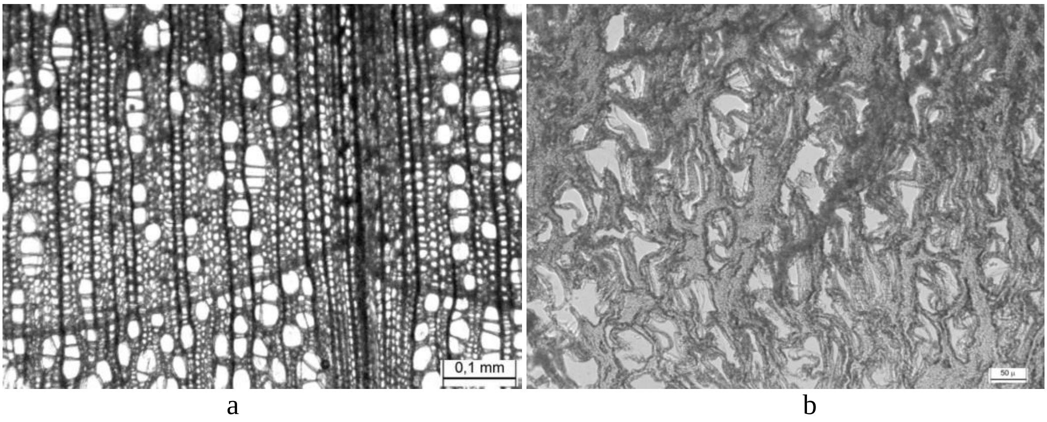
However, an anomalous result was obtained in the case of the V-M sample. From a simple consultation of the physical parameters, it is clear that this sample was seemingly in better conditions than the other alder samples: the MWC was only 204%, and the RBD was approximately 90%.

Table 4. Reference values for non-degraded wood of the same species also reported in Table 3. These values can be used as a comparison for the decayed wood

Wood Species	Lignin (%)	H/L	BD ($g \cdot cm^{-3}$)
Alnus sp.p.	23	3.2	0.40
Cupressus sempervirens	32	2.0	0.52
Picea abies	28	2.4	0.38
Quercus sp.p.	20	3.0	0.67

In contrast, the chemical parameters showed a high level of decay: the value of the H/L ratio was the lowest (0.4), and lignin constituted 70% of the wood tissue (this value was 23% for non-degraded alder), thus signifying that most of the polysaccharides had been lost. On the other hand, the amount of ash could not justify the diagnostic differences between the MWC and the H/L ratio, because this amount was only 4%.

It was possible to explain said incongruence after the micromorphological analysis, which showed that the V-M sample had collapsed. This fact apparently indicated that there was less room for water in this particular sample (Figure 11).



a b

Figure 11. Light microscope pictures of the transverse sections of fresh, non-degraded, alder (a) in comparison with the V-M sample (b). Diffused collapses are well evident in (b).

A third example, also reported in [29], concerns a sample coming from the excavation where the ancient ships of Pisa were found [1, 24]. Sample PA-A1 showed a low MWC value (261%) that did not correspond to the very low H/L (0.1) and RBD (46%) values (Table 3). The micromorphological observation showed a partial collapse involving fibers and radial parenchyma, but excluding the large vessels of the oak sample.

In the latter case, the contrast between the values measured in each single analysis was not as apparent as it was in previous cases.

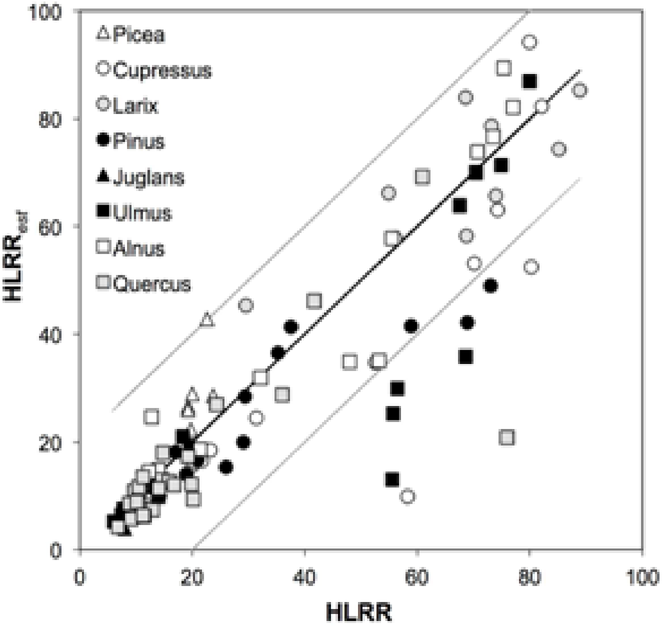
Therefore, this example also shows how insidious it can be to place excessive confidence on one single type of evaluation.

However, as proposed previously, there is a method to identify eventual outliers when both physical and chemical parameters are measured on the same sample [30]. This method is based on the estimation of the parameter HLRR, on the basis of both physical and chemical evaluations through the following expression:

$$HLRR_{est} \cong \left(\frac{H}{H_{NDW}} \right) \cdot RBD \quad , [\%] \qquad (9)$$

where HLRR$_{est}$ represents the estimated value of the parameter HLRR and H_{NDW} the holocellulose value of non-degraded material of the same wood species. As evident, by comparing HLRR$_{est}$ with the experimental value of HLRR (obtained by means of chemical analysis, Equation 7) it is possible to evaluate the congruence of the data obtained, thus to detect possible anomalies.

The comparison of the data obtained in several tens of samples evidenced that most of the experimental values are within ±20% compared to the expected one (a lower number of samples than those reported in [30] is shown in Figure 12).



Adapted from [30].

Figure 12. Plot of the parameter HLRR$_{est}$ (Equation 9) vs. HLRR calculated on the basis of experimental data (Equation 7). The black line represents the straight-line y = x (that is, HLRR$_{est}$ = HLRR), whereas the two other straight-lines are: y = x + 20% and y = x – 20%. Each symbol represents a sample.

How Results Can Be Used to Identify Degradation Trends in Waterlogged Archaeological Wood

Values obtained directly from both physical and chemical characterizations of wood samples can be hardly used to identify species-related degradation patterns in waterlogged archaeological wood. This because it is unreliable to compare the following among each other:

a) samples of different species;
b) samples in different states of preservation.

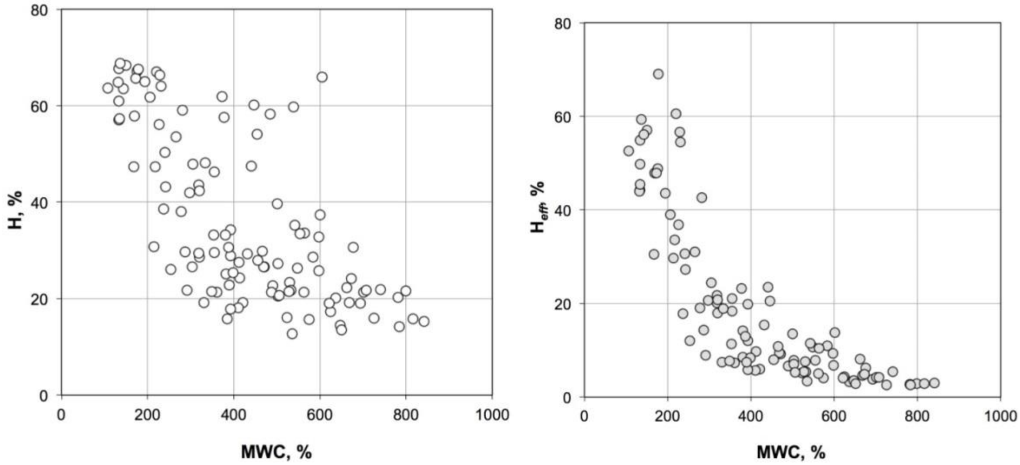
The reason of such occurrence can be better explained by the following examples: if a value of, e.g., 0.30 g/cm^3 is found for the Basic density of a sample, the same value evidences different states of preservation depending on the wood species: in the case of spruce (whose Basic density at the not-decayed state is 0.38 g/cm^3, Table 4), the sample would be in good conditions, whereas in the case of oak (whose Basic density at the not-decayed state is 0.67 g/cm^3, Table 4) it would be in quite bad conditions.

Likewise, if a value of, e.g., 50% is obtained for residual lignin in one sample, it simply evidences the relative enrichment in lignin in that sample (amount of lignin in non-decayed material is 20-30%, Table 4), but no information about the possible real decrease (or decomposition) in lignin is obtained. The best way to proceed is to combine raw parameters in order to obtain more representative information on the actual state of preservation of samples. If chemical raw parameters, P, obtained for a sample are multiplied by Residual basic densities (RBD) measured on the same sample, the effective value of that parameter, Peff, can be obtained:

$$P_{eff} = P \cdot RBD \text{, [\%]} \qquad (10)$$

It can be easily shown that the advantage of using effective parameters consists in the fact that chemical measurements can be referred to the presumed original mass of wood (i.e., before burial and therefore before any process of decay) rather than the mass of degraded, ash-rich, archaeological material [30]. Therefore, values of various archaeological samples are related to the same reference calculation basis as for non-degraded wood of the same species.

The practical advantage of using the effective parameters instead of the raw ones is well evident in Figure 13, which shows the comparison between graph H vs. MWC (a) and H_{eff} vs. MWC (b) for the same samples. It can be seen how the parameter H_{eff} is appreciably less scattered compared to H, which makes it easier to compare the values and to visually evidence the presence of possible trends. In such way, effective parameters may be used to evaluate the real effect of decay on the structural chemical components of cell walls in waterlogged archaeological wood.

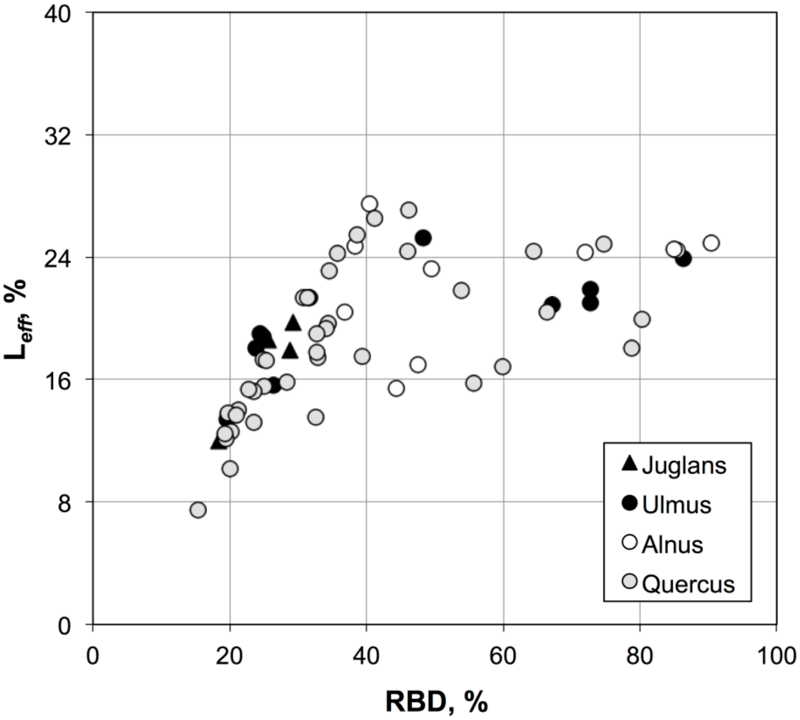


a b

Figure 13. Behavior of the raw holocellulose amount, H, vs. the MWC (a), and between the effective holocellulose, H_{eff}, vs. the MWC (b), in both cases for the same samples. It is apparent how values of H_{eff} were appreciably less scattered than H (graph (b) was adapted from [30]). Each circle represents a sample.

In the case of lignin, Figure 14 shows how L_{eff} appreciably decreases by increasing the decay in wood (the lower the RBD, the more decayed is the wood). Although only hardwoods are shown in Figure 14, the same behavior also applies to conifers [30]. The rate of L_{eff} decrease is quite low, or even absent, for high values of RBD (i.e., for wood in good conditions), whereas it is high when values of RBD are low (i.e., when wood is in bad conditions). If a limit has to be given, as evident in Figure 14, this limit should be comprised between 30% and 40%. Above said limit, the rate of lignin depletion becomes significant [30]. On the other hand, this same evidence has been already revealed by other (more sophisticated and less widespread, and also of non-immediate interpretation) techniques: Colombini et al. [44] found (by using Py-GC/MS, GPC and NMR) that lignin was subjected to partial depolymerisation, with the cleavage of ether intermonomeric bonds and the production of a higher concentration of free phenol groups in highly decayed archaeological samples of beech (*Fagus sylvatica*), elm (*Ulmus* sp.p.) and maritime pine (*Pinus pinaster*), whose residual lignin amount ranged from 68% to 77.5%. Analogously, Alesiani et al. [56] evidenced, by using CPMAS NMR analysis, a reduction of signals belonging to aromatic rings and side chains carbon of the lignin of waterlogged archaeological fir (*Abies alba)*. The depletion of lignin, although reasonable for highly decayed material, goes against the fact commonly thought that the amount of lignin is unchanged in waterlogged archaeological material [33], owing to the fact that this polymer is generally considered stable in waterlogged conditions.

As for the polysaccharide fraction (holocellulose), Figure 13 already showed how H_{eff} decreases by increasing MWC (that is, by increasing the decay in wood). If only conifer samples are plotted, it is clear that the observed trend is quite uniform (Figure 15), whereas the same does not apply for hardwoods: alder samples and oak/elm samples are aligned on different curves (Figure 16), the latter having a more asymptotic trend. By comparing Figure 15 and Figure 16, it can be observed how decay in conifers is slower than in both oak and elm (the same asymptotic value of 3-5% is reached more quickly).



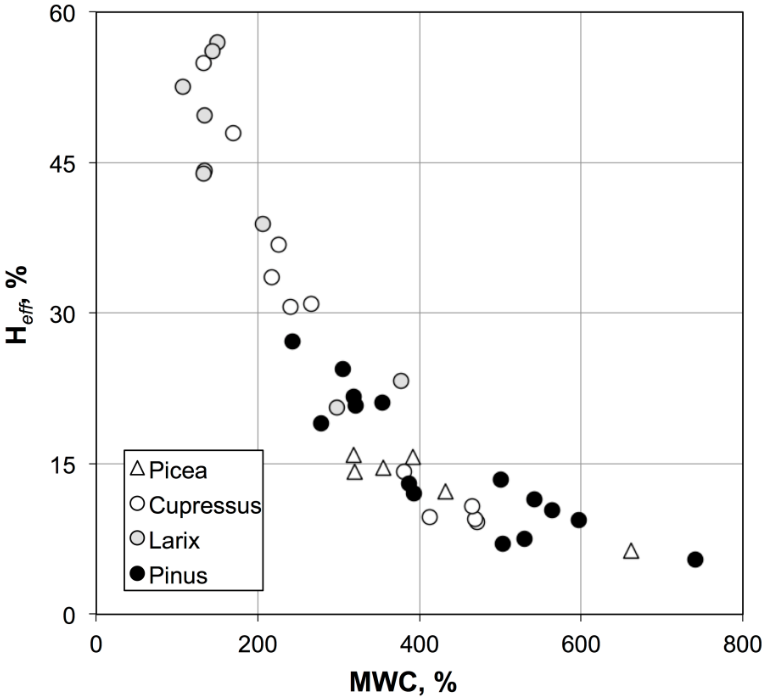
Adapted from [30].

Figure 14. Relationship between the effective lignin amount, L_{eff}, and the Residual Basic Density (RBD) in the case of hardwood samples. Each symbol represents a sample.

This behavior is imputable to a generic better resistance to decay of conifer holocellulose, owing to both chemical and anatomical reasons. In fact, hemicelluloses in conifers are richer in galactoglucomannans, which are mainly constituted by galactose, glucose and mannose [42].

These sugars are more resistant to biotic decay compared to xylose and acetyls, which constitute glucuronoxylans, the main components of hardwoods' hemicelluloses [33, 57]. Moreover, the protective action of lignin is less effective in case of hardwoods because of its composition, including syringyl groups in addition to the guaiacyl ones. Syringyl groups are commonly considered more easily attackable by biotic agents [44, 56, 58]. However, differences can be observed if different hardwoods are compared: for instance, decay in alder is slower than in oak/elm (Figure 16). From the chemical point of view, the structural biopolymers (lignin, hemicelluloses and cellulose) of both oak and alder do not differ appreciably in composition [42]. On the other hand, oak is richer than alder in extractives [59, 60] and is generally considered more durable, also in the marine environment [61].

Therefore, the better resistance to decay observed for alder can be imputed, by exclusion, to anatomical characteristics: alder is a diffuse-porous wood species, whereas oak is ring-porous, with bigger vessels, and very big rays [62], which apparently constitute a preferential way of access to bacteria.



Adapted from [30].

Figure 15. Relationship between H_{eff} and MWC for conifer samples. Each symbol represents a sample.

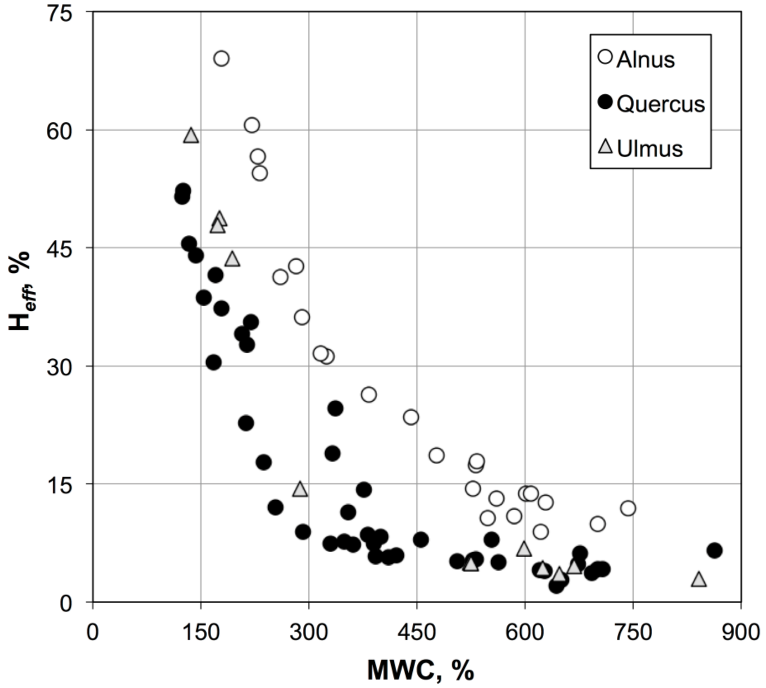


Figure 16. Relationship between H_{eff} and MWC for alder (of 4 different excavations), oak (8 excavations) and elm (4 excavations). Each symbol represents a sample.

Examples of How Diagnosis Is Useful for the Conservation of Waterlogged Archaeological Wood

A correct diagnostic evaluation may give important suggestions for a proper approach toward the conservation of waterlogged archaeological wood. The best way to proceed is presenting some useful examples in which said aid has been practical in real cases in which an intervention plan had to be setup.

Recently, some wonderful artefacts (several pieces of valued furniture) made of wood and coated by carved ivory layers were discovered at Villa dei Papiri, in Herculaneum. It was an exceptional discovery because of the quality of the materials and the complexity of the decorations full of Dionysiac symbols and figures [63]. The ancient town of Herculaneum was buried by high-temperature volcanic streams, which in general charred (entirely or partially) the organic material. However, apparently, in the above mentioned case anoxic conditions quickly arose, which preserved wood from burning or becoming destroyed. Perhaps, the same ivory layers played a role.

Actually, both the wood frame and the ivory layers were found in an apparently excellent state of preservation, although they both became very browned [64].

The diagnostic analysis carried out on the wood frames enabled to establish that all analyzed objects were made of ash (*Fraxinus excelsior* L.), which however had lost its original appearance (fresh ash generally has a light, whitish, color). Moreover, while the external visual aspect of the objects was very good, analyses revealed that the material constituting the wood frames was limitedly decayed, mainly in the internal parts (the outer layers were more decayed): the H/L ratio was close to 1, and MWC values allowed classifying the elements in classes II and III according to the criterion proposed in [65], briefly reported further on.

Based on the results of the diagnostic evaluation, it was decided to start a conservation project in which probe samples decayed by brown rot were used. In fact, this kind of fungi induces in wood the depletion of the polysaccharide fraction, whereas lignin is almost unaltered (at least, quantitatively). This occurrence causes a decrease in the H/L ratio and a corresponding decrease of mass (that is, in practice, the decrease of RBD), thus inducing a decay similar to that caused by bacterial attacks in waterlogged archaeological wood. The probe samples were obtained by inducing the fungi growth in laboratory starting from non-degraded ash samples, and by stopping it when both mass loss and chemical parameters similar to those of archaeological findings were obtained. Followingly, samples were filled with water in autoclave in order to simulate the waterlogged conditions, and a series of treatments were applied. The best combination selected on that basis was also applied to a small archaeological ivory-layered object, and the results obtained with probe specimens were also confirmed in that archaeological sample (unpublished data). Then, the selected procedure was extended to the treatment of all archaeological objects.

An additional example is the one related to some timber elements (as large as 30 by 20 cm^2 in section, and 6-7 m in length) recently found in an excavation in Italy. These elements were of fir (*Abies alba* L.) and constituted the roofing of a Roman house close to Naples. Diagnostic analyses evidenced a strong gradient in decay: the H/L ratio was higher than 1.7 in the internal portions, whereas it dropped to about 0.5 in the outer layers. In the same way, RBD passed from an average value of 80-90% to 40%, respectively. This huge variation in the state of preservation of the material suggested a conservation treatment in which a small molecule is used, thus favoring its penetration also in the more sound part of the timber without excessively slowing down the whole impregnation process. More specifically, in said case the suggested consolidant was a melamine resin, considering that melamine is one of the smallest molecules among those commercially available able to consolidate waterlogged archaeological wood [66]. Furthermore, melamine-treated wood is lightweight, which is an important characteristic to be considered in said case, considering the size of the elements to be treated. On the other hand, the main disadvantage of this consolidant, that is the induced discoloration of treated samples which become lighter in color [67], is not an actual drawback to be overcome, also considering that fir wood is usually a quite whitish material.

As evidenced by the examples reported above, a correct diagnostic evaluation helps not only in understanding the new properties of decayed wood and in identifying its degradation models, but also in setting up the more appropriate approach for the possible conservation of the objects to be treated. Within this perspective, it is highly interesting to arrive at a well-assessed classification of the waterlogged archaeological material according to its true level of decay, thus enabling to plan a suitable intervention on the basis of reliable knowledge of the characteristics of the material to be conserved. Some attempts at classifying waterlogged archaeological wood have been already proposed [65, 68]. These approaches were based on measurements of MWC, or on the execution of a pin test on the wood surface. Three classes have been distinguished according to wood decay: “Class I, the most deteriorated wood, contains over 400% water and virtually no core; Class II is 185%-400% water with a core present; and Class III with less than 185% of water and only surface degraded” [69]. However, on one hand the considerations and the examples presented here well evidence how relying on only one diagnostic parameter can be misleading not only for the possible errors associated to a single measurement, but also because a same MWC can be related to different degrees of decay, for instance depending on the wood species taken into consideration. On the other hand, MWC is a too rough parameter because it can represent the state of preservation only indirectly, that is as an indirect evaluation of residual porosity. Such parameter can be measured only when wood is in waterlogged conditions; otherwise, it is useless if the conditions of the object had to be verified sometime after its treatment. It is possible to find some examples in which this need has occurred several years after conservation such as the case of the Vasa wreck and the Viking Age objects exhibited at the Museum of Cultural History in Oslo [70, 71].

Currently, archaeological artefacts are always treated before being put on display in a museum [72–74]. A correct classification can enable to identify the best way to proceed with treatments (from the selection of the consolidant, also including its proper molecular weight, to the duration of the impregnation), and even, in perspective, to tailor the treatment method on the basis of this classification. In selected cases, it can even be possible to avoid the phase of impregnation with consolidants, at least when the normal checks that develop in wood after drying can be tolerated (for instance, when objects do not show colors or woodworking signs on their surfaces).

CONCLUSION

Waterlogged archaeological wood findings have become more and more important over the last decades, due to excavations carried out all over the world which have enabled to bring to light valuable examples of artefacts.

In most cases, the aesthetical aspect of the artefacts, which often is beautiful, does not correspond to the state of preservation of their constituting material. Waterlogged archaeological wood artefatcs are in fact fragile, and their manipulation and management from the very starting point of their retrieval to their conservation are crucial for the future fruition of the findings.

Starting from the description of the preliminary phases of the conservation process, this chapter has described the whole process with the aim to understand the material state of preservation.

The diagnosis phase is central for a correct and informed design of the conservation process, also including the consolidation treatment. However, diagnostic results have to be consistent in order to be useful. The three-step methodology (based on micromorphological, physical, and chemical analyses) described herein enables to reach a deep and reliable knowledge of the real conditions of the material.

In this perspective, some misleading results obtained without cross checking the single (i.e., anatomical, physical and chemical) results are described.

Moreover, this chapter showed how a consistent diagnostic evaluation helps in understanding the new properties of decayed wood and, in perspective, in classifying material according to its true level of decay.

Finally, some examples given exemplified the possible use of diagnostic results for the purpose of conservation.

It has been highlighted how a correct diagnosis can help conservators not only to constitute reference data useful for controlling the efficacy of the consolidation intervention just after its completion, but also to verify the evolution in time of the conditions encountered by the new composite constituted by the archaeological wood and the consolidating product.

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Chapter 8

ADVANCED NUCLEAR MAGNETIC RESONANCE METHODOLOGIES IN CULTURAL HERITAGE

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ABSTRACT

In recent years nuclear magnetic resonance (NMR) techniques have been increasingly applied to investigate, characterize and monitor objects of interest for cultural heritage. These techniques are considered non-destructive because the sample can be fully recovered after performing the analysis. NMR is a very powerful tool in the chemical characterization of materials; it allows light to be shed on pictorial techniques used by artists, and can provide knowledge about materials constituting artifacts. High resolution NMR spectra are the fingerprint of organic materials, such as paper, wood, textiles, parchments, adhesives, varnishes, binders, natural and synthetic resins. As a consequence, knowledge of the causes of degradation of artifacts may also be obtained by studying the chemical-physical transformation and structural modifications caused by ageing. NMR also provides an insight into the molecular structure of inorganic materials, such as pottery, stones and glass. NMR is not confined to a few specific applications, but can be successfully extended to a wide range of cultural heritage issues.

A breakthrough has surely been the recent development of portable NMR instruments. These devices can be applied directly to large objects such as *frescoes*, monuments, and buildings in general, preserving the integrity and dimension of the object under investigation. NMR parameters are important to establish the state of degradation of objects, to evaluate the performance of consolidation and water repellent treatments on porous materials, to monitor the detachment of painted layers from supports and to quantitatively map dampness in wall paintings. A further development of portable NMR devices is the availability of sensors to produce NMR stratigraphy with micrometric spatial resolution for investigating the layer structure of paintings, for obtaining information on the working practice and techniques of the artist, and for helping in selecting correct and suitable conservation and restoration procedures.

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In this chapter case studies will be reported to show how NMR spectroscopy, NMR relaxometry, and portable NMR can play an important role in the field of cultural heritage.

Keywords: NMR, non-invasive characterization, portable NMR, aging detection, moisture detection, protective, consolidation, archeological artifact, painting, stone, paper, wood

INTRODUCTION

Although Nuclear Magnetic Resonance (NMR) [1] has been a powerful tool in many fields of research for many years, its application to cultural heritage [2-5] is rather recent. One reason is that in its initial decades of existence, NMR was mainly a tool for the analysis of samples in the liquid phase, whereas many materials of interest for cultural heritage cannot be solubilised without definitely changing or even destroying their molecular structure. Nowadays, cryoprobes and microprobes [6,7] enable NMR analysis down to the μg scale, making NMR spectroscopy in solution a suitable technique for the analysis of soluble materials of interest for cultural heritage. Such materials are usually only available in tiny amounts. A typical application is the use of NMR to identify soluble organic residues in ancient artifacts [8].

With the development of high resolution solid state NMR techniques [9,10], NMR has become a powerful tool for characterizing solid materials. The amount of material needed for solid state analysis has progressively decreased from 400-500 mg to a few mg. Almost any element of the periodic table may be analyzed in the liquid or solid state, the only limitation being natural isotopic abundance and sensitivity to the NMR experiment.

Figure 1a shows a superconducting magnet operating at the proton frequency of 600.13 MHz. It consists of an outer stainless steel Dewar flask containing liquid nitrogen and an inner Dewar flask containing the superconducting coil immersed in liquid helium. The very low temperature must always be maintained, because at higher temperatures the coil is no longer superconducting. The sample to be investigated must be placed in a sample holder (a glass tube in the case of analysis in solution or a rotor in the case of solid state analysis) and placed in the magnet. The simplest NMR experiment consists of applying an rf pulse with a duration of few microseconds to the spin system. As the rf pulse is switched off, the nuclei relax back to equilibrium generating an interferogram (amplitude vs. time) known as free induction decay (FID). Signals in the time domain are converted to signals in the frequency domain (amplitude vs frequency) by applying a Fourier transformation to the FID. After this transformation, a spectrum is obtained with peaks of appropriate width and frequency (chemical shift). Nevertheless, we can also intervene directly on the FID [11] (NMR relaxometry or pulsed low resolution NMR). Figure 1b shows a photo of a magnet that is part of an NMR relaxometer used to measure FID and relaxation times in the frequency range 10 - 80 MHz.

Many materials of interest for cultural heritage may be considered to some extent porous, such as porous stones, plaster, mortar, wood, paper, wall painting, fired clay. Many properties of these materials are related to their porosity, and a number of different degradation processes affect the porous structure to different extents. Based on the measurement of relaxation times and the diffusion coefficient of water through the porous system, NMR can probe porous structure [12]. In fact, relaxation times of fluids confined in porous media are strictly related to structural geometry, as water in small pores relaxes rapidly, whereas water in large pores relaxes more slowly. Relaxation time distributions are linked to pore size distribution. In many cases the properties of porous systems may be resolved spatially by magnetic resonance imaging (MRI) [13].

There is growing understanding that monitoring and diagnosis of artifacts are mandatory to prevent or at least delay their degradation. Because the number and amount of samples obtained from precious artifacts to be analyzed must be reduced to a minimum, multi-analytical approaches where micro-destructive, non-destructive, and possibly non-invasive techniques are combined, are necessary. In this context, a breakthrough for application of NMR to cultural heritage has been the development of unilateral NMR sensors, which allow one to study arbitrarily sized objects non-invasively, combining open magnets and surface rf coils to generate a magnetic field external to the sensor and inside the object under investigation [14,15]. Although the magnetic field of these sensors is inhomogeneous, it is possible to measure NMR parameters, such as proton density and relaxation times, and even to collect correlation maps of unmovable and precious artifacts and monuments belonging to the cultural heritage. Because the NMR signal decays quickly in the inhomogeneous field generated by portable devices, the signal must be recovered stroboscopically [16]. As a consequence, the signal intensity is actually the intensity of the signal resulting after applying the Hahn echo pulse sequence. The inhomogeneous field is a further source of relaxation which makes the transverse relaxation time shorter than that measured in a homogeneous field [17].

To obtain different depths of measurement inside objects, the tuning frequency of these devices must usually be electronically switched. To do this, different probeheads, each tuned to the proper frequency, are used. Figure 1c shows a 2 kg palm-size NMR sensor. It consists of a U-shaped permanent magnet obtained using two anti-parallel permanent magnets mounted on an iron yoke with the rf coil positioned in the gap. The magnetic field is external to the device, enabling large objects to be studied without any sampling.

A recent development of single-sided NMR devices are sensors that can scan depths up to 2.5 cm, producing depth profiles with micrometric spatial resolution. This sensor generates a magnetic field with a uniform gradient to resolve the near surface structure of arbitrarily large samples [18]. To improve gradient uniformity, the device was optimized to work at a fixed depth from the sensor, where high depth resolution can be achieved. This strategy involves varying the relative position of the excited slice inside the sample, and is achieved by displacing the sensor using a high-precision lift that repositions the sensor with respect to the sample. Figure 1d shows such a device, consisting of a permanent magnet mounted on a precision lift. Application of these sensors to articles of cultural heritage has already opened a number of new possibilities [19-24].

In this chapter we report various case studies demonstrating that NMR is not confined to a few specific applications but can be successfully extended to a wide range of different issues regarding cultural heritage. NMR is a powerful tool for characterization of materials, providing insights into the techniques and materials used by artists. It can also be used to discover the causes of degradation of artifacts by studying chemical-physical transformations and structural modifications caused by ageing. NMR studies may also help in planning restoration.

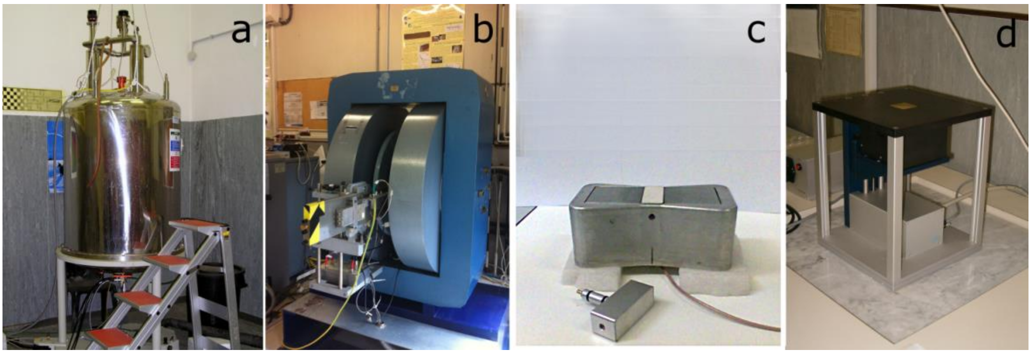

Figure 1. a) A superconducting magnet operating at a proton frequency of 600.13 MHz. b) An electromagnet for pulsed low resolution NMR. c) Portable single-sided NMR sensor. d) NMR depth profile sensor with lift.

EXPERIMENTAL

Materials and Methods

Porous Stones

Calcarenite was treated with a commercial solution of dimethylsiloxane in white spirit. White spirit is a mixture of saturated aliphatic and alicyclic C7 to C12 hydrocarbons with a 25% maximum content of C7 to C12 alkyl aromatic hydrocarbons. The hydrophobic treatment was absorbed by capillarity, keeping the specimens in contact with the solution for 5, 600, and 1800 s, respectively. A Mascia limestone specimen was treated with a mixture of butyl methacrylate (BMA)/ethyl acrylate (EA) 75/25 wt % polymerized *in situ* in acetone solution (20% v/v). The experimental procedure consisted of three steps: i) The polymerizing system (monomer or monomer mixture, initiator, and solvent) was absorbed from the specimen by capillarity. Absorption was achieved by placing the sample on a thick layer of cotton soaked in the reaction solution. The operation was carried out for 4 h at 4°C, in the absence of light; ii) Polymerization was performed for 24 h at 30°C; iii) Traces of solvent and unreacted monomers, still present after the polymerization, were removed over several days by air evaporation.

Paper Coated with Waterborne Polyurethanes, Biodegraded by Enzyme Attack

Two commercial waterborne polyurethanes from ICAP SIRA S.p.A. (Italy) were used. A preliminary investigation established that polyurethane had to be applied by brushing, because this was the only way to check the amount of product applied to the sheet. The next step consisted in determining the best solution concentration to improve paper strength without altering its flexibility. All samples were treated with polyurethane before and after dilution with water. Each specimen was brushed with the solution on one side and dried in air. Coating regularity depended on the manner in which brushing was carried out. After treatment, the amount of applied polymer was about 10–12% without altering the typical appearance, handling, and flexibility of the paper. Paper sheets were cut into strips and washed twice in 20 mM Tris-maleate pH 6.0 buffer for 20 min at 37°C under gentle shaking to eliminate soluble sugars that could initially be released from the paper. Enzyme-degraded samples were prepared by incubating strips in 2 mL 20 mM Tris-maleate pH 6.0 buffer at 37°C under gentle shaking at 40 rpm with 200 μg mL^{-1} cellulosomes. Cellulosomes are large extracellular enzyme complexes that degrade cellulose, hemicellulose, and pectin; they are produced by anaerobic bacteria such as the mesophilic bacterium *C. cellulolyticum*. A negative control was prepared without any enzyme added.

Grafting Acrylic Polymers onto Oxidized Textiles

Photo-initiated grafting was carried out on artificially and naturally oxidized linen and cotton. Samples were swollen in deionized water for 24 h before the grafting reaction. The wet samples were placed in a quartz reaction vessel kept under vacuum for a short time. The liquid monomer was then loaded, vaporized, and diffused into the reactor. The monomer/cellulose ratio was varied between 1.5 and 3.3 mmol acrylate per gram of sample. Subsequently the whole unit was exposed at room temperature to UV radiation from a 400 W vapor lamp with a wavelength ranging from 180 nm to visible light, placed at a distance of 60 cm, so that no cooling system was required. Polymerization was stopped after 4 h. Samples containing grafted cellulose and ungrafted homopolymer were filtered and brought up to constant weight. A drawback of graft polymerization was the simultaneous and inevitable formation of the homopolymer, which was removed from the grafted material by extraction with acetone for 72 h at room temperature.

Samples for solid state high resolution NMR analysis were packed into 4 mm zirconia rotors with an available volume reduced to 25 or 12 μl, and sealed with Kel-F caps. Samples for pulsed low resolution NMR measurements were placed in standard 5 mm NMR tubes and sealed. In order to keep the sample within the NMR coil, the height of each sample was 0.4 cm. Measurements carried out with unilateral NMR sensors did not require any sampling.

^{13}C CPMAS NMR spectra were measured at 100.63 or 50.13 MHz, keeping the spin rate at 8 or 12 KHz. The contact time for cross-polarization was 1.5 ms and recycle delay was 3 s. Cross-polarization was carried out by applying the variable spin-lock sequence RAMP–CPMAS. The RAMP was applied on the ^{1}H channel, and during contact time RAMP amplitude was increased from 50 to 100% of its maximum value. Spectra acquired with a time domain of 1024 data points were zero filled and Fourier transformed with 4096 data points, applying exponential multiplication with 8 Hz line broadening. Chemical shifts were referenced externally to tetramethylsilane (TMS).

^{27}Al MAS NMR spectra were recorded at 52.15 MHz or 104.26 MHz with a pulse length of 2 μs and a recycle delay of 30 s (pottery) or 2 s (tuff). The spin rate was 13 KHz. Spectra were recorded with a time domain of 512 data points, zero filled and Fourier transformed with 2048 data points, applying exponential multiplication with 16 Hz line broadening. Chemical shifts were referenced externally to aluminum nitrate.

^{27}Al 3QMAS NMR spectra were recorded using a three-pulse sequence with zero quantum filter. In the 2D map, 64 regularly spaced increments were acquired in F1 frequency domain and the time domain in F2 was set to 512 data points.

^{29}Si MAS spectra were recorded at 39.76 MHz or 79.49 MHz with a pulse width of 3.5 μs and recycle delay of 60 s. The spin rate was 12 KHz. Chemical shifts were referenced externally to tetramethylsilane (TMS).

^{23}Na MAS NMR spectra were recorded at 105.88 MHz. Pulse width was 3.5 μs and 512 data points were collected with a recycle delay of 5 s. The spin rate was 12 KHz. Spectra were recorded with a time domain of 512 data points, zero filled and Fourier transformed with 2048 data points, applying exponential multiplication with 16 Hz line broadening. Chemical shifts were referenced externally to 0.1 M NaCl H_2O solution.

^{1}H pulsed low resolution NMR measurements in homogeneous field

Free induction decays (FIDs) were recorded with a time domain of 2048 data points and a $\pi/2$ pulse of 3.8 μs. Longitudinal relaxation times (T_1) were measured with the Aperiodic Saturation Recovery sequence [11]. This sequence consists of a train of $\pi/2$ pulses (15 in our case) spaced out in an aperiodic way by linearly decreasing the interval.

Transverse relaxation times (T_2) in a homogeneous field were measured using the CPMG pulse sequence [11] with an echo time of 40 μs. Depending on the sample, 512, 1024 or 2048 echoes were recorded.

Measurements with Portable NMR

Longitudinal relaxation times were measured with the Aperiodic Saturation Recovery sequence and a logarithmic increment. Transverse relaxation times were measured with the CPMG sequence, using the shortest possible echo time. Both sequences were adapted to be applied in a inhomogeneous field.

Depth Profiles

Depending on the depth required**,** depth profiles were obtained with an echo time ranging between 57 and 94 μs and a spatial resolution between 20 and 57 μm. Profiles were acquired by repositioning the single-sided sensor in micrometric steps to cover the desired spatial range.

Instruments

Solid-state high resolution NMR spectra were recorded with a Bruker Avance III spectrometer operating at a proton frequency of 400.13 MHz, or with a Bruker AMX spectrometer operating at a proton frequency of 200.13 MHz.

Pulsed low resolution ^{1}H NMR measurements in a homogeneous field were carried out at 20 or 81 MHz on a *Spinmaster* spectrometer (Stelar Srl, Mede, Pavia, Italy).

Measurements in an inhomogeneous field with inhomogeneous strong field gradient were carried out with a unilateral NMR instrument from Bruker BioSpin. The magnetic field penetrating the object was inhomogeneous and decreased with distance from the magnet surface. Measurements at different depths inside the object were carried out by changing the resonance frequency. Three probeheads were used, one, operating at 18.1 MHz, allowed measurements within the first millimeter of the sample, another, operating at 17.2 MHz, allowed measurements at a depth of 3 mm, and the third, operating at 16.3 MHz, allowed measurements at a depth of 5 mm inside the sample. All probeheads detected the hydrogen signal from the study object.

Depth profiles were obtained with a purposely built single-sided NMR sensor (RWTH Aachen University, Germany) [18]. This sensor generates a magnetic field with an extremely uniform gradient to resolve the near-surface structure of arbitrary large samples. Measurements were carried out at 13.55 MHz.

RESULTS AND DISCUSSION

Moisture in Wall Paintings

Water is a major cause of decay to building masonry in cultural heritage sites [25]. Detachment of wall paintings, efflorescence of salts, and decay of porous stones are water-related phenomena. Moisture rises through walls to the limit of capillarity or until it evaporates from the wall surface. Salts in the soil or mortar are drawn into solution in the porous network of the wall. When salt concentration exceeds the equilibrium constant and/or when ambient relative humidity is lower than the equilibrium relative humidity of the saturated salt solution, salts crystallize out, causing crumbling and fretting of the wall. Determining the course and distribution of water through the wall is a fundamental step in conservation work and is particularly true for wall paintings. In this case a number of important factors must be taken into account: for example, the vulnerability of extremely thin painted surfaces forming the interface between the plaster and the environment, the difficulty of controlling potential deteriogens, such as moisture and pollution, and the proximity of places crowded with people to the wall painting. In addition, the drilling of solid cores for gravimetric tests is obviously forbidden in ancient wall paintings.

The development of portable NMR devices has allowed non-destructive, non invasive mapping *in situ* of moisture distribution in ancient wall paintings [16, 26-31]. The magnetic field is applied to one side of the object. Its integrity and shape is therefore preserved (Figure 2).

Figure 2. Portable unilateral NMR instrument measuring the moisture content in the wall painting *Saint Clement at mass and the legend of Sisinnius* in St. Clement’s Basilica, Rome.

The intensity of the signal detected by unilateral NMR is directly proportional to the water content. By performing a suitable number of measurements and processing the experimental data in a proper way, a precise moisture distribution map may be obtained. This method [28,29] was recently used to map the moisture distribution in the wall painting *St Clement at mass and the legend of Sisinnius* dating to 1080 AD. The wall painting is in the second underground level of St. Clement’s Basilica, Rome. A watercourse under the foundations of the basilica is a cause of the rising damp in the walls of the archaeological site. Because of the critical microclimate (high humidity and low temperature throughout the year) of the underground chamber, the conservation of wall paintings is challenging. The masonry and wall paintings show the typical degradation caused by high humidity, including salt efflorescence, encrustations, and biological colonization.

In the present case, the damage due to capillary rise of water in the wall was so severe that reduction of dampness and stabilization of moisture content were mandatory before planning any restoration. To reduce rising damp in the masonry, a horizontal cut was made through the bricks of the wall just above floor level, and a hydrophobic mixture of polyester resin and marble powder was injected into the wall. The evolution of moisture distribution in the wall painting was monitored by unilateral NMR before and after the operation.

NMR measurements were carried out on the first layers of the wall painting and at a depth of 0.5 cm in the plaster. In the former case a probehead operating at 18.1 MHz was used to detect at a depth of 0.1 cm under the surface. In the latter case a probehead operating at 16.3 MHz was used to detect at a depth of 0.45 - 0.55 cm, disregarding the signal of the surface.

To detect moisture in the wall painting, measurements were carried out choosing a matrix of points on the painted surface. Each experimental point had an area of 2 x 5 cm^2, equal to the area of the probehead. During the three measurement sessions (February 2008, November 2009, and February 2010), the same matrix of points was investigated.

The data was processed to obtain contour plots which are 2D representations of 3D surfaces. In these contour plots x and y are the coordinates of the measured area of the painted wall and z is the integral of the NMR signal, which is proportional to the water content. The maps thus obtained allow easy visualization of the detailed distribution of moisture in the wall painting, see Figure 3.

In these maps, the difference in the moisture level is encoded as a gray scale, dark regions indicating the highest moisture content, and vice versa. Although the maps differentiated wall painting areas as a function of moisture content, a further step was necessary to calibrate the NMR signal to assess the precise amount of moisture in each area. The NMR signal was calibrated using four specimens prepared by restorers according to the ancient original recipe to reproduce the mortar used in the wall painting. The detailed calibration procedure has been reported elsewhere [28]. According to this calibration procedure, each area of the map corresponds to an exact amount of moisture.

The maps obtained at a depth of 0.1 cm are shown on the left side of Figure 3, and those recorded at a depth of 0.5 cm on the right. Maps in Figure 3a and 3b were recorded in February 2008 before intervention to reduce rising damp. Maps recorded in November 2009 and February 2010 after intervention are shown in Figure 3c, d and 3e, f, respectively.

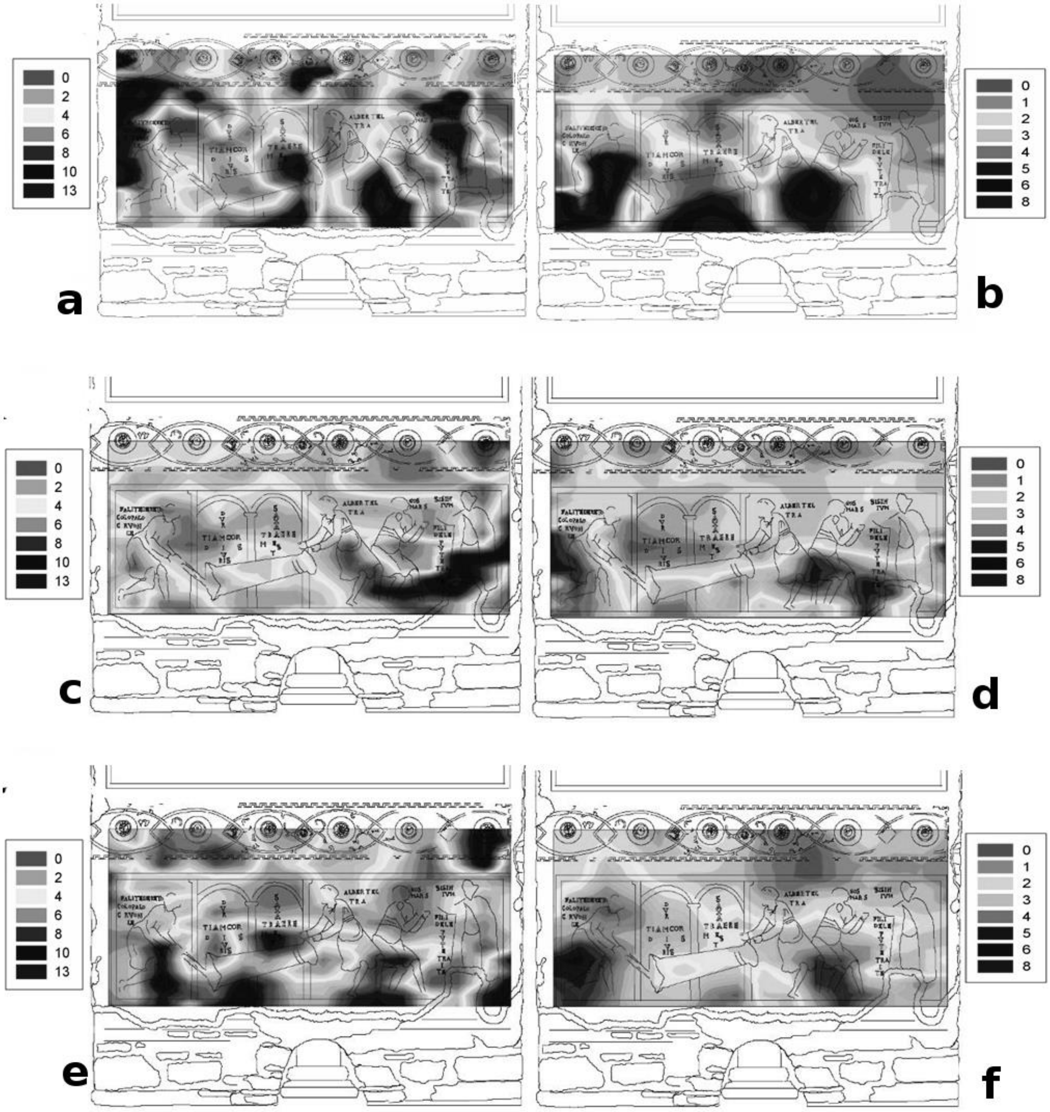

Figure 3. Moisture distribution maps obtained by unilateral NMR at a depth of 0.1 cm (left), and at a depth of 0.5 cm (right). Maps recorded in February 2008 before intervention to reduce capillary rise of water through the wall, (a) and (b). Maps recorded in November 2009 four months after intervention and in the presence of a scaffolding mounted near the wall painting, (c) and (d). Maps recorded in February 2010 seven months after intervention and after removal of the scaffolding, (e) and (f). Data adapted from [29].

It is noteworthy that all maps obtained at a depth of 0.5 cm gave a clear image of the path of rising damp. After intervention, the maximum water content measured in November 2009 and February 2010 was about 3% lower than that measured in February 2008 before intervention. The moisture distribution maps obtained four and seven months after intervention clearly show a lower rise of moisture and a net reduction in wet areas.

Maps obtained at a depth of 0.1 cm showed that maximum water content was 12-13% in February 2008, 10-11% in November 2009, and 11-12% in February 2010. It is worth noting that these maps do not give information about the path of rising damp: the measurements at 0.1 cm depth regard a slice very close to the painting-environment interface, which is also affected by the microclimate of the underground environment. The influence of microclimate on the quantitative moisture distribution in the first layers of the wall painting was evident in November 2009, when scaffolding caused a net lowering of relative humidity in proximity to the wall painting. In fact, monitoring of thermohygrometric parameters conducted simultaneously with the NMR measurement showed that outside the scaffolding, mean relative humidity was about 98%, whereas inside it was about 88%, and the temperature inside the scaffolding was, on average, one degree higher than outside.

The map obtained in November 2009 (Figure 3c) shows more dry areas than that recorded in February 2008 before intervention (Figure 3a) and that collected in February 2010 after removal of the scaffolding (Figure 3e). The maps recorded at a depth of 0.1 cm before and after intervention and after removal of the scaffolding are very similar and seem little affected by the intervention. Actually, the moisture content in the surface layers of the wall painting was found to be largely affected by the particular microclimate of the underground chamber.

NMR Stratigraphy of Painting Layers

Paintings consist of many layers, such as pigments, binders, primer, varnishes, and so on. Knowledge of the layer structure or stratigraphy of the artwork provides information about the materials used and the state of conservation, indicating suitable conservation and restoration procedures. The common way of obtaining information about stratigraphy is to cut cross-sections from the painting and analyze them by otpical microscopy, scanning electron microscopy, micro-Fourier transform infrared spectroscopy, and other techniques.

Recently, portable NMR equipped with a single sided sensor generating a magnetic field with an extremely uniform gradient was successfully used to reveal the stratigraphy of painted wooden panel [19,32]. The stratigraphy obtained encodes the amplitude of the ^{1}H NMR signal as a function of the depth scanned. Layers of different materials can be detected, their thickness measured, and information on the pictorial technique obtained. The intensity of the signal indicating hydrogen content enables one layer to be differentiated from another.

By way of example, the stratigraphy of a purposely prepared tempera specimen and the corresponding optical image are reported in Figure 4a and b. Based on variation in signal intensity, the stratigraphy indicates four well-defined layers: the first (0.2 mm thick) is the pictorial layer, the second (0.5 mm thick) is the primer, the third is the *incamottatura* (canvas+glue), and the fourth is the wood of the panel. The layers and their thickness match those observed by optical microscopy.

This non-invasive, non-destructive technique was recently used to study the stratigraphic structure and state of conservation of the *Adorazione dei Magi*, a wooden panel painted by Bartolo di Fredi in the second half of 14th century. Figure 5 shows an NMR stratigraphy recorded on an area of the painting by scanning from the surface to a depth of 5 mm. Three different layers are evident, the first from the surface to 1 mm consists of pigment and binder, the second, about 0.8 mm thick, is primer, and the third is the wooden panel, detected at a depth of 1.7 mm to 5 mm.

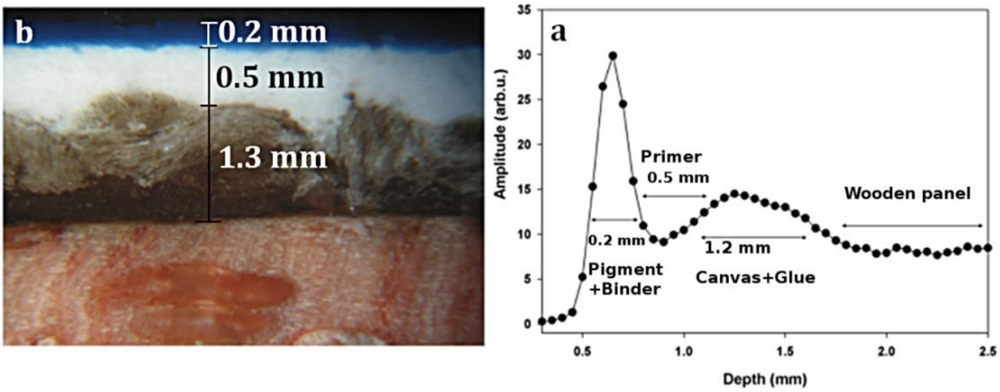

Figure 4 .a) NMR stratigraphy of a purposely prepared tempera specimen showing four layers: the first is the painted layer, the second the primer, the third the *incamottatura*, and the fourth the wood. b) The corresponding optical image.

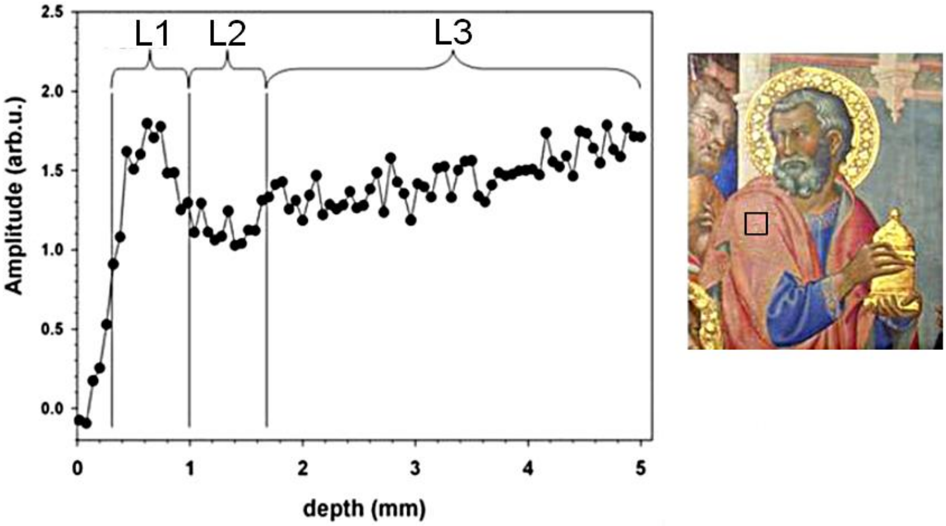

Figure 5. NMR stratigraphy of an area of the *Adorazione dei Magi,* a 14th century wooden panel painted by Bartolo di Fredi. Three layers are evident: L1 consisting of pigment and binder, L2 primer, and L3 wood. Data adapted from [32].

NMR Stratigraphy of Detached Mural Paintings

Under critical environmental conditions of conservation, such as flooding and risk of collapse, wall paintings must sometimes be detached from the wall and fixed on a new support in order to save and protect them. One of the methods used to detach mural paintings is known as *strappo* [33]. After the *strappo* a complex artifact is obtained. Besides the pigments and layers of plaster of the original mural, the inorganic and organic materials used during the *strappo* also become parts of the artifact. The complexity of such articles and often the lack of information about the *strappo* procedure used make analytical study challenging.

However, determination of the stratigraphy and chemical composition of the layers are essential for planning restoration.

We recently used NMR stratigraphy to plan restoration of a detached ancient Nubian mural from the archaeological site of Sonqi Tino, Sudan (Figure 6).

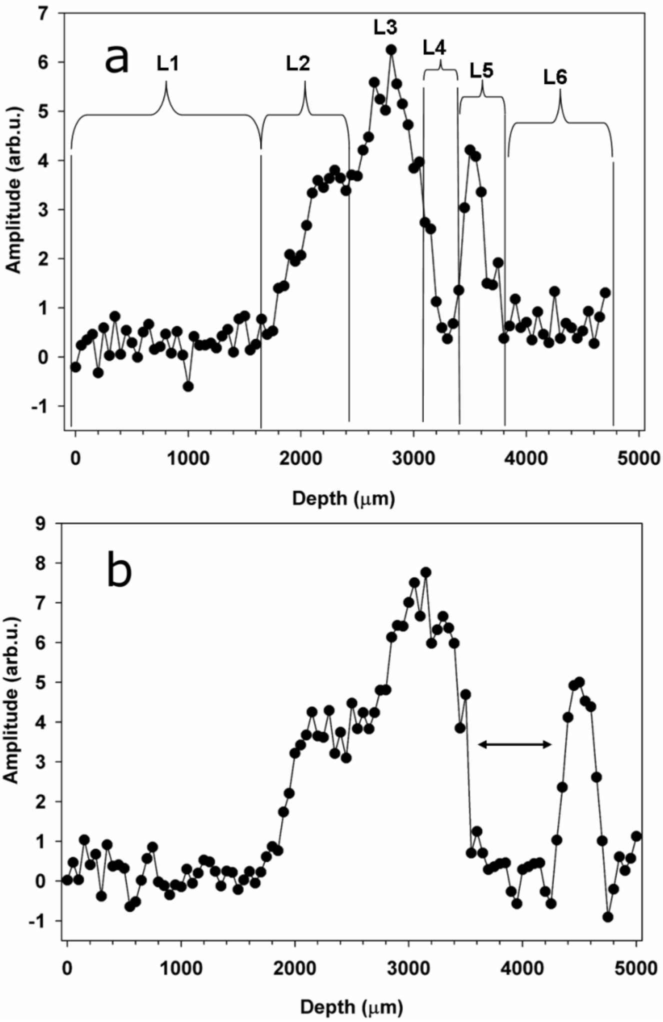

Figure 6. NMR stratigraphy of regions a and b of a detached mural painting consolidated and applied to a new support. Six layers are observed in both cases.

Six layers were evident. L1 and L6 showing weak intensity were due to inorganic pigments and clay, and to the material constituting the support, respectively. Layers L2, L3 and L5 were due to resins used to consolidate the detached painting and to attach it to the new support.

A further layer, L4, characterized by the absence of any NMR signal and by variable thickness, was detected in some regions between layers L3 and L5. Figure 6 shows the comparison of two regions where different thicknesses of layer L4 were found. In regions where layer L4 was found to be thick, detachment of the backing of the painting from the supporting panel was postulated, whereas this layer was found to be very thin in regions where layers L3 and L5 were bonded together. Thus the thickness of layer L4 provides important information on the state of conservation of the mural.

NMR Stratigraphy for Monitoring the Effectiveness of Cleaning Treatments of Wall Paintings

Removal of patinas of organic deterioration from paintings is a widespread problem. Shellac is a natural organic resin of animal origin that was widely used as a varnish for wall paintings. When it ages, it becomes insoluble, changing colour, and is very hard to remove. Many old paintings become yellowish due to a shellac coating.

NMR stratigraphy was used to non-invasively assess the effectiveness of a cleaning procedure. The procedure was tested on a calcarenite specimen coated with shellac that acted as an inert support to simulate the cleaning of a wall painting. The calcarenite specimen was scanned before treatment (UT), after coating with shellac (T), and after cleaning (TC) (Figure 7).

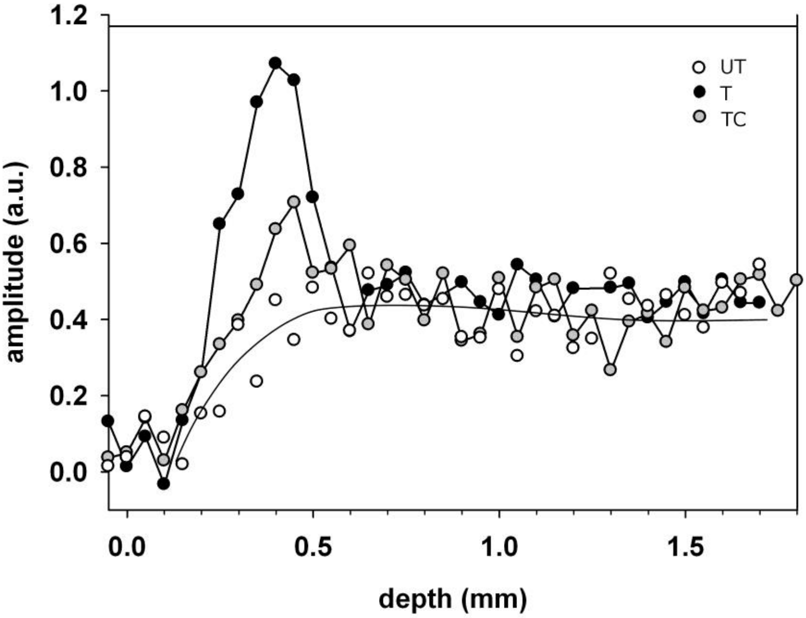

Figure 7. Depth profiles of untreated calcarenite (UT), calcarenite coated with shellac (T), and calcarenite coated with shellac and then cleaned (TC).

The profiles show two regions, one at a depth of more than 0.7 mm, where the three profiles merge together and show a weak signal amplitude, due exclusively to moisture in the porous structure. Between 0.2 and 0.7 mm, the profile of the specimen coated with shellac shows strong intensity due to the abundance of hydrogen atoms in shellac. In the same depth range, the intensity profile of the specimen coated with shellac and then cleaned is definitely weaker than before cleaning, due to a decrease in hydrogen levels. The profile of the untreated specimen is flat. The intensity profile between 0.2 and 0.7 mm indicates treatment efficiency: the more effective the treatment, the lower the level of hydrogens encoded by the profile.

This method can be used to monitor the efficiency of any cleaning procedure aimed at removing any type of organic patina and to measure the thickness of the patina. The method can also be applied *in situ*.

Porous Stone

Water is a main cause of degradation of ancient and modern inorganic porous materials such as stone, concrete, bricks, and mortar [34]. Water acts in a direct way by dissolving, and in an indirect way through freeze/thaw cycles, pollutant transport, and soluble salt hydration. It may also promote the growth of organisms that may help to degrade the material. Hydrophobic treatment is a major method in the conservation of stone artifacts and monuments [35]. The choice of hydrophobic products and the application methodology should be aimed at preventing the penetration of liquid water, allowing vapor leakage, delaying the degradation process, and avoiding modifications in the optical properties of the material [36]. Knowledge of the penetration depth of a treatment in a porous structure is important for deciding the treatment to apply [37].

The penetration depth depends critically on the porosity of the material to be treated and on the chemical physical characteristics of the treatment compound. Another critical requirement for stone conservation is that the compound absorbed by the stone should not create regions with sharp variations in the amount of absorbed product. Such variations mean chemical and physical discontinuities between the impregnated layers and the layers underneath. These layers may respond differently to changes in thermo-hygrometric conditions; for example, the volume expansivity of close layers may be very different, causing mechanical damage to the porous structure. In such cases, the treatment may cause worse damage than natural aging [38]. It is difficult to know the penetration depth of a treatment in a porous material and whether or not there are discontinuities. The requirement of a non-destructive method to apply *in situ* also excludes most analytical techniques [39,40].

MRI and ^{1}H NMR relaxometry were used to investigate stone porosity and treatments of porous stone [4, 41- 49]. Portable NMR was used to investigate the pore size distribution and effectiveness of protective and consolidating treatments on stones [50-55].

Non-invasive Monitoring of Hydrophobic Treatment of Porous Stone

Unilateral NMR was recently used for non invasive study of the hydrophobic effect of dimethylsiloxane on sandstone and calcarenite specimens in relation to treatment time [22]. By way of example, Figure 8 shows depth profiles measured in water-saturated calcarenite specimens, untreated or treated with the hydrophobic agent for 5 s, 600 s, and 1800 s.

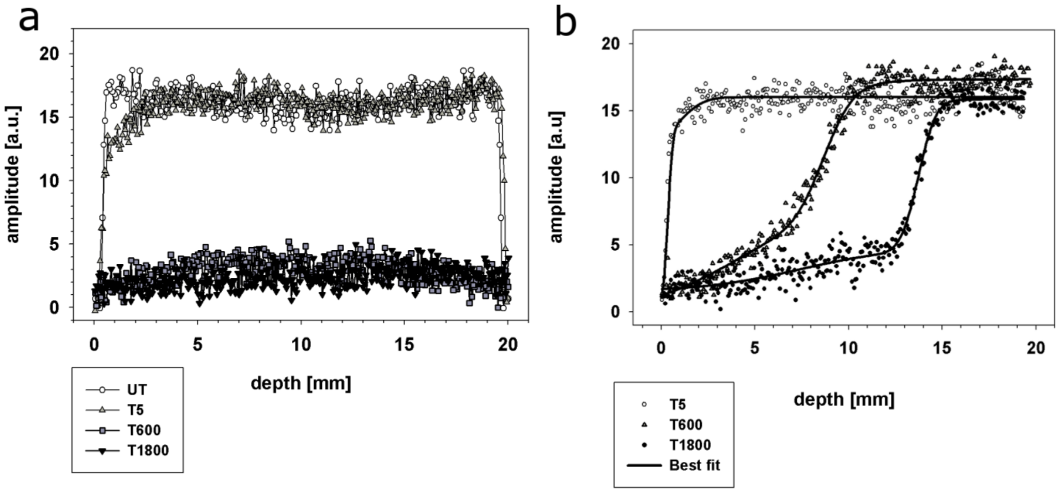

Figure 8. Depth profiles of calcarenite. Profiles reported in (a) were obtained after making the specimens absorb water from the treated side, whereas profiles reported in (b) were obtained after making the specimens absorb water from the untreated side. UT: untreated, T5: treated for 5 s, T600: treated for 600 s, and T1800: treated for 1800 s. The solid lines in (b) were obtained fitting the experimental data to a purposely designed equation. Data adapted from [22].

These profiles describe water absorption throughout the specimens as amplitude (proton spin density) variations with a resolution of 20 μm. To understand the meaning of the depth profiles, it must be born in mind that the amplitude is directly proportional to the amount of absorbed water. By comparing the amplitude of depth profiles of untreated and treated specimens, it is possible to obtain information about the amount of water absorbed and therefore to determine the hydrophobic action of treatment times.

The profile of the specimen treated for 5s showed an amplitude slightly lower than that measured in the untreated specimen in the few first layers of the specimen, while at a greater depth the amplitude increased up to the value measured in the untreated specimen (Figure 8a). The 5s treatment therefore only showed some hydrophobic action in the few first layers of the specimen, but not at greater depth. The profiles of specimens treated for 600 and 1800 s clearly showed a very low amplitude throughout the specimens revealing that water absorption was impaired. Under these circumstances, no information was obtained about the depth of penetration of treatments. Visual inspection of the profiles suggest that the treatment had been absorbed from one side to the other of the specimens. To clarify this point depth profiles were measured again, after making the calcarenite specimens absorb water by capillarity from the untreated side (Figure 8b). These profiles clearly showed that treatment had not penetrated through to the opposite untreated side of the specimen, as it was possible to precisely measure the penetration depth. Depth profiles of specimens treated for 600 and 1800 s clearly showed hydrophobic action deep down in the specimens, where the amplitude of profiles was definitely lower than that measured in the untreated specimen. On the contrary, the profile of specimen treated for 5 s showed a trend very similar to that obtained after making the specimen absorb water from the treated side (Figure 8a and b). In this case a very weak hydrophobic action was only observed in the first layers of the specimen.

To evaluate the penetration depth of treatment, the experimental depth profiles f(x) were fitted to the following equation:

$$f(x) = \sum_{k=1}^{N} \frac{w_k}{2} \operatorname{erf}\left[\frac{x_k - x}{\sqrt{2}\Delta_k}\right] + q_0 \qquad (1)$$

where N is the number of inflection points, Δ_k the half width of the transition of the amplitude from low to high spin density, w_k the spin density, q_0 the lowest spin density, and x_k is the depth at the inflection point, namely the penetration depth of the treatment.

To evaluate the speed of the variation of the amplitude of the profile, slopes b_k at the inflection points may be calculated. The detailed calculation is reported in ref. [22]. Basically, a high b_k value indicates a sharp variation of the amount of absorbed water, whereas a low b_k value indicates a gradual variation of the amount of absorbed water.

Depth profiles reported in Figure 8b were fit to equation (1) with k=2. The parameters obtained are reported in Table 1, and slopes at the inflection points in Table 2.

Table 1. Parameters obtained fitting depth profiles to equation (1) with k=2**

Specimen	x_1 (mm)	Δ_1 (mm)	w_1 (a.u.)	x_2 (mm)	Δ_2 (mm)	w_2 (a.u.)	q_0 (a.u.)	R^2
T5	0.28±0.01	0.12±0.03	12.5±1	1.0±0.6	1.0±0.3	3.5±1	0.00±0.05	0.82
T600	4.1±0.3	1.5±0.3	4.1±0.7	8.7±0.1	1.3±0.1	11.3±0.7	1.8±0.2	0.99
T1800	7.4±0.5	4±1	3.1±0.8	13.7±0.1	0.75±0.06	11.1±0.6	1.6±0.3	0.98

** Depth profiles were obtained after allowing specimens to absorb water from the untreated side.

Table 2. Slopes at inflection points of depth profiles shown in Figure 8b

Specimen	b_1 (mm^{-1})	b_2 (mm^{-1})
T600	0.971	3.030
T1800	0.300	5.263

In the case of the specimens treated for 5 s, x_1 and b_1 only included the first few points of the profile, which rapidly increased up to the values measured in the untreated specimen. Neither the low x_1 value nor the high b_1 value may be considered an actual penetration depth and an actual slope at the inflection point, respectively, being affected by the proximity to the air–water–specimen interface. The very weak hydrophobic effect observed in the first layers was expressed by x_2. The fitting of depth profiles of specimens treated for 600 and 1800 s allowed the determination of two actual inflection points, along with the corresponding slopes. The former inflection point x_1 was related to a thickness in the specimen where the treatment was efficient enough to impair water absorption, the measured amplitude being definitely lower than that measured in the untreated specimen (Figure 8b). The latter point x_2 was related to a depth in the specimen where the treatment was unable to impair water absorption, as indicated by the progressive increase in amplitude detected. In particular, due to a deeper penetration of the hydrophobic treatment, in the specimen treated for 1800 s, both x_1 and x_2 were found to be greater than those measured in the specimen treated for 600 s. In specimens treated for 600 and 1800 s, slopes at the first inflection point b_1 indicated the rather gradual increase in the amplitude of profiles, which corresponded to a gradual increase in the amount of water absorbed. Slopes at the second inflection point b_2 were definitely greater than those at the first inflection point, as they included a region where a rather sharp increase in the amount of absorbed water occurred.

The depth profiles describe water absorption throughout the specimen as amplitude variations. Provided profiles allow determination of the depth of treatment penetration, the amount of absorbed water is obviously modulated by penetration of the treatment into the specimen. In this case a depth profile of water absorption may be thought of as a sort of negative image of the absorption profile of the hydrophobic compound. The profile of the absorbed compound is easily calculated point by point using equations reported in ref. [22].

Figure 9 shows the absorption profiles of the hydrophobic compound in calcarenite treated for 600 and 1800 s. Angles α are analytical parameters allowing us to evaluate the changes in slope. Note that the smaller the angle α, the steeper the change in slope, and the greater the angle α the smoother the change in slope. Changes in slope are closely related to inhomogeneities in the stone: the sharper the change in slope, the sharper the inhomogeneity. In the case reported in Figure 9, all profiles showed a single change in slope indicated by angle α. In both specimens, α was an obtuse angle; however, in the specimen treated for 1800 s it was definitely less obtuse than in the specimen treated for 600 s. These values clearly indicated that the longer treatment gave rise to a steeper change in slope than the treatment for 600 s. The treatment showing deeper penetration of the stone also showed a sharper discontinuity, whereas the treatment showing shallower penetration showed a smoother discontinuity.

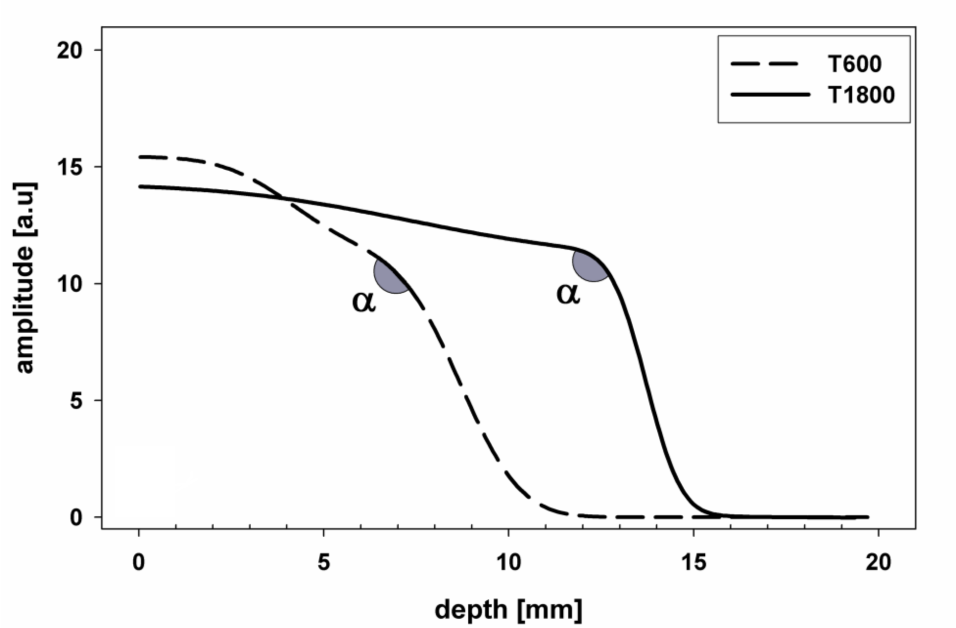

Figure 9. Depth profiles of calcarenite indicating absorption of the compound through the specimen due to hydrophobic treatment. Dashed and solid lines refer to specimens treated for 600 and 1800 s, respectively. Angles where changes in slope occur are also indicated. Adapted from [22].

Knowledge of α may help avoid sharp discontinuities in the stone by choosing one treatment with respect to another and suitable treatment times and methods. As a rule, both the analytical parameters obtained by NMR, namely penetration depth and degree of inhomogeneity, are useful for assessing the performance of a treatment.

Transverse Relaxation Times and Pore Size Distribution in Porous Stone

With portable NMR instruments it is possible to measure parameters known as relaxation times that provide information closely related to the porosity of the material [12,56]. Transverse relaxation times T_2 are time constants of multi-exponential CPMG decay [11]. They depend on the degree of confinement of a liquid (water) in a porous structure. Because T_2 depends on the surface-to-volume ratio, water in small pores relaxes rapidly, whereas water in large pores relaxes more slowly. Measurement of T_2 of a liquid confined in a porous matrix enables study of pore size distribution. Mono- or multi-exponential decay of magnetization vs echo time is obtained applying a CPMG sequence. In the case of bulk water, mono-exponential decay is measured, whereas in the case of water confined in a heterogeneous porous structure, multi-exponential decay is measured. The amount of water associated with each T_2 component is defined as the spin population or spin density of that component. The sum of spin populations is normalized to 100%.

T_2 measurements are particularly useful for comparing materials having different degrees of porosity, for investigating degradation processes affecting a porous structure, and for studying changes in the degree of open porosity resulting from hydrophobic and/or consolidating treatment.

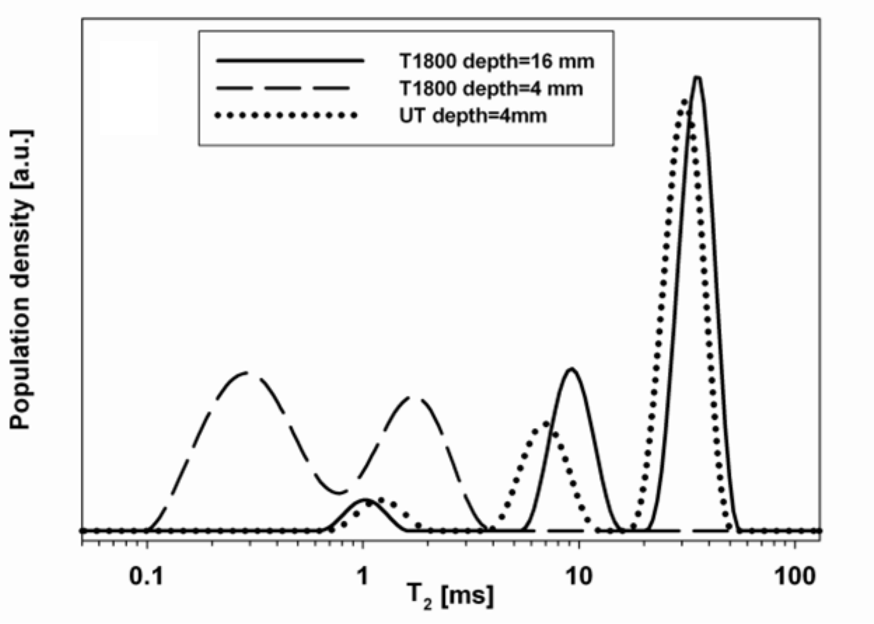

Figure 10. T_2 relaxation time distributions in untreated (UT) calcarenite at a depth of 4 mm (dotted line), in calcarenite treated for 1800 s (T1800) at a depth of 4 mm (dashed line) and at a depth of 16 mm (solid line). Measurements were carried out after allowing specimens to absorb water from the untreated side. Adapted from [22].

The experimental data obtained applying the CPMG pulse sequence is fitted to the equation:

$$Y(t) = C_0 + \sum_{i=1}^{n} W_i e^{\frac{-2t}{T_{2i}}} \tag{2}$$

where n is the number of magnetization decay components, W_i the spin population of the i^th component, C_0 the offset value adjusting for measurement noise, and T_{2i} the relaxation time of the i^th component.

A regularized inverse Laplace transformation [57,59] applied to the echo envelopes obtained from the CPMG sequence provides a distribution of T_2 relaxation times, where the peaks of the distribution match the most probable T_2 values, and the area of each peak matches the normalized spin population.

Figure 10 shows the T_2 relaxation time distribution obtained at a depth of 4 mm in untreated calcarenite and the distributions obtained at depths of 4 and 16 mm in calcarenite treated for 1800 s.

Measurements were carried out after allowing specimens to absorb water from the untreated side. At a depth of 4 mm in the untreated specimen (dotted line), three well-separated peaks centred at 1.3, 7.2, and 32 ms with spin populations of 6%, 21%, and 73%, respectively, were observed. In this case, a considerable amount of water (73%) was confined in large pores. The same trend was observed at a depth of 16 mm in the specimen treated for 1800 s (solid line), whereas a remarkable loss of water in large and medium-sized pores was observed in the same specimen at a depth of 4 mm (dashed line, Figure 10). In fact, only two T_2 peaks were observed centred at 0.3 and 1 ms with relative spin populations of 61% and 39%, respectively, whereas the largest T_2 peak was lacking. The small amount of absorbed water was therefore confined in small- and medium-sized pores. The distributions of relaxation times were in line with the depth profiles reported in Figure 8b, which showed that at a depth of 16 mm, no treatment impaired water absorption, whereas at a depth of 4 mm, the 1800-s treatment showed strong hydrophobic action.

Non-Invasive Monitoring of Consolidation Treatment of Porous Stone

Consolidation treatment of three limestones from Finale, Liguria (Italy) were investigated by portable NMR [60]. Mascia, Castelgavone and Pale Finale limestone has been used as building and/or ornamental stone since ancient times. Ancient roman bridges of Finale stone in Liguria are still fit for use. The capillary water absorption curves in Figure 11a clearly show their different water absorbing capacities: Pale > Mascia > Castelgavone.

The trend of the curves perfectly matches the trend observed by conventional MRI technique on water-saturated specimens (Figure 11b, c, and d). In the images, bright areas indicate areas filled with water, whereas dark areas indicate the absence of water. The image of Pale Finale limestone is the richest in bright areas, indicating the large amount of water absorbed into the porous structure. The image of Castelgavone limestone is the poorest in bright areas, indicating very little absorbed water in pores. Mascia limestone shows an intermediate pattern. The trend of the intensity of the NMR signal detected by portable NMR in water-saturated specimens at a depth of 3 mm matches the trend observed by MRI and capillary absorption curves. Indeed, the strongest signal is observed in Pale limestone, the weakest in Castelgavone, and an intermediate pattern in Mascia limestone.

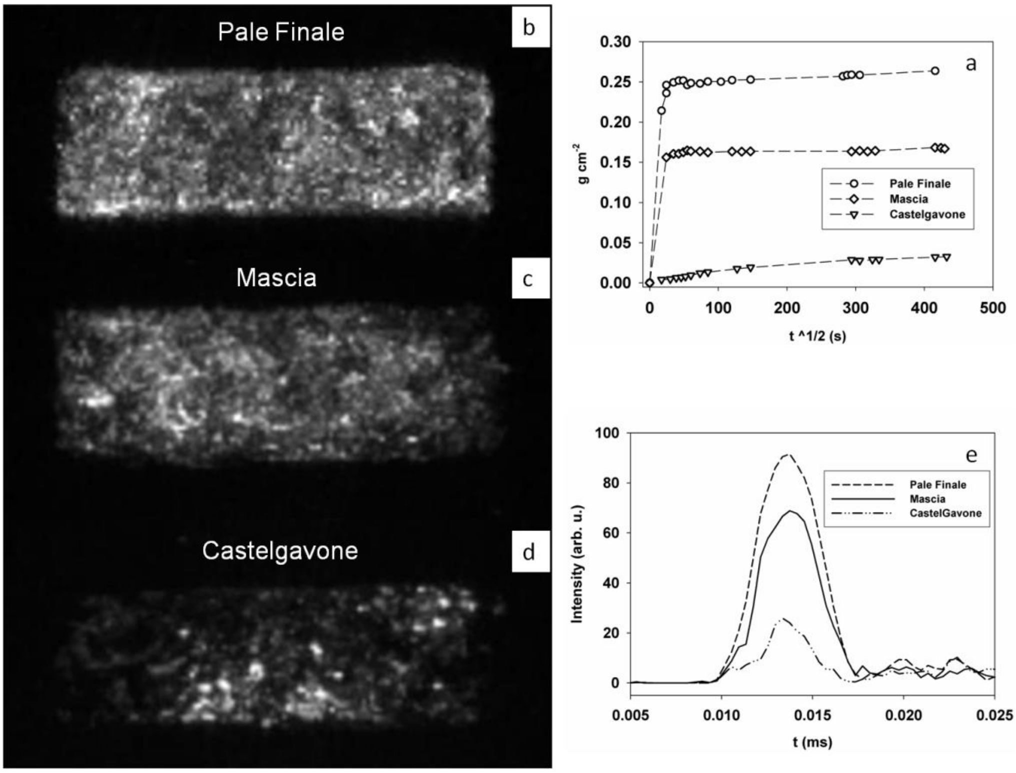

Figure 11. Capillary water absorption curves of untreated Pale Finale, Mascia, and Castelgavone limestone (a). MRI images (5 cm x 2 cm) of untreated Pale Finale (b), Mascia (c), and Castelgavone (d) limestone. Signal detected non-invasively by portable NMR at a depth of 3 mm in Pale Finale, Mascia, and Castelgavone stone (e).

To consolidate the stone, a mixture of butyl methacrylate and ethyl acrylate (BMA/EA) was permeated by capillarity, and then polymerized *in situ* [61]. Stone treated with Paraloid B72 was used for comparison.

Table 4. T_2 transverse relaxation times and spin populations measured in untreated Mascia limestone, Mascia limestone treated with Paraloid B72, and Mascia limestone treated by polymerizing *in situ* a mixture of BMA/EA absorbed by capillarity

Mascia limestone	W_a%	T_{2a} (ms)	W_b(%)	T_{2b}(ms)	W_c(%)	T_{2c}(ms)
Untreated	18	0.573±0.09	35	10.2±0.5	47	45±3
Paraloid B72	27	0.404±0.050	28	7.8±0.4	45	29±2
BMA/EA	53	0.255±0.020	22	4.6±0.1	25	28±2

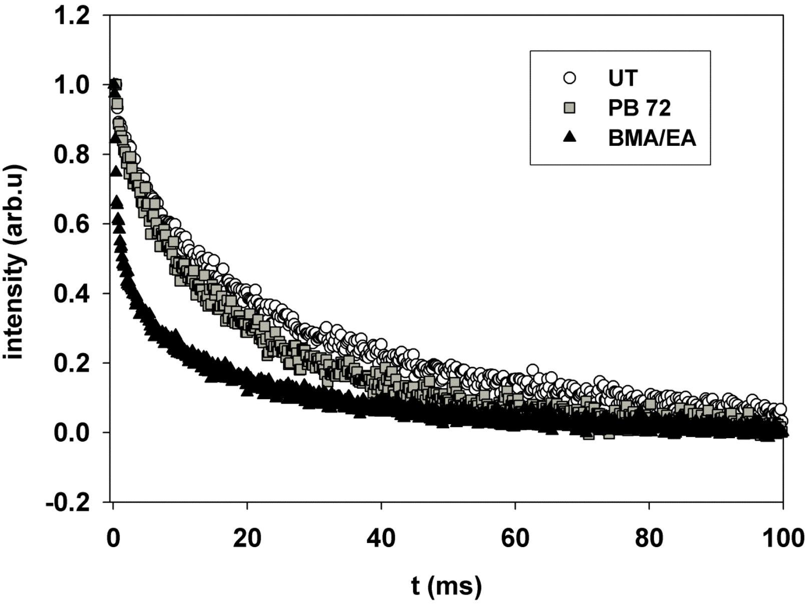

Figure 12. CPMG decay measured in untreated Mascia limestone (UT), Mascia limestone treated with Paraloid B72 (PB 72), and Mascia limestone treated with a mixture of BMA/EA polymerized *in situ*.

By way of example, Figure 12 shows CPMG decays measured at a depth of 3 mm in untreated and treated specimens of Mascia limestone.

The slowest decay was observed in the untreated specimen, the fastest in Mascia limestone treated with BMA/EA, polymerized *in situ*, whereas the decay measured in the specimen treated with Paraloid was slightly faster than in the untreated specimen. T_2 relaxation times were obtained by fitting the CPMG decays to three-exponential decays. The resulting parameters are reported in Table 4.

The longest T_2 values were measured on untreated Mascia, the shortest on Mascia polymerized *in situ*, whereas values measured on Mascia limestone treated with Paraloid B72 were intermediate.

Because transverse relaxation times in porous media decrease with decreasing fluid saturation [12], these results indicate that the treatment with BMA/EA mixture polymerized *in situ* has the strongest ability to impair water absorption.

Water-saturated Mascia limestone specimens, untreated and polymerized in situ, were scanned to obtain the depth profiles shown in Figure 13, where the unbroken lines through the experimental points were obtained by fitting the data to equation (1).

The hydrophobic action of the treatment is evident from the amplitudes of the two profiles. Depths of penetration of treatment were 16.7 mm and 18.1 mm. At depths less than about 16 mm the amount of water absorbed was much less than that absorbed by the untreated specimen. At depths of more than 18 mm, where the hydrophobic effect of the treatment decreased, the amount of water absorbed increased to about a half of the amount of water absorbed by the untreated specimen. In fact, at a depth of about 19 mm, the amplitude of the NMR signal in the treated specimen was about 2, whereas in the untreated sample it was about 4 (Figure 13).

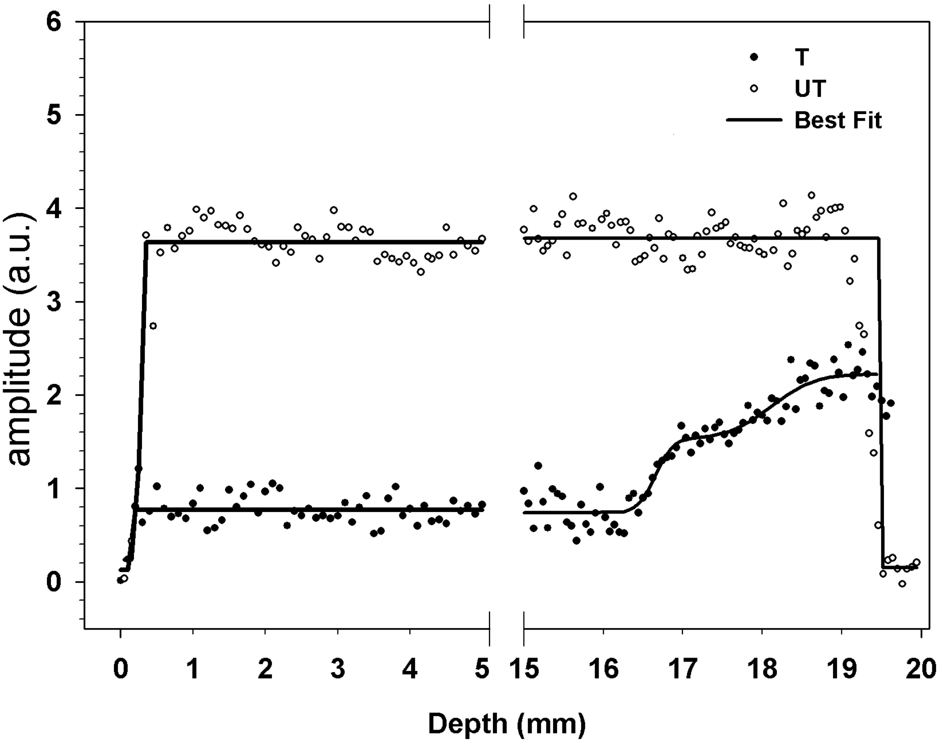

Figure 13. Depth profiles of water-saturated Mascia limestone specimens, untreated (UT) and treated with a BMA/EA mixture polymerized *in situ* (T). Unbroken lines were obtained fitting the experimental data to equation (1).

Clay and Pottery

NMR spectroscopy is almost equally useful for probing the atomic environment of disordered and ordered single crystal systems. NMR can be used to monitor changes occurring in the atomic environment when materials change from one state of structural disorder or heterogeneity to another, such as nucleation of polycrystals from glass and the formation and growth of crystalline phases when minerals react or change phase by heating or mechanical grinding. Such systems often lack the long-range order necessary for conventional diffraction studies.

Investigations on clays used for manufacturing ceramic artifacts in antiquity and their possible areas of origin are of great interest for archaeologists and art historians. Much effort is devoted to characterizing ancient ceramic artifacts and investigating the possible sources of primary materials and the technology of production. Many studies of ancient ceramics concern composition, firing, manufacturing methods and technological variability. The firing process involves the breakdown of some phases and the formation of new ones. The growth of new phases is related to firing temperature and the composition of microsites in which the phases grew. Clay artifacts are therefore regarded as artificial rocks formed in a kiln.

A multi-technique study, including ^{27}Al and ^{29}Si solid state NMR, was carried out to research the modifications induced by firing on illite-rich clay from Deruta, as a preliminary step for obtaining information about ancient ceramic technology [62].

Another study was carried out on pottery and clay from Acquapendente, Viterbo district (Italy), a ceramic production area since the Middle Ages. In addition to other conventional techniques, ^{27}Al MAS and 3QMAS, as well as ^{29}Si and ^{23}Na MAS NMR spectroscopy were used to determine the structural features of the raw material and the structural modification due to the firing.

For nuclei with spin I>1/2, the non-spherical charge distribution of the nucleus gives rise to an electric quadrupole moment which interacts with electric field gradients surrounding the nucleus. The quadrupolar interaction is only partially averaged by spinning the sample at a high rate (MAS). To obtain better spectral resolution, MQMAS [63,64] may be performed, which allows refocusing of the second order quadrupolar effects that broaden ^{27}Al MAS spectra.

By way of example, Figure 14 a and c shows ^{27}Al 3QMAS maps of a raw ancient clay and a pottery fragment both obtained from excavations at Acquapendente.

The raw clay map shows Al in octahedral (O_h) and tetrahedral environments (T_d). At least four peaks indicating the presence of T_d environments are observed in the map: a main peak centered at 54.8 ppm in F1 dimension and 64.4 ppm in F2 dimension (1) and other weak peaks (2,3,4). The ^{27}Al MAS spectrum is reported in F2 dimension. It is worth noting that in the 2D map, peaks of Al in T_d environments are resolved, whereas in the 1D MAS spectrum they merge.

The map also shows significant axes, such as C_{IS} (axis with slope 1), Q_{IS} (axis with slope -17/10) and A (the line parallel to F2 drawn through the intersection of the C_{IS} and Q_{IS} axes). The position and distribution of peaks along these axes provide the isotropic chemical shift and the second order quadrupolar factor of each peak, and enable qualitative observation. A peak parallel to the F2 axis indicates that the width of the peak is mainly due to second order quadrupolar broadening, whereas a peak parallel to C_{IS} indicates that the width of the peak is determined by a distribution of chemical shift, and the closer the peak is to the C_{IS} axis, the smaller the quadrupolar coupling. The O_h peak observed in the map of Figure 14a shows a distribution of chemical shift and second order quadrupolar broadening, whereas the main T_d peak mostly shows second order quadrupolar broadening, being aligned in the direction of C_{IS}. The centre of gravity of peaks in the MQMAS map may be used to evaluate major structural parameters such as isotropic chemical shift δ_{iso} and second order quadrupolar effect SOQE. These parameters may then be used as initial guesses in a spectral deconvolution procedure. Figure 14b shows the experimental and deconvoluted spectra obtained for raw clay.

Figure 14c shows the map of a pottery sample obtained from the fragment shown in Figure 14d. Firing caused break down of the structure of the clay used to manufacture the pottery and formation of new phases, all with Al in tetrahedral environments, as indicated by peaks 1’, 2’, and 3’. The absence of any Al in an octahedral environment indicates that the firing temperature was certainly higher than 850°C.

^{29}Si NMR spectroscopy is also a powerful tool for detecting various structural environments and distortions in silicates and aluminosilicates due to the relation between chemical shift and structure.

Figure 15, left, shows the ^{29}Si MAS spectrum of the fragment of pottery from Acquapendente (Italy) (a) compared with the spectrum of a fragment from Sonqi Tino (Sudan) (b). Although both spectra are rather broad, they differ from each other. For example, a very sharp and intense resonance of quartz is observed at -107 ppm in the fragment from Acquapendente, whereas this resonance is less intense and broader in the fragment from Sonqi Tino. To summarize, ^{27}Al MAS, MQMAS and ^{29}Si MAS spectra may be used with other techniques to discriminate different types of clays and to obtain information about firing temperature.

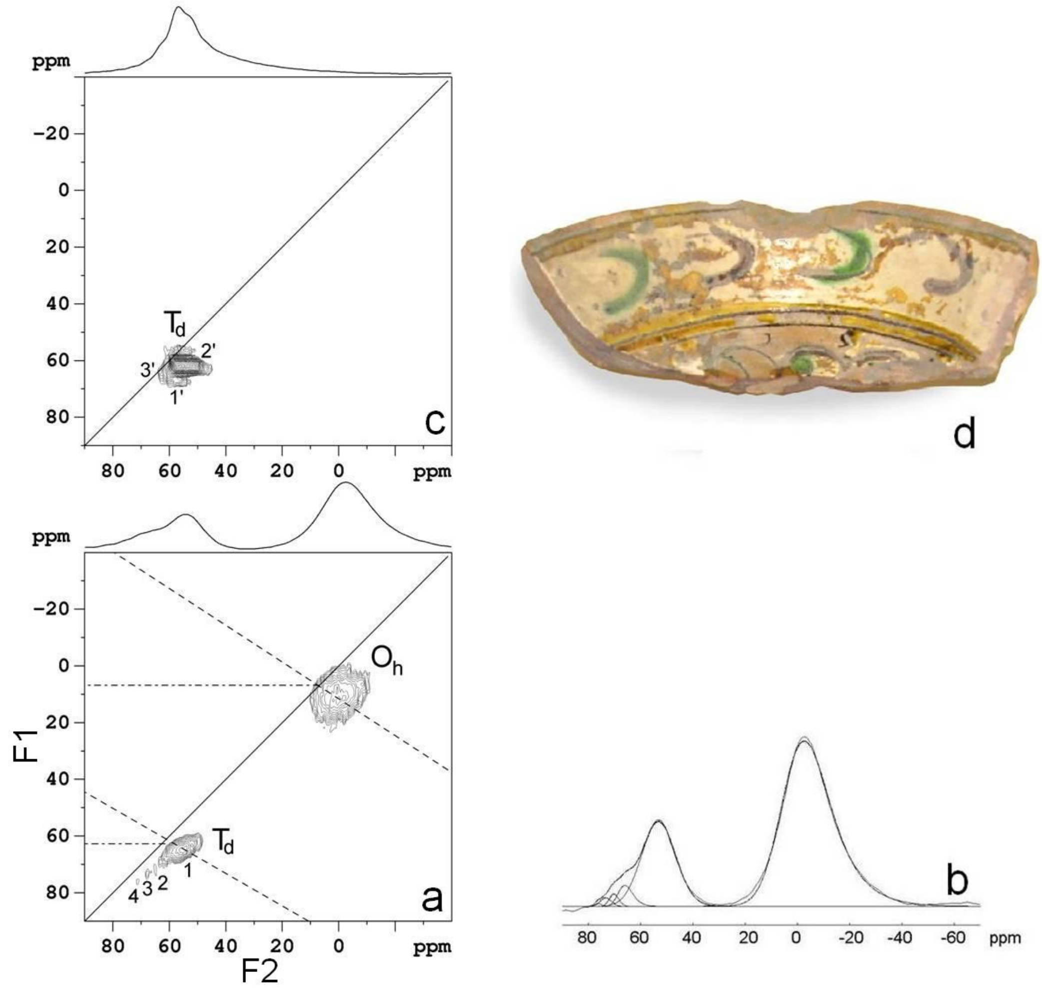

Figure 14. Sheared ^{27}Al 3QMAS spectra at 104.13 MHz of raw clay (a) and a fragment of ancient pottery from Acquapendente, Viterbo district, Italy (c). Experimental and deconvoluted ^{27}Al MAS spectra of the raw clay (b). A piece of pottery from Acquapendente (d) kindly donated by *Archeoclub* (Acquapendente Section). One of the main activities of the association is the valorization and tracing of local pottery.

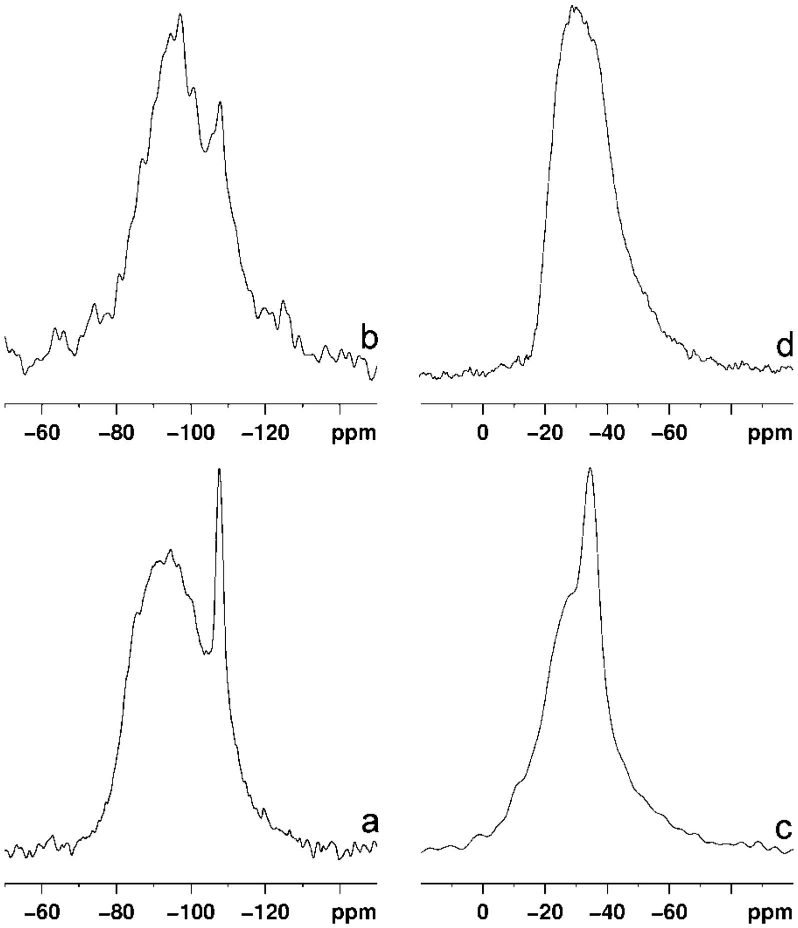

Figure 15. ^{29}Si (left side) and ^{23}Na (right side) MAS spectra at 79.49 MHz and 105.84 MHz, respectively, of a fragment of pottery from Acquapendente (Italy) (a, c), and a fragment of pottery from Sonqi Tino (Sudan) (b, d).

Although rarely applied, ^{23}Na MAS NMR may also be informative for characterizing pottery. Figure 15, right, shows the ^{23}Na spectrum of the fragment from Acquapendente (c), compared with that from Sonqi Tino (d). The spectrum of the former fragment is sharp, while the spectrum of the latter sample is typical of a more disordered and/or amorphous material. Both spectra deserve further investigation.

The porous structure of pottery depends on the heating-cooling cycles, raw material, and production technology used. Study of pore size distributions in ceramics may therefore be of interest for characterizing pottery. Portable NMR instruments allow measurement of relaxation times at different depths in water-saturated ceramic material. Because the distribution of relaxation times, especially transverse relaxation times, is closely related to pore size distribution in ceramic material, portable NMR allows the mapping of porosity [65]. By this technique, layers with different pore size distributions may be detected.

Figure 16 reports the transverse relaxation time distribution measured at different depths in the water-saturated pottery fragment from Acquapendente: 0.5 mm (a), 1.5 mm (b), and 3 mm (c). The distributions show three peaks corresponding to small, medium, and large pores in the ceramic material.

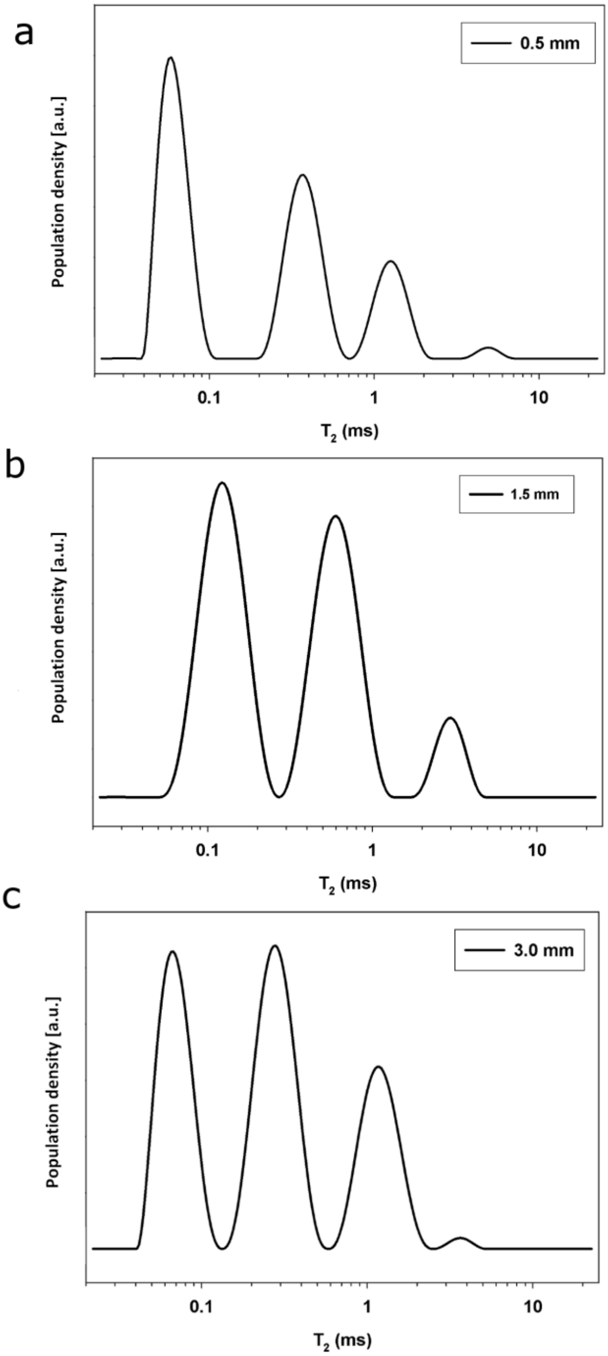

Figure 16. Distribution of transverse relaxation times measured at depths of 0.5 (a), 1.5 (b), and 3 mm (c) in a water-saturated fragment of pottery from Acquapendente.

At 0.5 and 3 mm of depth the maxima are centered at T_2 most probable values of 0.07, 0.3, and 1.3 ms, whereas at a depth of 1.5 mm the porosity seems slightly different with the maxima centered at longer values, 0.1 ms, 0.6 ms, and 3.1 ms respectively.

Recently, T_1-T_2 correlation experiments have been also employed to study water-saturated archaeological ceramics from Italian archaeological sites [66,67]. Basically these experiments generate maps of the spin population distribution on the basis of relaxation times.

As a matter of fact, the actual potentiality of NMR in obtaining a sort of fingerprinting of the structure of pottery and in recognizing mineralogical phases in the ceramic body as a function of the production technology and firing process in ancient times, deserves further investigation. Because of the widespread use of ceramic materials, information obtained with this method might also be of interest in the field of the industrial ceramic production.

Characterization of Tuffs from Ancient Monuments

Volcanic tuffs are rocks composed of a consolidated ash matrix containing different amounts of lithic (xenoliths of sedimentary origin and lava fragments), vitric (pumice fragments and glass shards), and crystal clasts (primary and accessory minerals). Large differences in texture and chemical and petrographic composition are observed among tuffs. In fact, these rocks are formed from pyroclastic flow or plinian and surge and fall deposits, and numerous factors, such as the nature of the primitive magma, the deposition and compaction of the emitted material, and post-depositional processes concur to define the final product. Besides the relative content of clasts, the nature of the matrix also differs, and a distinction is made between welded and lithified tuffs. The term “welded” tuffs identifies rocks bonded by sintering and compaction of glass in the matrix. Because the welding process occurs when the deposit is still hot and plastic, large vitric scoriae, deformed into disk-shaped lenses known as *fiamme*, often occur in these tuffs. The term “lithified” tuffs applies to rocks whose original ash matrix has undergone such profound chemical alteration that authigenic minerals, mainly composed of zeolites, act as binding agents [68].

Both welded and lithified tuffs have been extensively utilized as building materials since early times, mainly because they are light and easy to cut and shape. Tuffs have been used in the construction of monuments and artifacts representative of the cultural heritage of northern Latium (Italy) since the 6th century BC.

Recently, a multi-technique study including solid state NMR spectroscopy was carried out to characterize tuffs from different sources [69]. Samples were investigated by ^{27}Al, ^{29}Si, and ^{1}H MAS NMR. ^{27}Al MAS spectra of tuffs showed a peak centered at about 60 ppm typical of Al in a tetrahedral environment, but with tailing at higher frequency (Figure 17).

^{27}Al 3QMAS maps allowed spectral resolution to be improved, and isotropic chemical shift as well as second order quadrupolar effect to be obtained and used as initial guesses in the deconvolution procedure for experimental MAS spectra [70].

As an example, Figure 18 shows the 3QMAS maps of two tuffs, one lithified (a) and the other welded (b), both from the Etruscan Necropolis of Norchia, Viterbo (Italy) dated between 4th and 2nd century BC. Note that the map of the welded tuff also shows a weak peak at about 5 ppm ascribed to Al in an octahedral environment, possibly due the presence of clays.

In the case of lithified tuff, the relative content of Al in the crystalline and amorphous phase was determined from the respective integrals of the two phases by deconvoluting ^{27}Al MAS spectra. In the case of welded tuff, the spectra were fit to a model used for amorphous/disordered materials that accounts for chemical shift and quadrupolar coupling constant distributions [70].

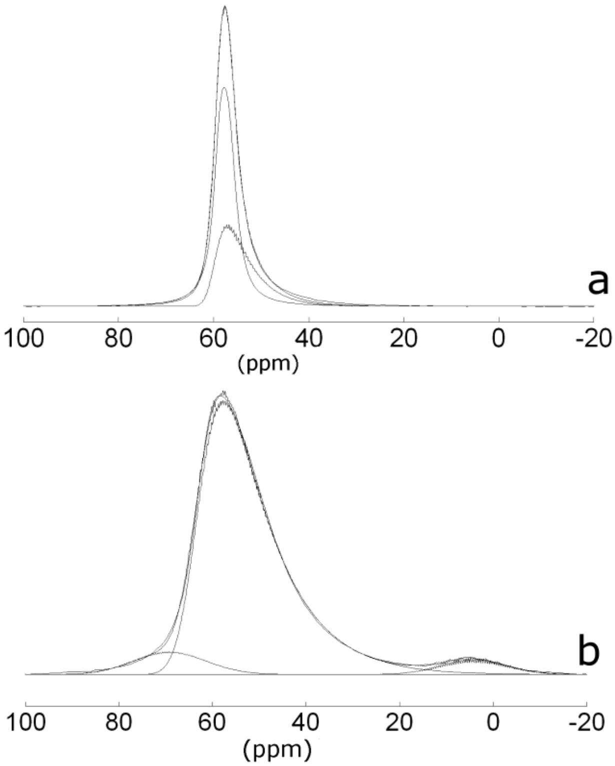

Figure 17. ^{27}Al MAS spectra at 104.13 MHz of a lithified (a) and a welded (b) tuff from the Etruscan Necropolis of Norchia. The deconvoluted spectra are superimposed on the experimental ones.

The prevalent zeolitic or glassy nature of the matrix can be assessed by ^{29}Si MAS NMR. In fact in the zeolite-cemented tuff, the intense peaks of zeolites are prominent in the spectrum (Figure 19a), whereas broad and unresolved peaks are observed in that of the welded tuff, see Figure 19b.

Figure 19c shows the spectrum of a zeolite-cemented tuff obtained from the surface of a tomb in the necropolis. This tuff did not appear very different from the intact material, although it was so mechanically weak that it crumbled in the hand.

Tuffs exposed to atmospheric agents undergo chemical transformation, resulting in progressive changes in their physical, chemical, and geological properties. Frequent penetration and evaporation of water from stone material is known to be one of the primary processes causing alteration of the mineral composition and matrix of tuff. These surface alterations cause a progressive loss of stone fragments. The lithified tuff found in the Necropolis is known to be highly susceptible to degradation due to wet-dry cycling because it is highly porous, mechanically weak, and cemented by zeolites. The weathered tuff was investigated by ^{29}Si MAS NMR to see if alteration had also affected the order-disorder of cementing zeolites.

The deconvolution of ^{29}Si spectra of the two lithified tuffs, one unweathered (Figure 19a) and the other weathered (Figure 19c), allowed the relative integrals of all peaks to be obtained. The integral of resonances generated by Si-tetrahedral sites (SiO_4) linked to a different number of Al atoms was used to calculate the Si/Al ratio [71].

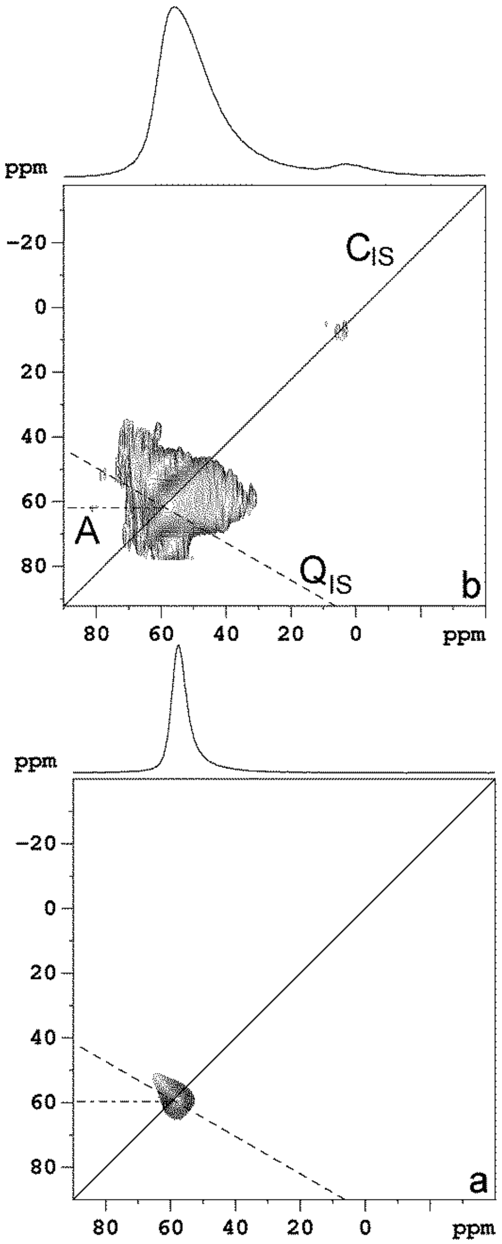

Figure 18. Sheared 27Al 3QMAS spectra at 104.13 MHz of a lithified (a) and a welded tuff (b) from the Etruscan Necropoli of Norchia, Viterbo (Italy).

In the case of the unweathered lithified tuff, Si/Al was found to be 2.42, whereas a definitely lower value of 1.98 was found for the naturally weathered lithified tuff, indicating that weathering had caused Si – Al substitutions in the zeolitic component. In conclusion, the Si/Al ratio obtained by ^{29}Si NMR analysis differentiated well preserved lithified tuffs and lithified tuffs in which natural weathering had occurred.

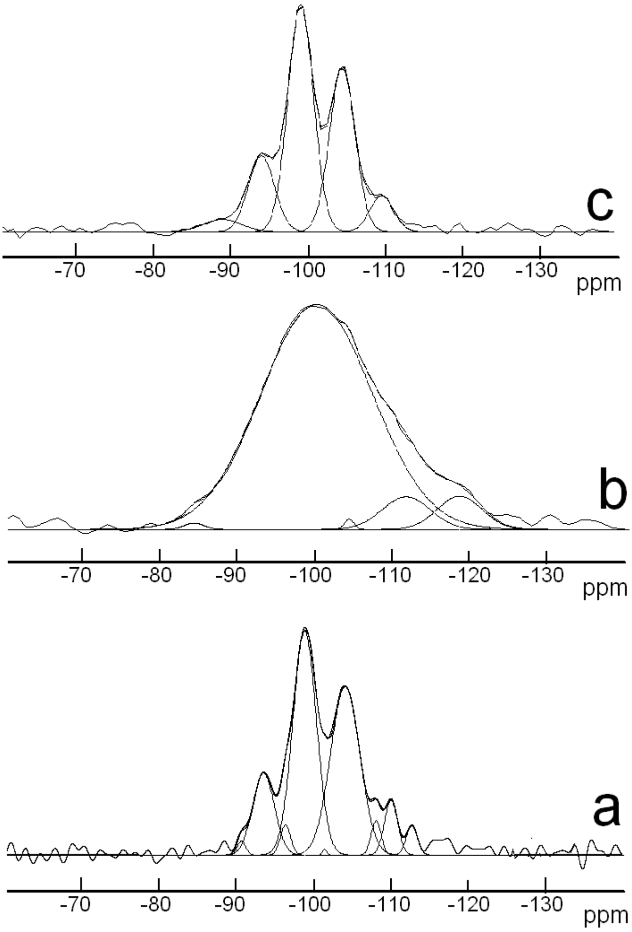

Figure 19. ^{29}Si MAS spectra of tuffs from Etruscan Necropolis of Norchia. Experimental and deconvoluted spectra of a lithified tuff (a), a welded tuff (b), and a weathered lithified tuff (c).

Parchment

Parchment has been used for centuries as a writing material, bookbindings, scrolls, maps, and substrata for paintings. Although parchment has continued to be used primarily for official documents, it ceased to be a primary choice for artists by the end of 15th century when it was largely replaced by paper. It is obtained from wet, unhaired, and limed animal skin (calfskin, sheepskin or goatskin) by drying on a stretching frame. After flaying, the skin is soaked in water to remove blood and grime. It is different from leather, being limed but not tanned. As a consequence it is very sensitive to changes in relative humidity.

Parchment consists mostly of collagen, which contains varying amounts of amino acids, with Gly, Pro, Ala, Hyp, and Glu being the most abundant residues. The structure of collagen has been described as a right-handed triple-helix with the three individual protein strands in the left-handed polyproline-II helix conformation [72]. The three strands of the helices are staggered by one residue, allowing for interchain hydrogen bonds. Gly-Pro-Hyp is the most common repeating sequence involved in the formation of the triple-helix conformation.

Large parchment collections in varying degrees of preservation are found in museums, archives, and in public and private libraries. Gelatinization of parchment may occur spontaneously even during normal storage conditions, leading collagen to lose its ordered triple-helix conformation. As a product of collagen denaturation, gelatin is regarded as a more disordered state of collagen, partially or completely lacking the tertiary, secondary, and to some degree, the primary structure of collagen. Gelatin may degrade further by hydrolysis of peptide bonds and crosslinks.

Solid state NMR was applied to characterize parchment and to evaluate the extent of degradation of historical parchments [73-75]. The ^{13}C CPMAS spectrum of a sample of historical parchment, dated 17th century, is shown in Figure 20. The assignment of the spectrum was carried out on the basis of assignments of amino acids, peptides and proteins reported in the literature [76,77]. Sometimes additional peaks assigned to calcite and aragonite were observed at 168.7 and 171 ppm (relative to TMS) respectively. The peak at 33 ppm, observed as a shoulder, was assigned to Val C-3, however an additional strong peak at the same chemical shift was also observed in the spectrum. Measurements of proton relaxation time in the rotating frame demonstrated that this peak is not from collagen carbons but belongs to a different proton reservoir compartment [73]. This additional peak was assigned to chain carbon of fatty acids.

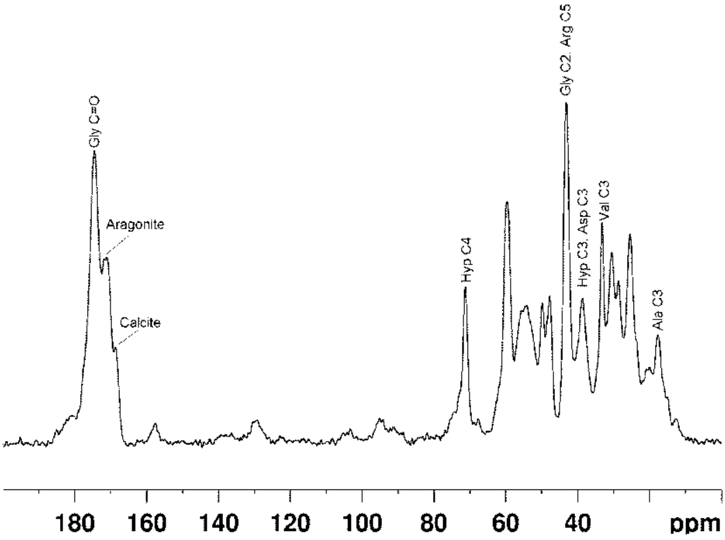

Figure 20. ^{13}C CPMAS NMR spectrum at 100.13 MHz of a 17th century parchment sample from a private collection, along with the assignment of few resonances.

The intensity ratio between the peak at 33 ppm and that at 43 ppm assigned to Gly C-2 and Arg C-5 allowed semi-quantitative comparison of lipid content between samples. In fact, these peaks correspond to the most intense signals of lipid and collagen, respectively. Comparing the spectrum of aged parchment with the spectra of well preserved collagen and gelatin, no significant changes in peak positions were detected, and no new peaks appeared as a result of ageing, whereas significant line broadening occurred on gelatinization. Well preserved collagen and gelatin are considered to be reference samples of well preserved and fully degraded parchment, respectively. In order to quantify the extent of degradation, Aliev [73] introduced a disordered ranking parameter R_d defined as:

$$R_d = \frac{\Delta \nu_{1/2} - \Delta \nu_{1/2}^{C}}{\Delta \nu_{1/2}^{G} - \Delta \nu_{1/2}^{C}} \tag{3}$$

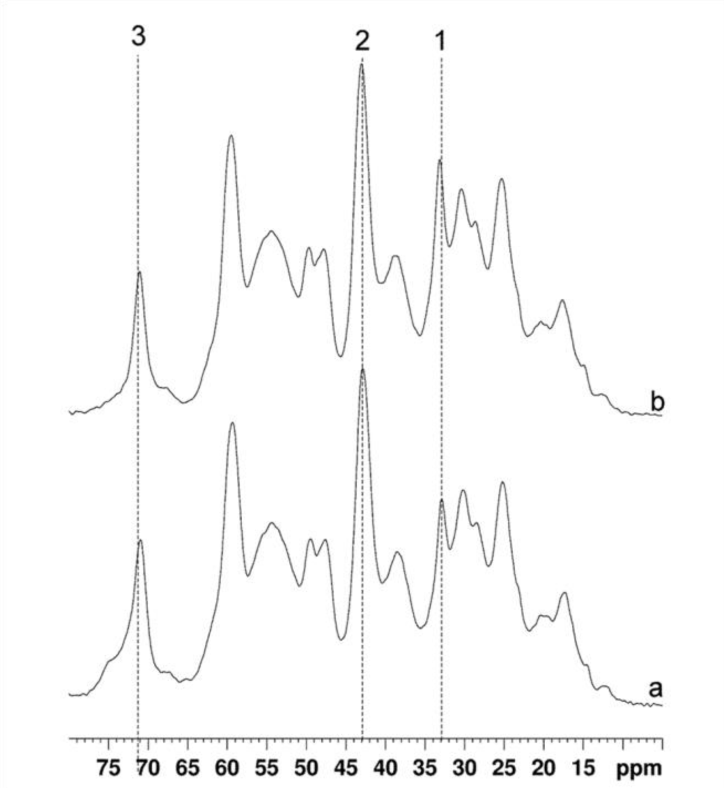

Figure 21. 5 to 80 ppm region of ^{13}C CPMAS NMR spectra at 100.13 MHz of two 17th century parchment samples.

where $\Delta \nu_{1/2}$ is the linewidth of the peak at 71 ppm assigned to Hyp C-4 and $\Delta \nu_{1/2}^{C}$ and $\Delta \nu_{1/2}^{G}$ are the line widths measured for collagen in new parchment and gelatin, respectively. By definition R_d ranges between 0 and 1 for historical parchments in their pre-gelation state, with higher R_d values corresponding to a higher level of degradation. With respect to gelatin, hydrolyzed collagen is a mixture of low molecular weight polypeptides, and may therefore be regarded as degraded gelatin, with $R_d > 1$ indicating the extent of gelatin disintegration. As a matter of fact, R_d obtained from the ^{13}C CPMAS spectrum is an index of parchment degradation.

Figure 21 shows the 5–80 ppm spectral region of two 17th century parchment samples.

According to the previously reported assignment [73], a semi-quantitative comparison of the lipid content of the two samples is obtained by the ratio of the intensities of peak 1 at 33 ppm I_1 and peak 2 at 43 ppm I_2. The I_1/I_2 ratio was found to be 0.72 in spectrum (a) and 0.59 in spectrum (b). The disorder ranking parameter R_d calculated from equation (3), where $\Delta\nu_{1/2}$ is the line width of peak 3, was found to be 0.4 in spectrum (a) and 0.31 in spectrum (b).

As a rule, to evaluate the state of degradation of historical parchment from the ^{13}C CPMAS spectrum, the spectra of reference samples, i.e. new parchment and gelatin, must also be collected to obtain $\Delta\nu_{1/2}^{C}$ and $\Delta\nu_{1/2}^{G}$.

Paper

Paper is one of the oldest precious man-made materials. For centuries paper has been used to record important cultural achievements all over the world. The deterioration of paper as it ages is a serious problem for archival communities throughout the world. This material is often exposed to usage or storage conditions that affect its chemical stability. Paper degradation is due to reactions inducing physical and chemical changes in its polymeric matrix. Degradation occurs through acid hydrolysis, oxidation, cross-linking, ring opening, chain scission and variations in the amorphous/crystalline ratio. These reactions are affected by synergic action of external factors such as light, temperature, humidity, oxygen and micro-organisms. Paper deterioration is also related to its quality: modern paper is usually more vulnerable to degradation than older paper. The quality of ancient paper is always particularly high as it was manufactured from cotton rags containing few impurities. Due to an enormous increase in demand, after 1850 paper was produced by an industrial manufacturing process and its quality worsened. Wood pulp was added to cellulose, together with various fillers, sizing, dyes, pigments and metal ions. The animal glue originally used for sizing was substituted by rosin and alum. These industrial processes considerably reduce the physical-chemical and mechanical properties of paper, damaging its structure, increasing its brittleness and causing an overall loss of material quality.

High quality paper is a two-component material consisting of almost equimolar quantities of cellulose and water, with traces of impurities. The interaction between water and cellulose can be studied using ^{1}H pulsed low resolution NMR. The free induction decay (FID) of paper shows a fast decaying component due to the polymeric matrix, and a slow decaying one due to confined water (Figure 22a).

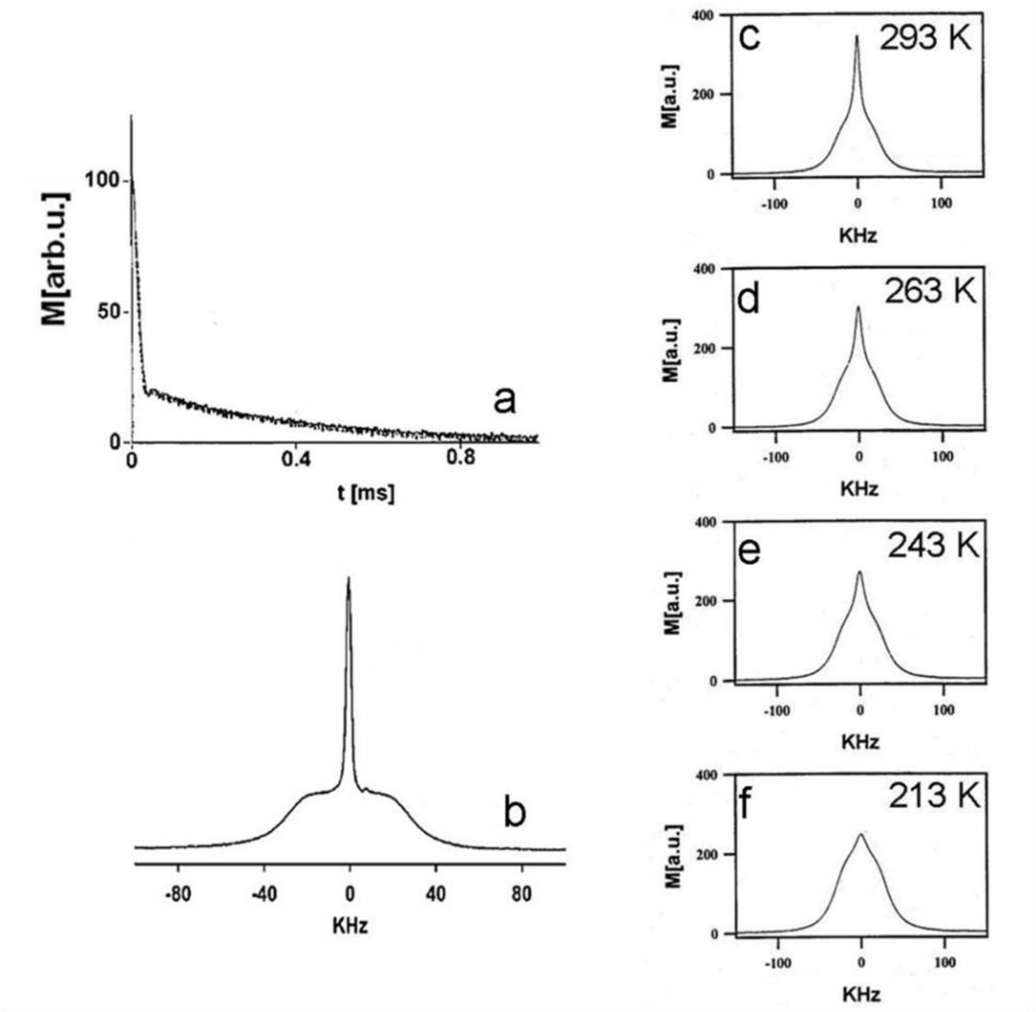

Figure 22. Linters paper. Free induction decay: the fast decaying component is from cellulose, the slow decaying one is due to water (a). ^{1}H proton wide line NMR spectrum: the broad line is from cellulose (line width at half height about 64 kHz), and the sharp line is due to bound water (line width at half height about 1.5 kHz) (b). ^{1}H wide line NMR spectra at 81 MHz collected at different temperatures: 293°K (c), 263°K (d), 243°K (e), 213°K (f). The sharp water peak progressively broadens as the temperature decreases.

After Fourier transformation, see Figure 22b, the cellulose component appears as a broad hump, on which a rather sharp resonance due to water is observed. To obtain the molar ratio between the water and the polymeric component, FID may be fit to a function obtained by adding a Gaussian and an exponential function [78], the former function accounting for the cellulose component, the latter for the water:

$$Y = C_0 + \left[W_{cell} \exp\left(-\frac{t^2}{G_{cell}^2} \right) \right] + \left[W_w \exp\left(-\frac{t}{E_w} \right) \right] \tag{4}$$

where W_{cell} is the spin population of cellulose, W_w is that of water, C_0 is the average noise level, and $E_w = T_2^*$, T_2^* is the transverse relaxation time obtained from fitting FID, known, however, to be always shorter than T_2 measured with the CPMG pulse sequence [11]. In the case of the Gaussian function G(t), a characteristic decay time can be defined as the time T_2 required for G(t) to decay to 1/e of its starting value G(0), and therefore $G_{cell}=T_2$. The water/cellulose molar ratio was found to be characteristic of different types of well preserved paper. As an example [79], in good quality paper this ratio was found to be about 0.9, whereas in low quality paper this ratio was about 1.7.

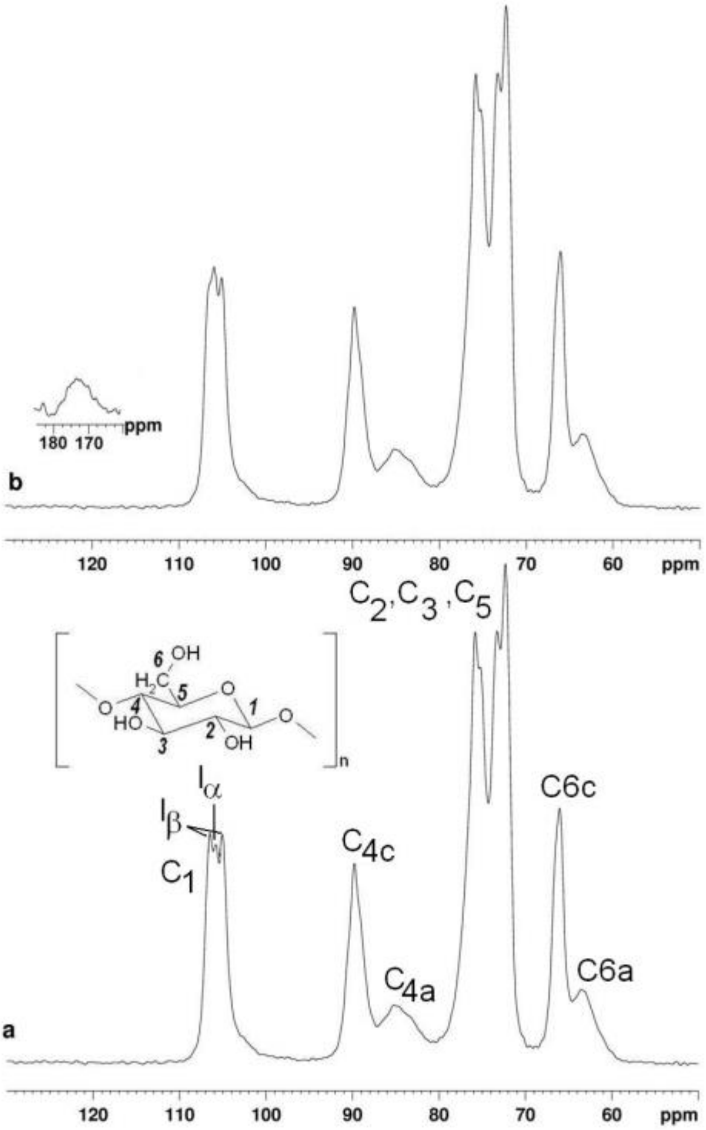

Figure 23. ^{13}C CPMAS NMR spectrum at 100.13 MHz of Linters paper with resonance assignments (a). ^{13}C CPMAS NMR spectrum of a sample of ancient deteriorated paper from a book dated 1662 (b). Insert shows the resonance of carboxyl carbons with vertical multiplication.

At room temperature, the water resonance of paper is a sharp peak on the broad cellulose component (Figure 22c). With decreasing temperature, the water resonance progressively broadens, but can still be observed at 213°K, indicating that the freezing point of the bound water in paper is below 213°K. The freezing point is related to the nature of hydrogen bonds between the water and the cellulose. In general, the physical properties of a liquid confined in pores are different from those of the bulk liquid. In particular, the melting point of confined liquid is depressed in relation to pore size [80]. Paper can therefore be treated as a porous system with a mobile species, water, embedded in a rigid polymeric matrix [81].

The degradation of paper and generally of cellulose-based materials can be monitored with ^{13}C CPMAS NMR spectroscopy. In fact, the ^{13}C CPMAS spectrum may be regarded as the "fingerprint" of the solid component of the paper. By way of example, the spectrum of a sample of pure cellulose is reported along with the assignment of carbon resonances (Figure 23a).

The sharp resonances are due to long fibers of cellulose in crystalline domains, while the broad ones are due to cellulose in amorphous domains. In particular, the resonance at 106.3 ppm is that of the anomeric carbon atom C_1, those at 90.3 and 66.8 ppm are of C_{4c} and C_{6c}, respectively, in crystalline domains, while those at 85.4 and 64.5 ppm are of C_{4a} and C_{6a}, respectively, in amorphous domains. The shape of resonance C_1 clearly indicates the presence of microcrystalline polymorphous forms of the native cellulose I_α and I_β [82,83].

A cause of paper deterioration is oxidation occurring in the cellulose matrix. By way of example, the ^{13}C CPMAS spectrum of a sample of paper from a book dated 1665 is shown in Figure 23b. In the 60-110 ppm range, the resonances characteristic of cellulose with a good degree of crystallinity are observed; however, the broad weak signal at about 175 ppm due to carboxyl carbons indicates oxidation in the cellulose matrix [84]. Oxidation reactions in cellulose involve the primary and secondary hydroxyl groups of the pyranose ring, leading to carbonyl and carboxyl groups, which absorb UV and visible radiation. Both carbonyl and carboxyl groups are chromophores and their formation is responsible for the yellowing of paper. The oxidation reaction may also be accompanied by opening of the pyranose ring. In both cases, the glycosidic bond becomes weaker and the eventual formation of carboxylic acids increases the acidity of the paper. This leads to depolymerization of cellulose and a general worsening of physical and mechanical properties.

Papyrus is another early writing material, produced with the fibers of *Cyperus papyrus*. The ^{13}C CPMAS spectrum of a sample of modern papyrus is shown in Figure 24a. Besides the cellulose, the spectrum shows a considerable amount of lignin. Figure 24b shows the spectrum of an ancient papyrus specimen from the archeological site of Antinoe, Egypt. The degradation of lignin is evident from the broadening of all resonances, whereas the cellulose component is in a good state of conservation as it has the same shape as the spectrum of modern papyrus (Figure 24).

Deterioration of historic paper in libraries and archives is responsible for an enormous loss of documents. To understand and explain the degradation processes occurring in cellulose-based materials, many studies have been focused on monitoring paper weathering. Because natural weathering is too slow to observe changes in a reasonable time frame, methods of accelerated ageing under physical or chemical conditions have often been used to speed up weathering in cellulose-based materials.

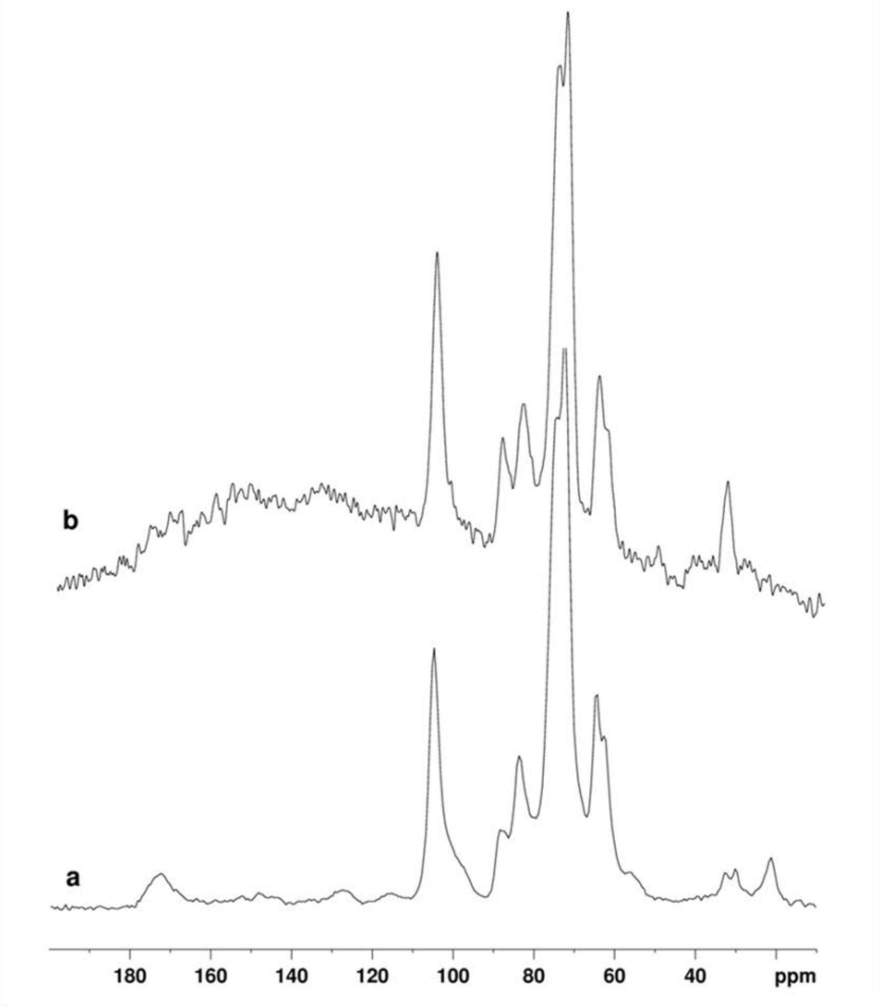

Figure 24. ^{13}C CPMAS NMR spectra at 100.13.MHz of modern papyrus (a) and ancient papyrus from the archaeological site of Antinoe, Egypt (b).

Whatman paper and papyrus have been studied before and after physical and/or chemical aging [85]. In Figure 25, the ^{13}C CPMAS spectrum of untreated Whatman paper is compared with those of oven-aged paper (a), solarbox-aged paper (b) and paper oxidized with $NaIO_4$ (c).

Spectra of weathered samples showed a modest broadening of peaks. The spectrum of solarbox-aged paper showed a detectable amount of carboxyl groups. The spectrum of the oxidized sample showed oligomers. Deconvoluting the spectra recorded before and after aging, we obtained the integrals of all peaks, allowing quantitative evaluation of modifications occurring in the cellulose matrix. In this study, relevant data were the integral of the broad shoulder between 90 and 100 ppm that provided the amount of cellulose oligomers, the ratio between the integrals of C_{4a} and C_{4c} that gave the crystalline/amorphous ratio, and the integral of the carboxyl group peak centered at 175 ppm. The crystalline/amorphous ratio was found to be 0.57 in the untreated sample, whereas after weathering in the oven and solarbox it decreased slightly to 0.53 and 0.47, respectively, indicating a modest decrease in the crystalline cellulose fraction after aging. The quantity of oligomers was 2% in the untreated paper and 4% in samples weathered in the oven and solarbox. In the oxidized sample the crystalline/amorphous ratio decreased slightly to 0.52, whereas the quantity of oligomers increased to 7.8%.

In the case of papyrus, oxidation mostly affected the cellulose matrix, whereas physical ageing, particularly weathering in the solarbox, mostly affected the lignin matrix. In Figure 26, the spectra of untreated and weathered papyrus are reported on an expanded vertical scale to highlight the modifications in lignin structure.

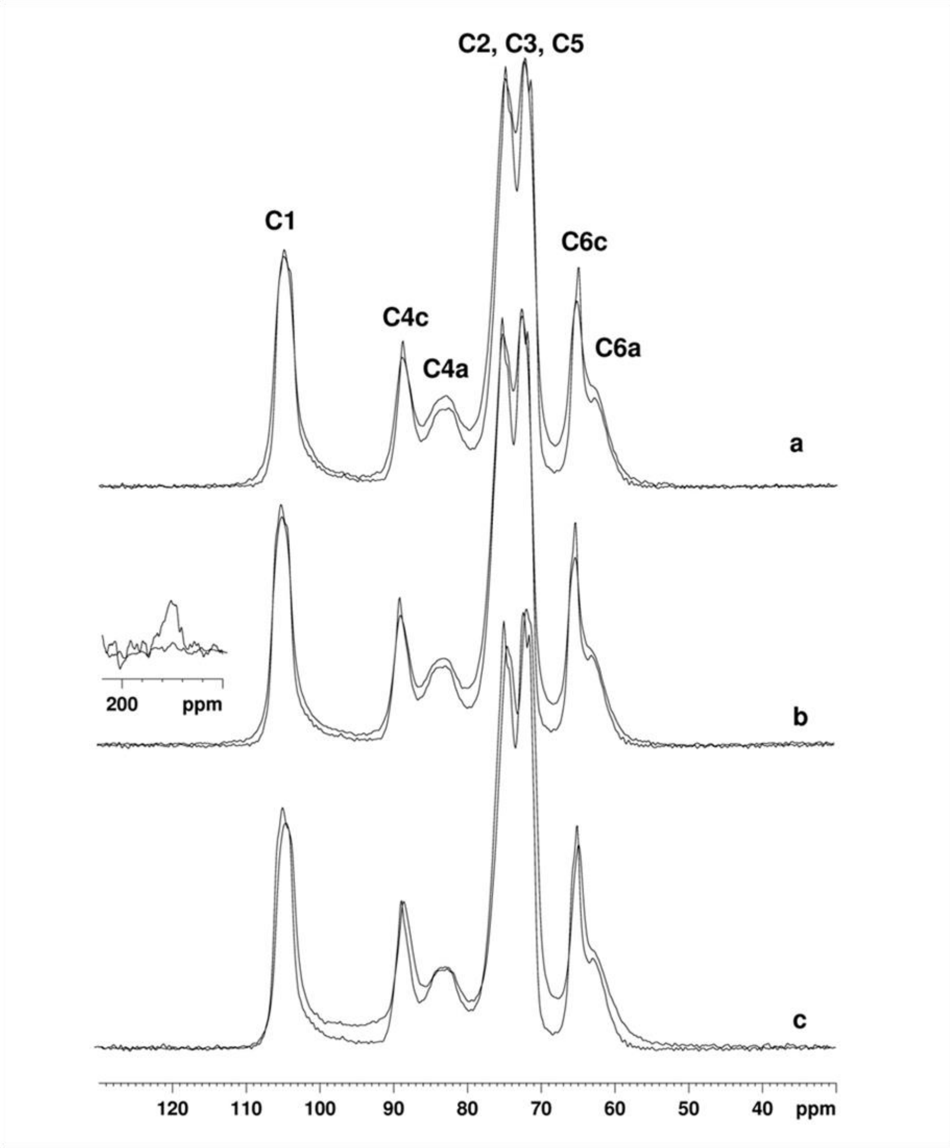

Figure 25. ^{13}C CPMAS NMR spectrum at 50.13 MHz of untreated Whatman paper compared with the spectra of oven-aged paper (a), solarbox-aged paper (b) and paper oxidized with $NaIO_4$ (c). Adapted from [85].

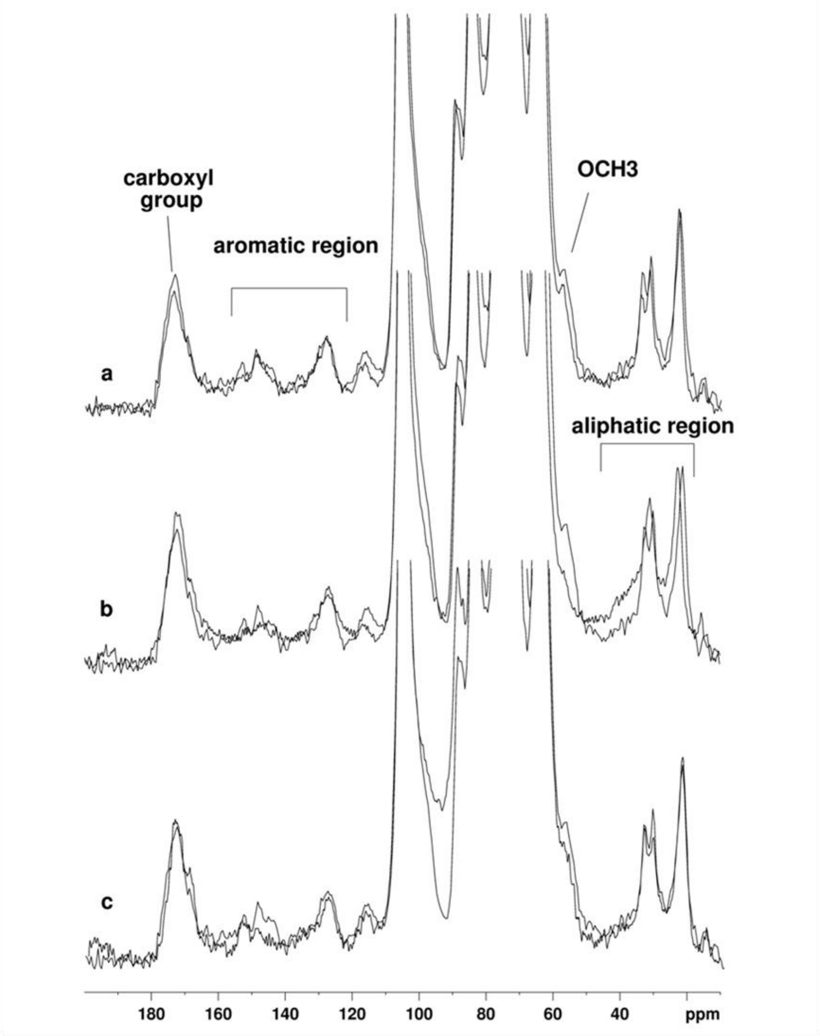

Figure 26. ^{13}C CPMAS NMR spectrum at 50.13 MHz of papyrus compared with the spectra of oven-aged papyrus (a), solarbox-aged papyrus (b) and papyrus oxidized with $NaIO_4$ (c). Adapted from [85].

The ^{13}C CPMAS spectra of papyrus after ageing in the oven and solarbox revealed a broadening of some aromatic carbon resonances and a net reduction in the intensity of OCH_3 groups. These modifications were much less evident in the sample weathered in the oven and in that oxidized with $NaIO_4$. A broadening of peaks in the aliphatic region between 15 and 40 ppm was also observed in the spectrum of the solarbox-weathered sample.

The effect of physical and chemical ageing processes was also monitored by NMR relaxometry, using both conventional and unilateral devices [86]. With this technique the longitudinal and transverse relaxation times T_1 and T_2 can be measured. By way of example, T_2 distributions measured by unilateral NMR in untreated and weathered Whatmann paper and papyrus are reported in Figure 27a and b, respectively. As degradation occurred, the maximum of T_2 distributions shifted to shorter values in all samples. The most pronounced shift was found in solarbox-weathered and oxidized samples, indicating that both treatments affected the samples. On the contrary, oven weathering had little effect on samples.

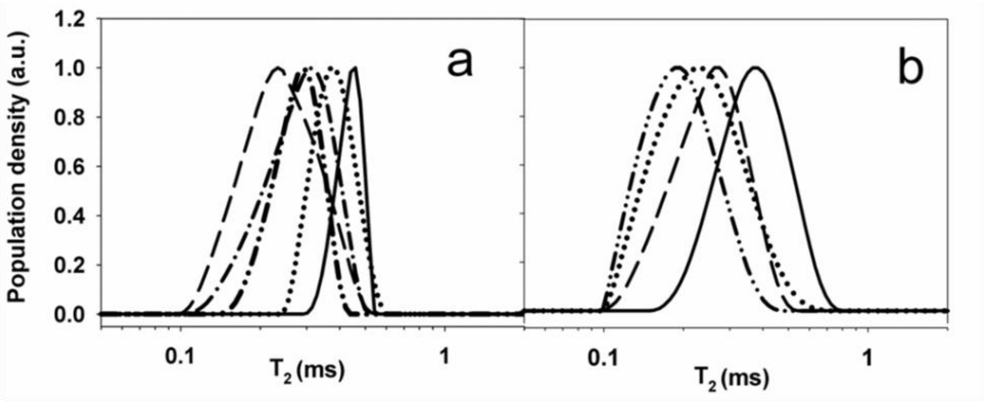

Figure 27. T_2 relaxation time distributions meausured by portable unilateral NMR on Whatman (a) and papyrus (b). Untreated samples (solid line), oven-weatherd samples (dotted line), solarbox-weathered samples (dash-dot-dot line) and samples oxidized with $NaIO_4$ (long dashed line). Adapted from [85].

Studies have been carried out on polymers to consolidate and protect oxidized paper [87]. Ethylacrylate (EA), methylacrylate (MA) and methylmethacrylate (MMA) were grafted onto cellulose by vaporised acrylic monomers. To simulate the ageing of paper, chemical oxidation with $NaIO_4$, a specific oxidizing agent, was performed before grafting. The oxidation process was needed to obtain dialdehyde groups where the acrylic monomers could be grafted. ^{13}C CPMAS NMR spectroscopy was used to follow the oxidation process in the paper and to confirm grafting on oxidized paper. At short oxidation times the spectra showed weak resonance at about 202 ppm, ascribed to dialdehyde groups. After prolonged oxidation, the spectra showed a general broadening of all resonances of cellulose, along with a substantial increase in resonances due to oligomers. Spectral deconvolution was used to quantify oligomers and the crystalline/amorphous ratio as a function of oxidation time. ^{13}C CPMAS spectra also made it possible to demonstrate the grafting of EA, MA and MMA on oxidized cellulose chains.

Fungal growth on paper is another cause of deterioration in archives and libraries. Fungi growing on paper may produce different hydrolytic enzymes, such as cellulases and ligninases [88]. This enzyme activity dissolves paper components by different mechanisms. Cellulose degradation arising from different types of fungi involves the synergic action of enzymes, such as exoglucanases, endoglucanases, and β-glucosidases. Biodeterioration of lignin, which occurs in most paper manufactured after 1850, depends on a complex of enzyme activities, such as lignin peroxidases, Mn-peroxidase and laccase. Ligninase and cellulase act in synergism to completely dissolve paper components. In order to study the effect of fungal attack on historical documents, a purified enzyme with a well defined activity, endoglucanase, was used on paper. NMR relaxometry proved valuable in assessing paper degradation, detecting early enzyme attack not observable by other methods [89]. Three series of samples were incubated with 5 and 10 units of cellulase of *Aspergillus niger* in citrate-phosphate buffered solutions (pH 4.0, 5.0, and 6.0). Three paper strips were also soaked in the buffered solutions without the enzyme and used as control. After soaking, all samples were dried at 60°C for 24 hours. Before subjecting the paper to enzyme attack by *Aspergillus niger,* the activity of the enzyme was tested on carboxymethylcellulose (CMC). One unit of enzyme was found to release 1.0 mole of glucose from CMC in 1h at pH 5 and

37°C. The activity of this enzyme generally decreases with increasing pH, and is no longer effective at pH > 6.

The most sensitive parameter to monitor the effect of enzyme attack by NMR was found to be transverse relaxation time T_2. Before and after enzyme attack on Linters paper and woodpulp, three T_2 components contributed to CPMG decay, namely slow, intermediate and fast relaxing components. The slow relaxing component was 9.0 ± 0.5 ms, the intermediate 0.1 - 0.5 ms and the fast 0.05 - 0.1 ms. The fastest component was due to tightly bound water, which was involved in a spin-diffusion process with the polymers (cellulose, hemicellulose and lignin) or was close to paramagnetic centres. The slowest component found in all samples did not occur in unsoaked samples. Thus this component was ascribed to a small amount of residual free water after soaking. The fastest and slowest components were found to be unaffected by enzyme attack. The intermediate component was much shortened after enzyme attack (Figure 28). In fact, T_2 values were about 0.3 – 0.4 ms in control samples and only about 0.1 ms in paper after enzyme attack. As well, the intermediate component clearly lengthened with increasing pH in control samples, whereas in samples incubated with the enzyme, it was only slightly affected by pH (Figure 28).

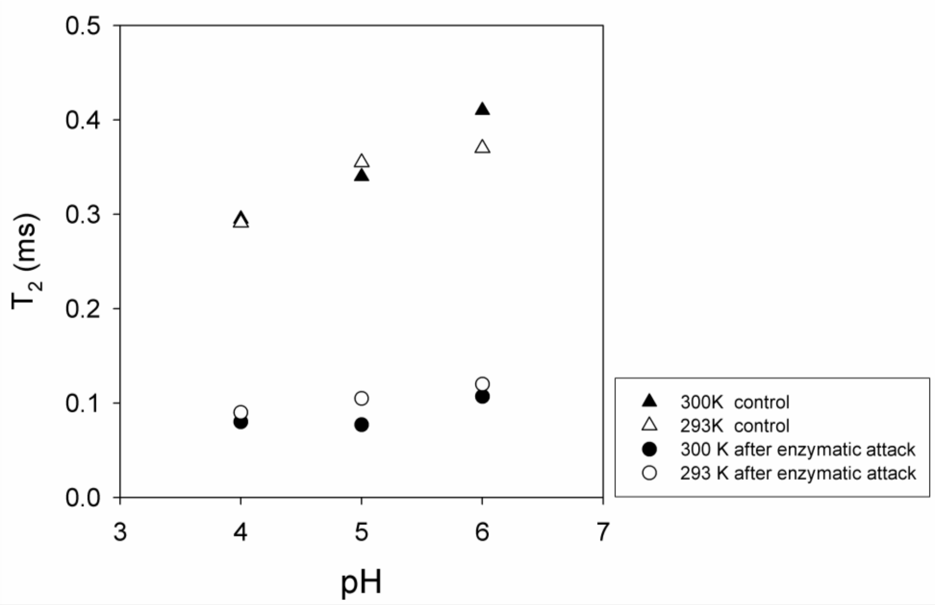

Figure 28. T_2 intermediate component measured in Linters paper used as a control (triangles) and in paper after enzyme attack (circles). Adapted from ref. [89].

Because the microbial degradation of paper is one of the most serious and unappreciated sources of damage to library and archived materials, it would be important to develop measures against this type of degradation. The protective efficacy of commercial waterborne polyurethanes against enzyme attack was recently tested on several types of paper [90]. The evolution of structural and physicochemical characteristics of uncoated and coated paper samples, before and after biodegradation, was monitored by several techniques, including ^{13}C CPMAS NMR spectroscopy. ^{13}C solid state NMR allowed the detection of structural modifications in the cellulose matrix of uncoated paper and paper coated with polyurethanes after different times of incubation with the enzyme complexes (cellulosomes). After 2 and 5 days of incubation, the cellulose structure of uncoated paper was essentially unchanged, but after 10 days of incubation, damage to the cellulose matrix was evident (Figure 29).

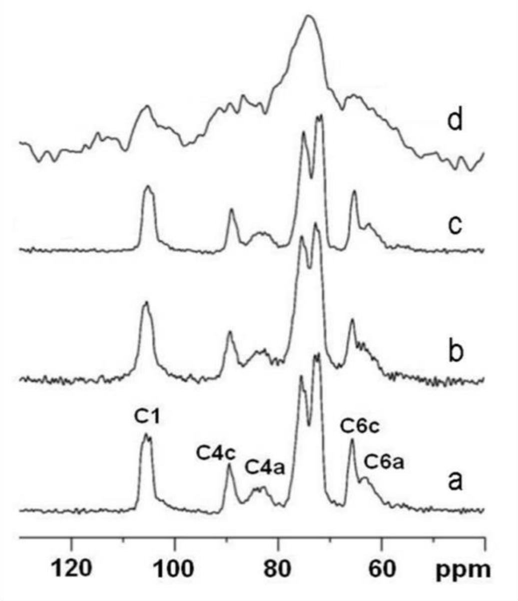

Figure 29. ^{13}C CPMAS NMR spectra at 50.13 MHz of paper: not incubated (a), incubated with enzyme for 2 days (b), incubated for 5 days (c), and incubated for 10 days (d). The assignment of carbon resonances is also reported. Adapted from [90].

In fact, after 10 days of incubation, all resonances clearly broadened and the intensity ratio C_{4a}:C_{4c} increased, indicating a net increase in the amorphous cellulose fraction. Broad shoulders between 93 and 100 ppm, possibly due to cellulose oligomers, were also observed. After 15 days of incubation, the uncoated paper was completely destroyed and no solid sample could be recovered from the aqueous solution where the paper had been soaked during the enzyme treatment. The paper coated with polyurethane showed prolonged resistance to biodegradation. In fact, the ^{13}C CPMAS spectrum of coated paper incubated for 10 days showed only a slight increase in the amorphous fraction. This effect was more evident after 15 and 30 days of incubation (Figure 30).

NMR spectra showed that the cellulose matrix of coated paper still existed after 30 days of incubation, albeit without crystallinity, whereas the cellulose structure of uncoated paper was completely destroyed by incubation times longer than 10 days. The polyurethane coating clearly delayed destruction of the cellulose matrix of paper subject to enzyme attack.

Unilateral NMR was used to investigate the degradation of precious old books non-invasively [91-93]. Historical 17th century books were measured by positioning the probehead directly on pages showing different degrees of deterioration. Transverse relaxation times were used to discriminate pages of the same book showing different degrees of degradation, as the longest T_2 values were obtained for relatively well conserved paper and the shortest for increased levels of degradation.

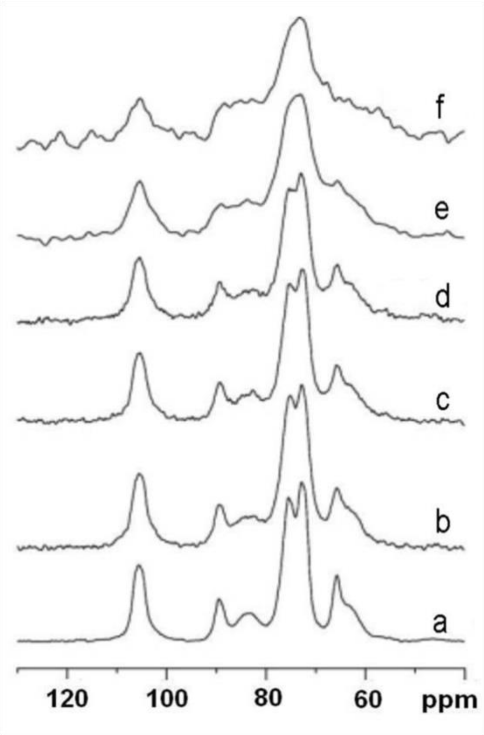

Figure 30. ^{13}C CPMAS NMR spectra at 50.13 MHz of paper coated with polyurethane: not incubated (a), incubated with the enzyme for 2 days (b), 5 days (c), 10 days (d), 15 days (e), and 30 days (f). Adapted from [90].

The state of conservation of ancient 17th and 18th century maps [94,95] was investigated by unilateral NMR, measuring T_1 and T_2 relaxation times at different points on the maps. T_1 measurements discriminated areas showing foxing (discoloration with brown spots - shorter T_1 values) from areas in a good state of conservation. T_1 also detected paramagnetic ions in areas with green ink where shorter T_1 values were measured. This result was confirmed by non-invasive X-ray fluorescence (XRF) analysis which revealed Cu and Fe ions in these areas. T_2 transverse relaxation times detected organic substances used in a previous undocumented restoration.

A novel application of unilateral NMR to paper, in which micrometer thick oil stains on paper were differentiated and characterized, was recently reported [23]. Oils can stain works of art on paper, such as manuscripts, photographs, and drawings. When the stains are visually disruptive and the damage is not considered part of the history of the object, art conservators remove them by applying a suitable conservation treatment that ideally reduces the stain without affecting the paper support, pigment or other media. The degree of cross-linking of the oil is a good guide to the choice of the treatment, but is not the sole identifying factor of the type of oil. The degree of crosslinking of oils was assessed non-invasively by tracking changes in T_2 transverse relaxation time. T_2 decreased with increasing crosslinking of the oil. The longest T_2 component measured in oil stains on paper was used to determine whether an oil stain was caused by a drying, semi-drying, or non-drying oil, and to follow up after stain removal, when the longest T_2 component converged to the T_2 value characteristic of the paper.

Wood

Wood is a complex natural composite material consisting of cellulose, hemicelluloses, lignin and water.

Lignin is a complex three-dimensional amorphous polymer synthesized by enzyme polymerization of p-coumaryl, coniferyl and synapyl alcohols, which are the respective precursors of p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) phenylpropanoid units linked by C – C and ether bonds. The most complex HGS lignins are typical of grasses, whereas hardwoods contain GS lignins, and G lignins are characteristic of softwoods. Hemicelluloses are relatively short-branched homo and heteropolymers made up of pentose and hexose sugars and their uronic acid derivatives. They constitute the alkali-soluble carbohydrate fraction of wood. Hemicelluloses and lignin interact with cellulose microfibrils giving rise to a rigid structure that strengthens the cell wall. Cell wall structure gives rise to chemical and anatomical properties which are highly variable and strongly dependent on plant species and age. Degradation of any of the components of wood decreases its mechanical strength and modifies its morphology.

Evaluation of the degree of deterioration of ancient wooden heritage artefacts is of interest for archaeology, archaeometry and conservation science. An assessment of the degree of deterioration of wood, characterized by its morphological, chemical and physical properties, is mandatory to plan an appropriate conservation approach.

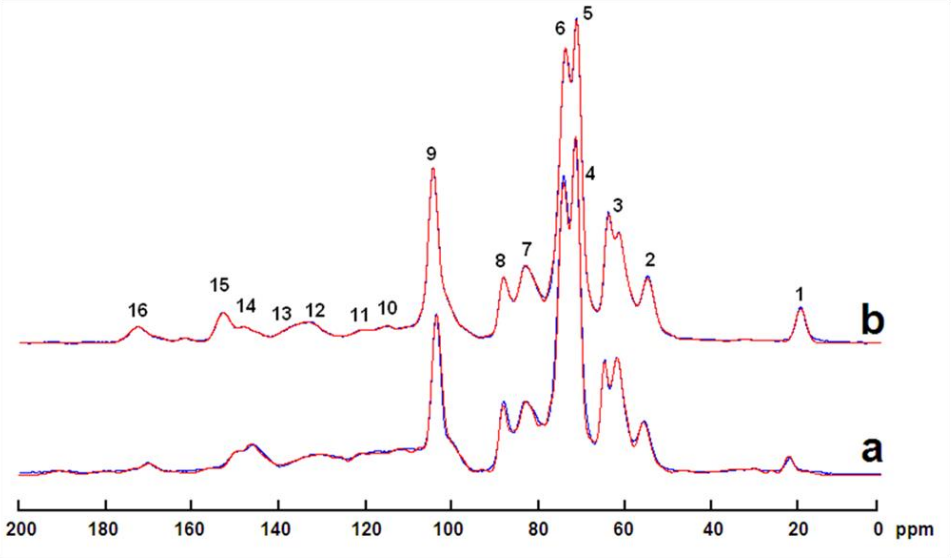

Figure 31. ^{13}C CPMAS NMR spectra at 100.13 MHz of a sample of modern seasoned yew wood (a), and modern seasoned poplar wood (b). The deconvoluted spectra are superimposed on the experimental ones. 1: carbohydrates $\underline{C}H_3COO$-; 2: lignin OCH_3; 3: lignin Cγ; 4: carbohydrates C6; 5: carbohydrates C2, C3, C5; 6: lignin Cα, carbohydrates C2, C3, C5; 7: lignin Cβ, carbohydrates C4; 8: carbohydrates C4; 9: carbohydrates C1; 10: lignin G5, G6, S2, S6; 11: lignin G6; 12: lignin S1(ne), S4(ne), G1(e); 13: lignin S1(e), S4(e), G1(e); 14: lignin S3(ns), S5(ne), G1, G4; 15: lignin S3(e), S5(e); 16: carbohydrates $\underline{C}OOR$-, $\underline{C}OOCH_3$. Note that S units are further labeled as S(ne) in non-etherified arylglycerol β-aryl ethers, and as S(e) in etherified arylglycerol β-aryl ethers.

^{13}C CPMAS NMR spectroscopy is a very powerful analytical technique [96,97] for studying structural changes occurring in ancient wood. The position, integral, and shape of each carbon resonance give information about the type of wood, namely hardwood (woody angiosperms) or softwood (woody gymnosperms or coniferous trees), as well as indicating the state of degradation of the wood.

Figure 31 shows experimental and deconvoluted spectra of a sample of modern seasoned yew wood (softwood) (a), and a sample of modern seasoned poplar wood (hardwood) (b).

The ^{13}C CPMAS spectrum of wood is actually a fingerprint of the wood. According to the literature [97,98], the weak signal at 21 ppm is assigned to the CH_3 carbon of the acetyl group in hemicelluloses. The peak at 55.6 ppm is assigned to methoxyl groups of aromatic units of lignin. The region between 60 and 105 ppm is dominated by the intense peaks mostly assigned to cellulose. Note that the peak at 88.7 ppm is assigned to C4 of crystalline cellulose, whereas the peak at 83.8 ppm is assigned to C4 of amorphous cellulose or less ordered surface cellulose molecules. The region between 105 and 160 ppm is specific to the aromatic carbons of lignin. The signal at 172 ppm is assigned to carbonyls in acetoxy groups of hemicellulose, and to acid groups possibly present in wood. Resonance 15 at 152.6 ppm is assigned to carbon atoms C3 and C5 of S(e) units, namely S3(e) and S5(e), and resonance 14 at 147 ppm is assigned to carbon atoms C3 and C5 of S(ne) units, namely S3(ne) and S5(ne), and to carbon atoms C1 and C4 of G units, namely G1 and G4. Applying a deconvolution procedure to the spectra in Figure 31 it was possible to obtain the integral of each resonance. The relative ratio of the integral of resonance 15 and that of resonance 14, makes it possible to distinguish between softwood and hardwood (Figure 31a and b, respectively). In degraded wood, the ratio of the integral of resonances 15 and 14 also allows one to estimate the depletion of β-O-4 linkages in lignin. Taking the integral of resonance 9 at 104.8 ppm I(9) as reference and the integral of resonance 2 at 55.6 ppm, I(2) (methoxyl groups of lignin), the relative amounts of carbohydrates and lignin can be evaluated. By way of example, $R=I(9)/I(2)$ was found to be 2 and 2.2 in modern seasoned poplar and yew wood, respectively, whereas in degraded wood from Dunarobba fossil forest (Terni, Italy), it was 0.78 indicating a marked depletion of carbohydrates (Figure 32).

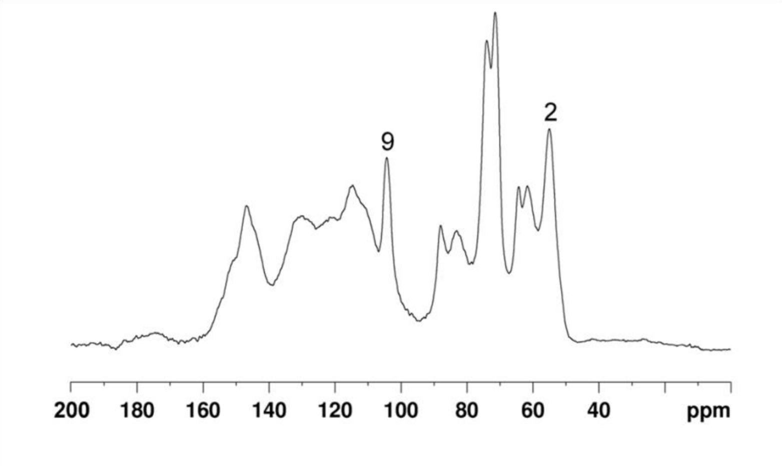

Figure 32. ^{13}C CPMAS NMR spectrum at 100.13 MHz of a sample of degraded wood from Dunarobba Forest (Terni, Italy).

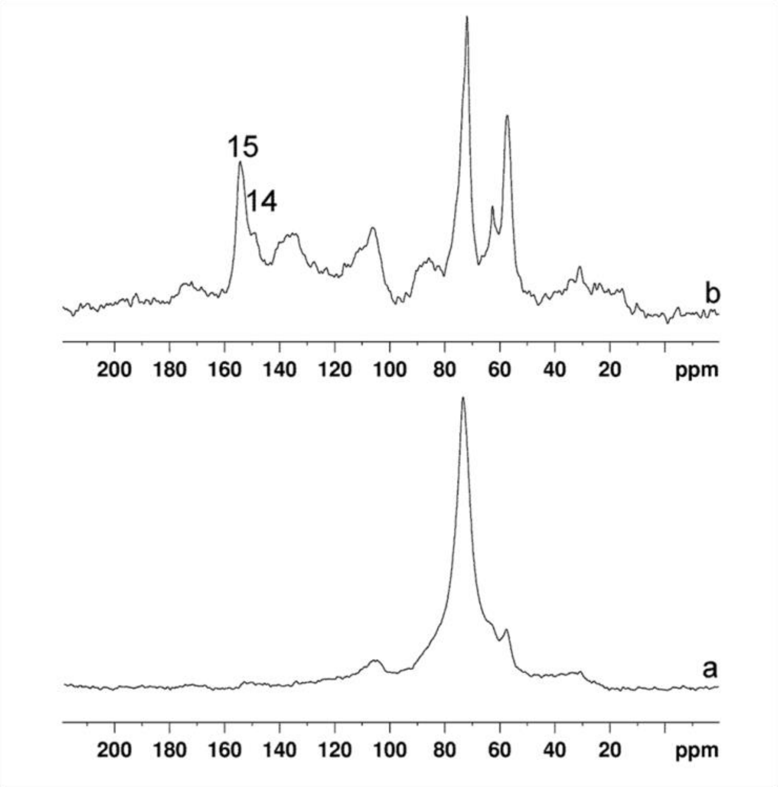

Figure 33. Archaeological wood impregnated with polyethylene glycol. ^{13}C CPMAS NMR spectra at 100.13 MHz collected with a contact time of 0.150 ms (a), and 4 ms (b).

^{13}C CPMAS NMR spectroscopy is a suitable analytical tool for investigating the structural changes occurring in wood after a long period under water, as the main components of wood, celluloses and lignins can be quantified [98]. Depending on the extent of degradation, spectra of waterlogged woods reveal net cellulose depletion explained by the leaching of carbohydrates [99-102].

Samples of archaeological wood impregnated with polyethylene glycol (PEG) may also be successfully investigated by NMR [103]. Choosing proper contact times in the ^{13}C CPMAS experiment, it is possible to selectively edit the spectrum of the wood components or that of PEG. ^{13}C CPMAS spectra of a sample of archaeological wood impregnated with PEG are shown in Figure 33; spectrum (a) was obtained with a contact time τ of 0.150 ms and spectrum (b) with τ of 4 ms.

The spectrum recorded with the shortest contact time was dominated by peaks of PEG. In fact, the intense peak at 72 ppm was assigned to carbons of CH_2O groups constituting the bulk of PEG, whereas the shoulder at 61.7 ppm was assigned to carbons of terminal CH_2 bound to hydroxyl groups. The spectrum collected at long contact time, besides peaks of PEG, showed signals of wood, which are mostly those of lignin moiety carbons. By comparing the peak at 104.8 ppm due to sugars with different peaks assigned to lignin, the level of degradation of the wood components may be evaluated. The sample showed net depletion of carbohydrates. The ratio of the integrals of resonances 15 and 14, both assigned to lignin, was the same as that found for a modern seasoned hardwood, indicating that β-O-4 linkages, the most frequent structure, are still present in the sample. Therefore the overall structure of lignin was not affected. To summarize, the ageing conditions experienced by this object led to strong degradation of cellulose and other sugars, which were leached from the wood, but did not affect the lignin moiety.

Wood impregnated with PEG may be considered a composite material. Measurements of proton relaxation times in the rotating frame $T_{1\rho}(^1H)$ may help to determine if this composite material can be considered a simple mixture of PEG and wood, or a molecular blend.

The pulse sequence to measure $T_{1\rho}(^1H)$ applied a spin lock time ranging between 0.05 and 20 ms, after cross-polarization with a contact time of 0.150 ms. The intensity of the two resonances, assigned to PEG at 72 ppm and lignin at 55.6 ppm, is reported against spin lock time in Figure 34 top and bottom, respectively.

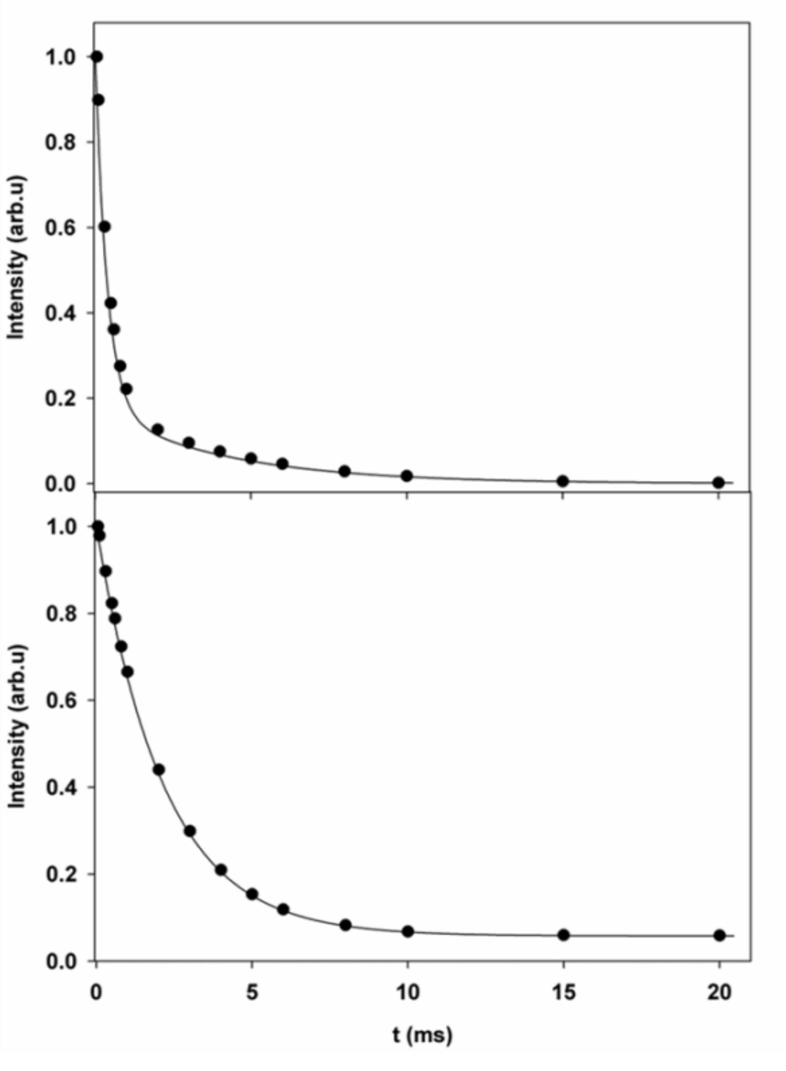

Figure 34. Decay of magnetization vs spin-lock time obtained from an experiment designed to measure $T_{1\rho}(^1H)$. Bottom, peak at 56 ppm; top, peak at 73 ppm. Experimental data was fitted to equation (5).

$T_{1\rho}(^1H)$ values were obtained fitting the experimental data to a mono or multi-exponential decay:

$$M(t) = C_0 + \sum_{i=1}^{n} W_i e^{\frac{-2t}{T_{1\rho}^{i}\left(^1H\right)}} \tag{5}$$

where n is the number of components of magnetization decay, W_i the spin population of i^{th} component, $T_{1\rho}^{i}\left(^1H\right)$ the relaxation time of i^{th} component, and C_0 the offset accounting for measurement noise.

The data reported in Figure 34, top and relative to PEG, was fitted to a bi-exponential decay, whereas the data reported in Figure 34, bottom and relative to lignin, was fitted to a mono-exponential decay.

In the former case, two $T_{1\rho}(^1H)$ values were obtained, 0.38 and 4.14 ms, with relative spin populations of 0.83 and 0.17, respectively; in the latter case a single $T_{1\rho}(^1H)$ value of 2.2 ms was obtained from the best fit procedure.

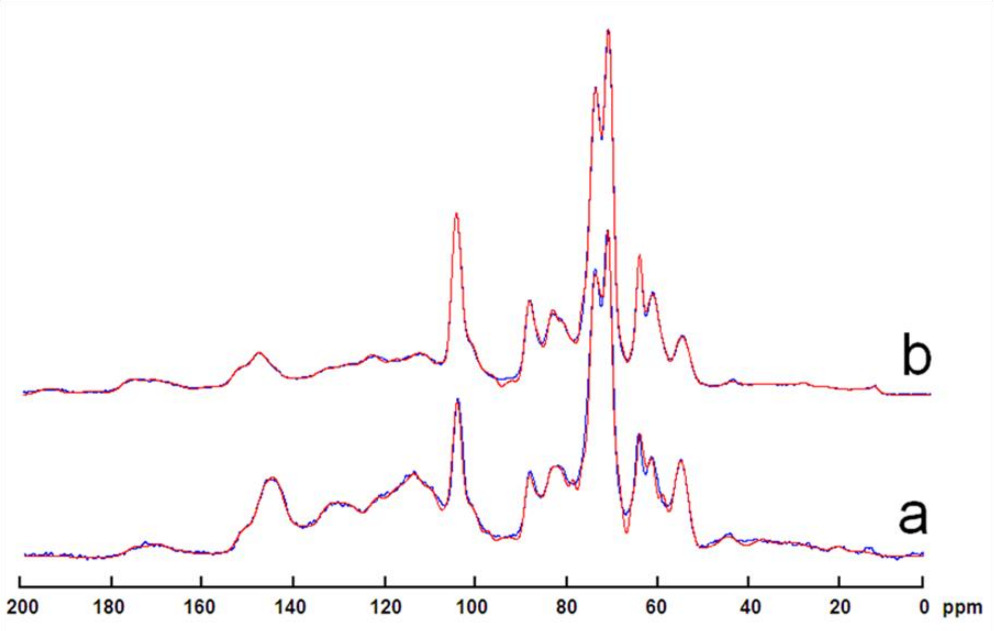

Figure 35. ^{13}C CPMAS spectra of a sample from the outer side of the panel of the sarcophagus (a), and a sample from the inner side (b). Deconvoluted spectra are superimposed on the experimental ones. Adapted from [21].

In polymers, $T_{1\rho}(^1H)$ values increase with the degree of crystallinity or the degree of order of the polymer chain, whereas a decrease in $T_{1\rho}(^1H)$ may indicate either an amorphous state or a decrease in the degree of order. The presence of a short and a long $T_{1\rho}(^1H)$ in PEG indicated that the PEG moiety in the wood consisted of two phases with different dynamic properties [102]: about 80% of PEG protons had dynamic behavior characteristic of a disordered phase (0.38 ms) and the remaining protons showed behavior characteristic of an ordered or even crystalline phase (4.14 ms). The presence of a single and rather long $T_{1\rho}(^1H)$ value in lignin (2.2 ms), of the same order of magnitude as the longest value found in PEG, provided evidence that about 20% of PEG was in close molecular interaction with lignin, whereas the remaining 20% did not interact with the residual wood components, fully confirming data previously reported in literature [102].

High and low resolution methods were also used [104] to investigate ancient and degraded larch and fir wood samples from the trussed rafter of 15th century Valentino Castle, Turin, Italy.

^{13}C CPMAS NMR spectroscopy was used [21] to evaluate the state of conservation of an ancient wooden panel of an Egyptian sarcophagus (XXV – XXVI dynasty, Third Intermediate Period). Figure 35 shows the spectra of samples from the outer (a) and inner (b) sides of the panel.

In Figure 35 the deconvoluted spectra overlap with the experimental ones. The deconvolution provided integrals of all peaks. The ratio of the integrals of resonances 15 and 14 enabled evaluation of the depletion of β-O-4 linkages in lignin. This ratio was found to be 0.25 in the sample from the outer side of the panel, and 0.48 in the sample from the inner side (Figure 35a and b, respectively). These results indicate that depletion of lignin β-O-4 linkages occurred in the sample from the outer side, whereas the sample from the inner side was only slightly affected, the ratio being about 0.51 in the seasoned well-preserved softwood. No peaks were observed at 21 ppm in either sample, indicating hemicellulose depletion. The intensity of lignin peaks was definitely higher in the sample from the outer side of the panel (Figure 35). In fact, R=I(9)/I(2) was found to be 1.58 in the sample from the inner side, and 0.87 in the sample from the outer side, and about 2.17 in a sample of well preserved seasoned softwood. These results indicate that carbohydrate depletion occurred in both samples and was higher in the sample from the outer side. The line widths of the signals did not significantly change in either sample, indicating that while ageing induced depletion of carbohydrates, no other chemical rearrangements occurred in the biopolymer network.

The state of conservation of the panel of the sarcophagus was also investigated by unilateral NMR. Because the wood of the panel was determined to be yew wood by optical microscopy, the transverse relaxation times measured on the inner and outer side of the panel were compared with those measured on a piece of seasoned yew wood.

It was previously shown [105] that analysis of transverse relaxation times measured in seasoned wood enables separation of water and detection of three populations: cell water with a short T2 value and lumen water with medium and long T2 values. T2 characterizes water in different internal compartments, being related to the size and proportion of wood tissue. It has also been shown that T_2 relaxation times in wood are clearly represented by applying an inverse Laplace transformation to decays obtained with the CPMG sequence. The transformed data shows well-separated T_2 peaks of cell water and lumen water.

Distributions of relaxation times measured in seasoned yew wood on the inner and outer sides of the sarcophagus panel are reported in Figure 36.

In this representation, the maxima (peaks) are centered at the corresponding most probable T_2 values, while peak areas correspond to the populations of T_2 components. The loss of water occurring in the wood of the sarcophagus is clearly observable, as in seasoned yew wood the distribution displays three peaks resulting from cell water and lumen water in two different environments, whereas in the inner and outer sides of the panel the peak centered at the longest T_2 value is missing, and also the amount of more confined lumen water measured on both sides of the panel is definitely lower than that measured in seasoned yew wood. Ageing of the panel was associated with an evident loss of lumen water. In addition, the longest T_2 component measured in the outer side of the panel clearly shifted to a value shorter than that measured on the inner side, showing that the wood on the outer side experienced more pronounced degradation than the wood on the inner side. This is in line with a previous observation indicating transverse relaxation times as a suitable parameter for evaluating the state of degradation of cellulose-based materials [89]. The result is also in line with that obtained by ^{13}C CPMAS NMR spectroscopy, which indicated more pronounced degradation on the outer than the inner side (Figure 35).

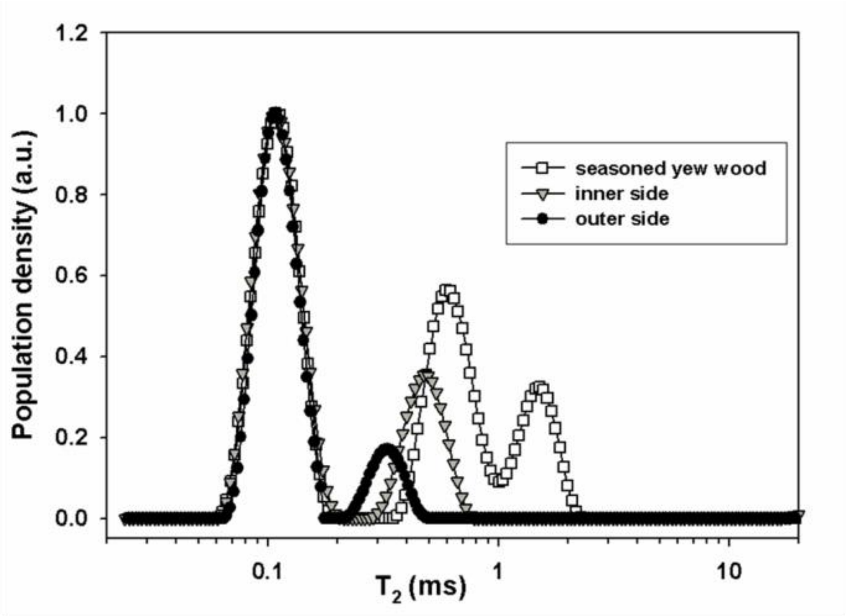

Figure 36. Transverse relaxation time distributions obtained for seasoned yew wood (squares) and for a region on the inner side (triangles) and outer side (circles) of the sarcophagus panel. Data adapted from [21].

Textiles

Historic textiles are a source of information on human history. Textiles degrade easily, showing effects like fading and uneven wear. The main component of major textiles, such as linen or cotton, is cellulose. The main degradation processes acting on the structure of cellulose in textiles are photodegradation, acid hydrolysis, oxidation and biodegradation.

Some studies have focused on *in situ* polymerization to strengthen the cellulose matrix in degraded textiles [106,107]. The method was tested on modern linen and cotton samples previously oxidized to induce the formation of carboxyl and carbonyl groups used as photosensitive agents. It was shown that the oxidation process affected linen more than cotton. Figure 37 shows the ^{13}C CPMAS NMR spectra of cotton (left side) and linen (right side) samples. The spectra of untreated cotton and linen are shown in a and e, whereas spectra of samples after oxidation with $NaIO_4$ for 2 h, 6 h, and 24 h are shown in b and f, c and g, and d and h, respectively. As previously observed in paper and papyrus, also the spectra of oxidized textiles show progressive line broadening with increasing oxidation time.

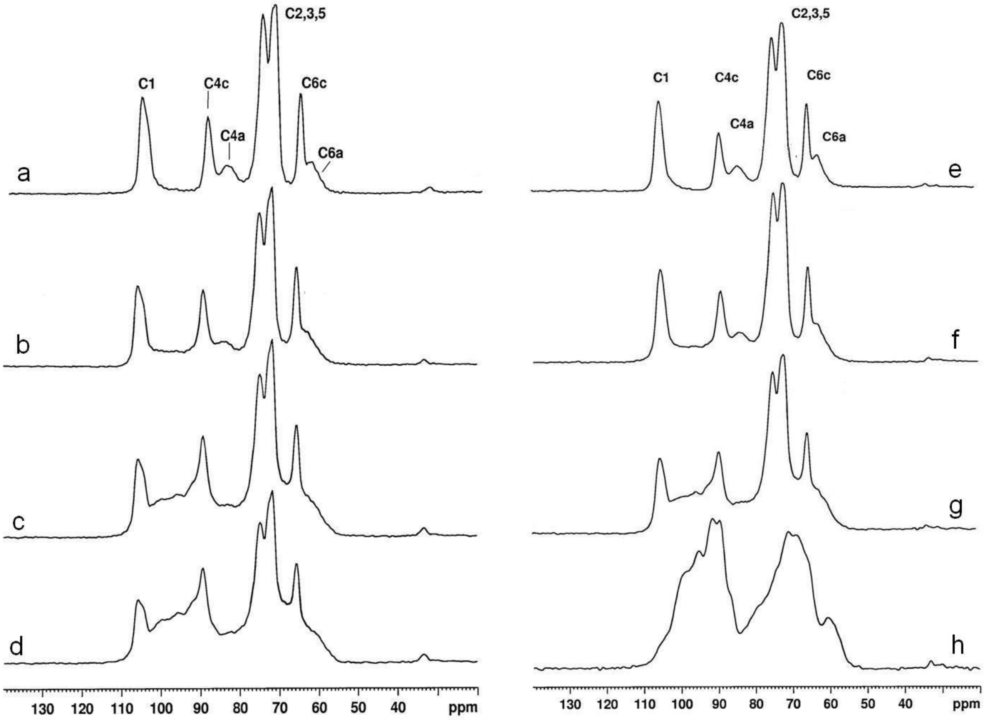

Figure 37. ^{13}C CPMAS NMR spectra at 50.13 MHz of untreated cotton (a) and linen (e) samples, and spectra of samples oxidized with $NaIO_4$ for 2 h (b), and (f), 6 h (c) and (g), and 24 h (d) and (h).

The broadening of resonances is mainly due to an increase in the cellulose amorphous fraction. The progressive formation of oligomers resonating at 90 - 100 ppm is also clearly evident. After oxidation for 24 h, the spectrum of cotton is broadened but still shows cellulose signals, whereas full degradation of the cellulose matrix is observed in linen (Figure 37d and h, respectively), indicating that linen suffered much greater degradation than cotton.

To strengthen the cellulose matrix, EA or MMA was grafted on naturally aged and chemically oxidized textiles irradiating with low energy ultraviolet for a short time. For naturally aged cotton, carboxyl and carbonyl groups caused by natural aging were used as photosensitive agents. By way of example, Figure 38 shows the spectra of untreated cotton (a) and cotton oxidized with $NaIO_4$ and grafted with MMA (b). The spectrum of the grafted sample shows cellulose carbon resonances and others due to MMA: that of methyl 5’ is at 17.8 ppm, quaternary carbon 2’ at 46.3 ppm, carbon resonance due to the OCH_3 group 4’ at 53.2 ppm, methylene carbon 1’ at 57.6 ppm and carbonyl carbon 3’ at 178.7 ppm. Resonances in the 60–110 ppm region were unchanged, confirming that cellulose bulk structure was unaffected. In order to test the suitability of the grafting method on real samples, the grafting reaction with MMA, previously performed on artificially aged cotton, was also performed on a naturally aged historical cotton sample. The ^{13}C CPMAS spectrum is reported in Figure 38c.

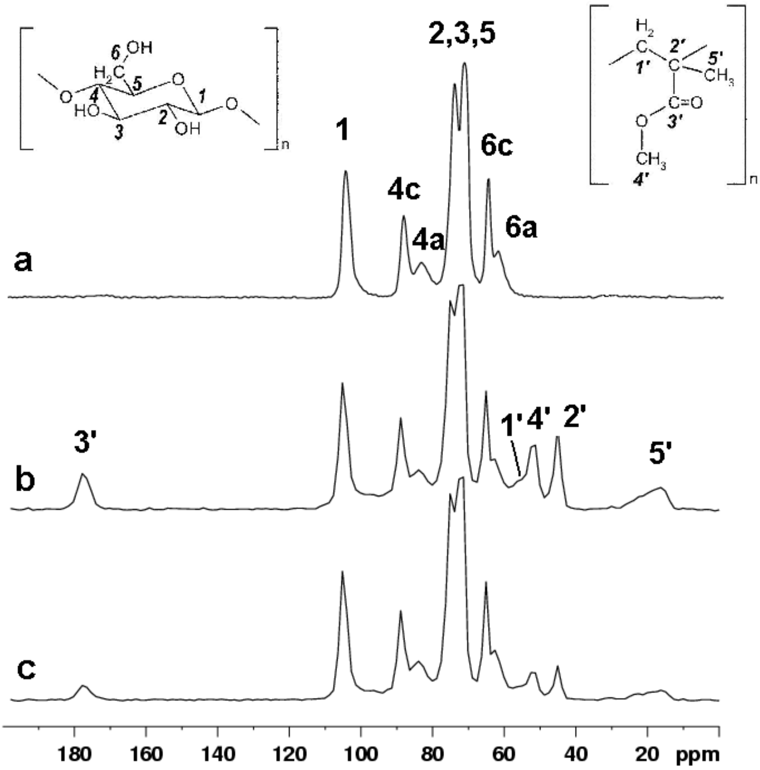

Figure 38. ^{13}C CPMAS NMR spectra at 50.13 MHz of untreated cotton (a), cotton oxidized with $NaIO_4$ and grafted with MMA (b), and a naturally aged historical cotton sample grafted with MMA (c). Adapted from [106].

Because the intensity of carbon resonance depends on the cross-polarization rate, which may be different for different carbon atoms [108], CPMAS spectra are not quantitative. A quantitative evaluation of the degree of grafting was performed by studying the full cross-polarization process. In Figure 39 the correlation between the intensity of the anomeric carbon resonance 1 and that of the carbonyl carbon resonance 3’ belonging to MMA, and the contact time τ, are reported for a cotton sample oxidized with $NaIO_4$ and then grafted with MMA (a), for naturally aged cotton grafted with MMA (b) and for a cotton sample oxidized with $NaIO_4$ and then grafted with EA (c).

Data reported in Figure 39 was fitted to the following equation:

$$M(\tau) = M_0\left[1-\exp\left(-\frac{\tau}{T_{CH}}\right)\right]\exp\left(-\frac{\tau}{T_{1\rho}\left({}^1H\right)}\right) \tag{6}$$

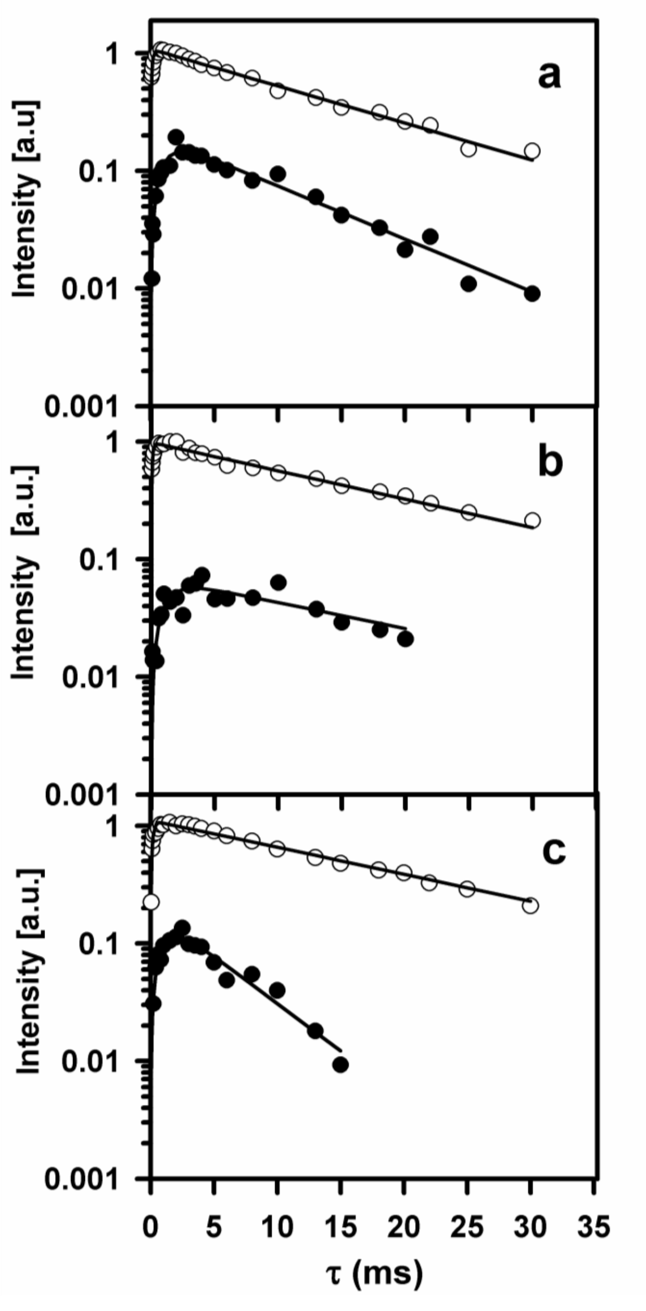

Figure 39. Intensity vs. contact time τ of anomeric carbon resonance 1 (white circles) and carbonyl carbon resonance 3’ of MMA (black circles) for a cotton sample oxidized with $NaIO_4$ and grafted with MMA (a), for naturally aged cotton grafted with MMA (b) and for a cotton sample oxidized with $NaIO_4$ and grafted with EA (c). Data adapted from [106].

where M(τ) is the intensity measured at contact time τ, M_0 the initial intensity of magnetization extrapolated back to τ=0, T_{CH} the cross-relaxation time between protons and carbons, and $T_{1\rho}(^1H)$ the proton spin-lattice relaxation time in the rotating frame. It is worth noting that M_0 may be used for quantitative analysis.

The value of $T_{1\rho}(^1H)$ may be obtained from the slope of the downward part of curves shown in Figure 39. The spin diffusion process is fully active in equalizing $T_{1\rho}(^1H)$ values of cellulose and the grafted monomer in cotton grafted with MMA (Figure 39a and b), but in cotton grafted with EA the spin diffusion process is interrupted (Figure 39c). In fact in the latter case the $T_{1\rho}(^1H)$ value of resonance 1 is definitely much longer than the corresponding one obtained for resonance 3', indicating that the system is inhomogeneous. The spin diffusion process does not average out $T_{1\rho}(^1H)$ values to a single value. In this case, to obtain a quantitative spectrum and a quantitative evaluation of the grafting yield, a ^{13}C single pulse excitation spectrum (without cross-polarization) was recorded with a long recycle delay.

To summarize, in cotton grafted with MMA, integrals obtained by fitting the intensity of resonances vs contact time made it possible to calculate a grafting percentage of 33% in the sample previously oxidized with $NaIO_4$ and 7% in the naturally aged sample. In the case of cotton grafted with EA, a grafting percentage of 40% was obtained by direct integration of resonances in the ^{13}C single pulse excitation spectrum.

CONCLUSION

In this review and discussion of the applications of NMR methodologies for characterizing and monitoring cultural heritage, the various case studies, though not exhaustive, clearly demonstrate that NMR is not confined to a few specific applications, but can be successfully extended to a wide range of different issues regarding cultural heritage.

Portable NMR was used to quantitatively and noninvasively map moisture distribution and its evolution in an ancient deteriorated wall painting, before and after work to reduce the capillary rise of water through the wall.

^1H-driven NMR stratigraphy enabled detection of different layers of paintings on a wooden panel and in detached mural paintings, and measurement of the thickness of each layer. The technique can be used to obtain information on pictorial techniques used by artists and the materials constituting artifacts.

^1H-driven NMR stratigraphy was used to investigate the effectiveness of a cleaning treatment aimed at removing a thick layer of degraded shellac, used in the past as a varnish for wall paintings.

Portable NMR methods were used to study porous stone subject to hydrophobic or consolidating treatments. The study was aimed at answering general questions, such as the penetration depth of treatment into a porous material, its capacity to prevent the water absorption, how treatment may change the open porosity available to water, and how treatment may affect the diffusion of water inside a porous structure. Inhomogeneity in treated stones due to sharp variations in the amount of product absorbed by the porous material was observed and scaled. Experimental data were processed to obtain new parameters. These parameters, namely hydrophobic efficiency, penetration depth, and angles describing changes in slope of depth profiles, provided important information for assessing treatment performance.

The structure of clay, pottery and tuff from archaeological sites was characterized by solid state high resolution ^{29}Si MAS, ^{23}Na MAS , ^{27}Al MAS and ^{27}Al 3QMAS NMR. The porous structure of pottery was investigated noninvasively by portable NMR, obtaining information about ancient firing technology. The potential of NMR to fingerprint pottery structure and recognize mineralogical phases in the ceramic mass in relation to production technology and ancient firing processes deserves further investigation. Because of the widespread use of ceramic materials, information obtained by this method may also be of interest in the field of industrial ceramic production.

Historical parchments were studied by ^{13}C CPMAS NMR spectroscopy. Based on changes in line width compared to new parchment, collagen, and gelatin, an index that allows assessment of degradation in historical parchments was obtained. The relative amount of lipids in parchment samples may also be established.

^{13}C CPMAS NMR spectroscopy and ^{1}H NMR relaxometry in homogeneous and inhomogeneous fields were successfully applied to the study of structural changes in naturally and purposely degraded paper. The protective effect of waterborne polyurethanes against enzyme attack on paper was monitored through changes in the structure of original and coated paper before and after biodegradation. The polyurethanes selected were effective in protecting paper against enzyme attack. Indeed, ^{13}C CPMAS NMR spectra revealed that the coating delayed destruction of the cellulose matrix.

The development of mobile NMR equipment allowed non-invasive study of historical books and maps, for which sampling of even a small amount of material must be avoided.

^{13}C CPMAS NMR spectroscopy and ^{1}H NMR relaxometry may be also used to investigate and quantify degradation in wooden artifacts. Case studies regarding an ancient Egyptian sarcophagus and archaeological wood were reported. Proton spin-lattice relaxation time measurements in the rotating frame enabled study of the interaction between the lignin matrix and PEG in PEG-impregnated archaeological wood specimens.

^{13}C CPMAS NMR spectroscopy was applied to the study of acrylate polymer grafted onto cellulose chains of chemically or naturally oxidized textiles. The aim of grafting was to improve mechanical strength, thermal stability, and resistance to chemical and biological agents. Quantitative evaluation of the grafting was performed by studying the dynamic cross-polarization process or by direct integration of resonances in ^{13}C single-pulse excitation spectra.

NMR studies on archaeological bones, mummies and amber, as well as identification of residues in archaeological findings reported in the literature demonstrate that although NMR has not yet been widely applied, it may also play a major role in the specific field of archaeometry. Since it can be performed on ever smaller amounts of sample, NMR will probably become more and more competitive with other analytical techniques for the analysis of samples in solution and in a soaked or solid state.

Portable instrumentation for investigating large objects without any sampling has been a major breakthrough. Successful application of NMR for monitoring artifact degradation and restoration treatments *in situ* has already demonstrated the potential of portable NMR devices.

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Chapter 9

X-RAY FLUORESCENCE SPECTROMETRY AS A DIAGNOSTIC TOOL IN CHARACTERIZATION AND CONSERVATION OF MANUELINE-ILLUMINATED MANUSCRIPTS

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ABSTRACT

In this chapter we will describe the capabilities of Portable X-ray Fluorescence Spectrometry to characterize illuminated manuscripts. As complementary techniques, Raman and SEM-EDS Spectroscopy will be also described. The use of these techniques is essential for the understanding of the artists working methods, which aids conservation and restoration of the manuscripts.

As a case study, the Renaissance foral charters, from the 16th century, belonging to the Portuguese National Archive, will be studied in detail. A complete characterization of parchments, pictorial materials and metallic coatings used in the production of illuminated manuscripts will be performed. Scientific identification of: i) inks used in the written texts; ii) pigments used in the production of coloring materials for the illuminations and inks for letterings, will be carried out. These results will be a key step in the work of conservation and restoration to be undertaken in many illuminated manuscripts, such as the aforementioned charters, which can present very high degrees of deterioration and need urgent intervention.

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INTRODUCTION

As the name implies, X-ray fluorescence spectrometry (XRF) relies on X-rays, which are photons of small wavelengths, in the 0.005 to 10 nm range of the electromagnetic spectrum. For low wavelength they overlap with γ rays, while in the high end they approach ultraviolet radiation. An enormous variety of analytical techniques, besides XRF, makes use of this bandwidth in the electromagnetic spectrum, such as X-ray imaging (XRI) and X-ray diffraction (XRD). X-ray fluorescence technique is based on the detection of characteristic X-rays from the elements present in the sample under evaluation. When an excited atom, with an inner-shell vacancy, decays to its electronic ground state, it emits radiation with energy equal to the energy difference between the electronic levels involved in the transition. If the vacancy is in the K-shell these X-rays are labeled $K_{\alpha,\beta,\ldots}$ depending on the provenance of the electron occupying the vacancy. The inner-shell vacancy, in this technique, is created by photoionization using high energy X-rays usually from X-ray tubes or radioactive sources, but in other techniques it can be created by electrons, protons or any other projectile. In Figure 1 a diagrammatic presentation of the characteristic X-rays for a given element is shown.

Every atom has a different electronic structure, and hence the inner-shell transitions have slightly different energies. An energy dispersive detection method will then give rise to a spectrum in which the characteristic inner-shell transitions can be separated, and thus the elemental composition can be inferred. XRF has continuously evolved either in the form of conventional energy-dispersive X-ray fluorescence (EDXRF) techniques or in the form of wavelength-dispersive X-ray fluorescence (WDXRF) techniques. In WDXRF a diffraction crystal is used in a rotating table to scan a single wavelength at a time, while in EDXRF, the dispersion and detection of fluorescence photons are performed using a solid-state X-ray detector and a multichannel pulse height analyzer (MCA), both of which produce accumulating digital spectra that can be processed further to derive the concentrations of the different elements present in a sample. Both analytical techniques are well-established for elemental analysis at the micro and trace levels, but the latter is by far the most cited analytical method in literature, dealing with cultural heritage investigations.

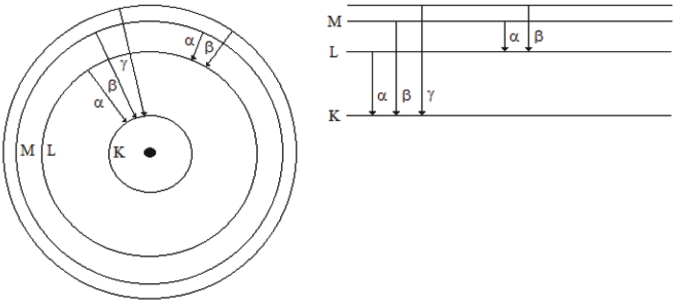

Figure 1. Characteristic inner-shell transitions.

This technique is non-destructive, and can be used to perform *in situ* measurements and usually presents sensitivities at the level of parts per million (ppm). The major advantages of X-ray spectroscopic methods are the simplicity of spectra treatment, its wide elemental range, minimal sample preparation, non destructiveness and good detection limits. This, coupled to the fact that the apparatus can be very lightweight and portable, allowing *in situ* analysis, makes EDXRF a benchmark technique in cultural heritage studies.

Synchrotron radiation XRF (SR-XRF) has also started to play an increasingly important part in cultural heritage analyses. The specific features of synchrotron radiation include energy tunability, a higher photon flux and a higher resolution.

Another major advantage is the application of XRF synchrotron beam to selectively identify areas of analyses. With the advent of new X-ray optics and the technological development of polycapillary lenses, a new tool for microanalysis arose: three dimensional micro-X-ray fluorescence spectroscopy (3D micro-XRF). This technique is based on the use of two polycapillary optics in a confocal arrangement. The overlap of the focuses of the two X-ray optics forms a probing volume from which fluorescence and scattered radiation is exclusively derived. This technique can be used for lateral and depth-resolved XRF measurements, allowing 3D mapping.

The versatility of EDXRF is however counterbalanced by its insensitivity to chemical bonding. The very small energy differences in inner atomic orbitals, when an atom is bonded in a molecule, cannot be resolved with this technique and hence only the elemental composition is obtainable but not its molecular state. This can be very important, for example, when analyzing pigments in a painting since their color can be due essentially to the molecular structure rather than the elements *per se*. For example, malachite ($Cu_2CO_3(OH)_2$) and verdigris ($Cu(CH_3COO)_2nCu(OH)_2$) only differ in the molecular arrangement and thus cannot be distinguished solely by XRF.

Another drawback of XRF spectrometry is the fact that the low energy X-rays (≤ 2 keV) are highly absorbed in air, and coupled to low detection efficiencies in that energy region, makes it impossible to detect low energy characteristic X-rays. Low atomic weight elements, below $Z = 13$, cannot be thus detected currently by EDXRF. In this work, we are interested in describing the XRF spectrometry as a diagnostic tool in conservation of cultural heritage samples, namely Portuguese illuminated manuscripts of the 16th century.

Complementary Techniques (Raman Spectroscopy)

Raman spectroscopy probes molecular and crystal-lattice vibrations and is therefore sensitive to the composition, bonding, chemical environment, phase and crystalline structure and orientation of the sample material. Its sensitivity to molecular bonding makes it a complementary technique to XRF, on account of the possibility of distinguishing different molecular arrangements of the same compound. The nondestructiveness and its applicability to samples of large or nonuniform shapes and relative immunity to interference, also qualifies it to be used in cultural heritage studies.

Raman microscopy has been used to investigate pigments and inks in illuminated manuscripts either by collecting micro-samples or by placing the manuscripts directly under the microscope [1-6].

Complementary Techniques (SEM-EDS)

Scanning electron microscopy (SEM) is also a very powerful tool in cultural heritage research because it provides knowledge about the surface topography of the studied objects. This kind of microscope uses electrons rather than light to form an image, and if it is coupled with an energy-dispersive detector, the information regarding the elemental composition is also obtained. SEM-EDS has been used recently in ancient manuscripts either to perform elemental micro-analysis [7] or to assess the damage of environmental impact on parchment [8]. This technique has been used mainly for investigating the caratage (gold content) of the silver and gold areas of the charters.

METHODS/EXPERIMENTAL

X-Ray Fluorescence Spectrometer

The EDXRF spectrometer used throughout this work consists on an Eclipse IV Oxford Instruments X-Ray tube (45 kV, 50 μA, 2.25 W max.) with a Rh anode. The radiation is collimated by a tantalum collimator allowing a 4 mm diameter beam on the sample, placed at 55 mm from the tube and 10 from the detector. The detector is an Amptek XR-100SDD with a 25 mm^2 detection area collimated down to 17.12 mm^2 and 500 µm thick fully depleted, and with a 12.5 μm Be window which has proven to be essential in cultural heritage studies due to the low detection limits and low energy efficiency for these matrices [9]. The energy resolution is 140 eV at 5.9 keV and the acquisition system is the Amptek DppPMCA. The angle between the incident and emitted beam is 90°. This geometry allows a minor background due to Compton scattering. The sample was positioned at the focal point of two laser beams, built in to better define the spectrometer geometry. The X-ray generator was operated at 35 kV and 40 µA, and an acquisition time of 200 s was used. It should be noted that trace amounts of Ti, Ni and Cu observed on the spectra originate in the spectrometer.

Raman Spectrometer

Raman spectra were obtained on micro-samples from the illuminated manuscripts using a Horiba-Jobin Yvon XploRA confocal Raman microscope, equipped with 532 nm, 638 nm and 785 nm laser diodes and an entrance slit of 100 μm. The collected scattered light was dispersed by a 1200 lines/mm grating onto an air cooled CCD array of an Andor iDus detector. A 100× magnification objective with a pinhole of 300 μm was used to optimize the spatial resolution and the Raman intensity.

These parameters, combined with accumulating times going from a few seconds to several minutes allows one to perform Raman microspectroscopy. Particles of pigment were selected with the help of a microscope. To reach an accurate identification of the materials under study, a polynomial baseline correction was carried out on the measured Raman spectra to remove the fluorescence contribution.

The identification of pigments was then made with accuracy by using literature [10-13] and several spectral databases (Crystal Sleuth, Spectral ID) implemented with some of our own references spectra (pigments and binders provided by Kremer).

SEM-EDS

Examination and analysis of the samples were carried out using a FEG-SEM model JSM 7001F by JEOL with an Oxford Si(Li) INCA PentaFet x3 detector. The samples were placed on the sample-holder with a double-coated conductive carbon tape. The voltage used was 20 kV, but decreased to 10 kV while dealing with parchment, because it is mainly constituted by low atomic weight elements.

ILLUMINATED MANUSCRIPTS

Illuminated manuscripts are documents, usually on parchment support, in which the text is surrounded by decorations such as colored initials, borders and miniature illustrations. The term illuminated originally denoted the embellishment of the manuscripts with gold or silver, giving the impression that the page had been literally illuminated. These illuminations were often loaded with symbolic information and sometimes carried as much information as the text [14]. The majority of surviving manuscripts and books are from the Middle Ages, although many Renaissance illuminated manuscripts can also be found in archives all around the globe. Since parchments were a rare commodity, the reuse of older books to produce new manuscripts was a very common practice, hence the very limited number of manuscripts from Late Antiquity. The Arquimedes Palympsest project, which lead, in 2011, to the discovery of a presumed lost Arquimedes manuscript [15], is a spectacular example of this practice. The rising awareness of the scientific community to the issue of preservation of cultural heritage, as well as the establishment of multidisciplinary teams comprising scientists, restorers and conservators, prompted an increased interest in the application of analytical methods to the study of illuminations. Such studies are of major importance to understand the artists working methods and materials, which are essential in the restoration and conservation processes. This characterization may also help in the assignment of probable manuscript ages [16]. Non destructive analytical techniques are required when dealing with most of the cultural heritage study objects, and due to their intrinsic value and/or dimensions, *in situ* analysis is an indispensable requisite, hence X-ray fluorescence spectrometry (XRF) has become a ubiquitous technique in this field.

Manuelin Foral Charters

Between 1495 and 1520, King D. Manuel promoted one of the most ambitious enterprises of his time by restructuring the charters produced since the 12th century onwards. The former charters, written in Latin, were copied in Portuguese into renewed codices to meet the 16th century legal requirements.

Figure 2. Illuminated frontispieces of the foral charters of the Portuguese towns of *Sintra*, *Teixedo* and *Setúbal* (top row) and *Sabugosa, Castanheira e Povos* and *Juromenha* (bottom row).

They were written on parchment in gothic style characters and illuminated with precious ornaments such as the coat of arms and the armillary sphere used to express the authority of the realm. This procedure was known as reform of charters, and the foral charters called Manueline [17]. These documents represent nowadays invaluable testimonies of the reality of Portugal five hundred years ago and deserve the utmost care. In this work we have studied the foral charters issued to the Portuguese towns of *Sintra*, *Teixedo*, *Setubal*, *Sabugosa*, *Castanheira* e *Povos* and *Juromenha* dated between 1510 and 1514, whose illuminated frontispieces are shown in Figure 2. The heraldic design of the charters is well represented in the figure, and corresponds to the royal statements for their production according to three different typologies, from which only two are represented in the studied examples. The ubiquitous coat of arms sports a golden crown which was particularly representative of the Kingdom of the Algarves since 1242. In the charters of type III, it is inserted in the initial D, while in charters of type I, it has a center role, surrounded by golden armillary spheres.

Parchment Fabrication

Parchment was a common writing support in the Renaissance, and it was made from the dermis layer of goat, sheep and calf skins. Fresh hides could be employed immediately after the slaughter of the animals, but it is mostly sun dried stiff skins or skins cured with salt that were the main raw material for parchment manufacture. To inhibit microbial activity and prevent green hides from decomposition prior to their transformation into parchment, sodium or potassium chlorides, ammonium chloride or sulfate in addition to lime (calcium containing inorganic materials, in which carbonates, oxides and hydroxides predominate) were part of the substances used in the conservation process [18, 19].

Parchment making required many steps, the most important of which are recorded here, because of their physical and chemical impact on the finished product [19]:

- Washing the fresh hides in running water to eliminate blood and waste, or the stiff skins cured with salt to turn them supple and remove salt;
- Liming by applying a slaked lime-based paste over the skins or by soaking the hides in a lime bath to make the hair fibers easier to remove;
- Scudding by cutting the most part of the hair fibers by hand and scouring the hides over a beam and removing all the hair with a dull knife (iron hand tool);
- Liming in plain lime baths containing or not orpiment (As_2S_3) to let the hides swell and degrease;
- Stretching the skins on a wooden frame in order for them to remain flat, be workable and dry slowly;
- Removing flesh and fat by scrapping vigorously the skins on the flesh side with a sharp knife and pumicing them with the aid of powdered lime or chalk (calcium carbonate);
- Shaving and scrapping with a sharp knife (iron hand tool) to get the desired thickness;
- Pumicing the skins on the flesh and hair sides by rubbing the surfaces with pumice stone (mainly composed of SiO_2 and Al_2O_3);
- Whitening both sides of the parchment by applying thin pastes of chalk or mixtures of lime, flour, egg whites and milk;
- Cutting the parchment into sheets of specific dimensions to transform them into a writing support.

From these procedures we can observe that the skins underwent important structural changes, mostly by the simultaneous action of stretching and drying, and by shaving/ scrapping. The stretching process allowed the three-dimensional fiber orientation within the dermal network to be deeply altered and permanently set in a new and highly taut form by drying, the fibers being aligned and more nearly parallel to the surface.

Generally, one or two layers of the skin dermis remained after the scrapping process: just the split of the skin (inner layer), or both the outermost (grain layer, with hair holes) containing a fine fiber structure and the more open Corium layer (larger collagen fibers constituting the layer near the flesh side). We are thus expecting to find large amounts of calcium, potassium, chlorine and sulfur in the parchment, which will obviously be present in any XRF measurement.

RESULTS

EDXRF analysis had to be performed *in situ* because the foral charters are part of the Portuguese national treasure, and hence are secure in the National Archive. An average of 50 points was analyzed in every charter, covering all the pigments, inks, silver and gold coatings and different parchment zones. The analysis revealed information on the elemental composition of the area covered by the X-Ray beam of the portable XRF spectrometer.

Complementary micro-spectroscopy techniques (Raman and FTIR) were only possible due to a previous conservation study in which micro-samples of some charters were taken, although the number of data points was scarce and did not cover all of the pigments and inks. They were, however, fundamental in identifying the molecules associated with the elemental composition revealed by EDXRF. While EDXRF took into account an area of about 9 square millimeters and gave an average result on all the elements present in this area, micro-techniques, with the help of the associated microscope, were applied on grains of pigments of a few square microns.

Parchment

In all the studied foral charters, Cl, K and Ca together with traces of Si, S, Mn, Fe and Cu were detected in parchment by EDXRF. The presence of Ca was already expected given the treatments employing lime (CaO, $CaCO_3$, $Ca(OH)_2$) for dehairing, and chalk ($CaCO_3$) so as to give parchment a whiter surface, as seen above. The presence of Mn is not surprising because of the abundance of this element in natural calcite [20]. In addition, as much K as S may originate from the potassium chloride or sulfate used as preservative in the drying conservation process of the animal skins, as already mentioned. Furthermore, Ca is expected to be associated with S and even aids sulfur uptake from the atmosphere because of the reaction of sulfur acids with alkaline lime, a classical exothermic acid/base neutralization reaction over time [21]. Fe and Cu are not surprising either since they occur naturally at low concentrations in leather and parchment [22]. The scrapping procedures in the parchment usually employed iron tools as well.

Inks

In the written text and outlining of the heraldic designs of all the foral charters, iron-based inks were found. Their elemental composition can be seen in the EDXRF spectra, of which some examples are presented in Figure 3. These spectra suggest the use of iron gall inks, which were by far the most used ink type in ancient European manuscripts. This ink type is basically made from galls, vitriol ($FeSO_4$), gum Arabic as binder and an aqueous vehicle such as wine, beer or vinegar. Since vitriol, the main source of iron in these inks, could be obtained from different mines, the elemental composition of these inks could present other metals, such as Cu, Al, Zn and Mn, in addition to the iron sulfate [23, 24]. This variation in elemental composition can be used to infer on the possible location of the workshops in which the manuscript was fabricated, by correlating the vitriol composition of known extraction mines in a given geographical region. Raman spectra of the inks used throughout this work unambiguously show the presence of iron sulfate ($FeSO_4$) [25].

Zinc As a Preserver

The migration processes of the minor elements in the iron gall inks, compared to that of the major constituent Fe, has been extensively studied [26], and the mobility of the Zn and Cu ions through the support has been found to be much higher than the Fe ions.

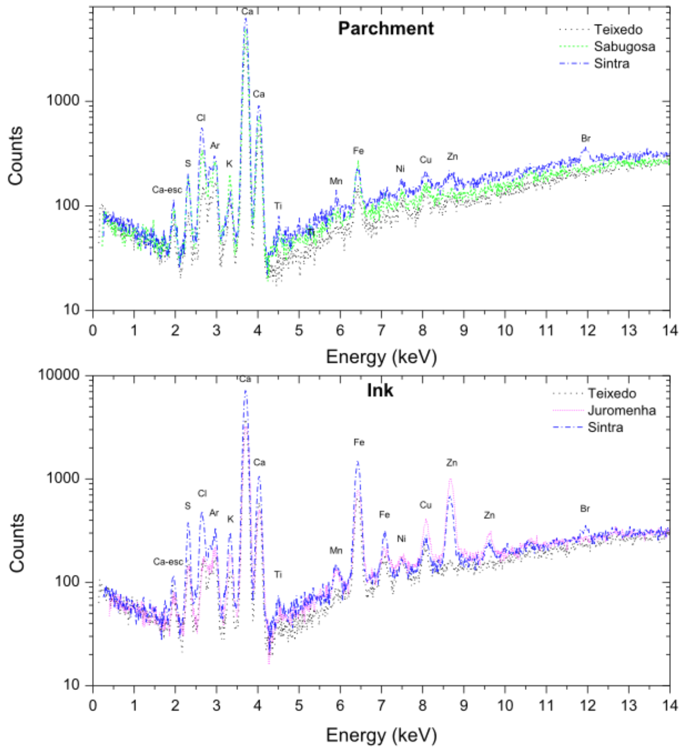

Figure 3. EDXRF spectra of the parchment and ink of Manueline foral charters.

The Fe^{2+} content on the analyzed inks is found to be a chemical indicator of the degree of corrosion in ancient manuscripts, and it has been found that the presence of Cu ions enforces the photo-reduction process of iron by acting as a catalyst. Micro-XRF measurements have thus confirmed that the discolored inks in historical documents contain high amounts of Cu (compared to Fe), possibly containing a complex mixture of several decomposition products such as purpurogalline or ellagic acid [27].

However, as shown by Kanngiesser *et al.* [26], the support degradation in historical manuscripts is not only a question of iron oxidation, and other metals could play an important role. In the foral charter of *Sintra*, two iron gall inks were identified (see Figure 4), one containing mainly Fe and another Fe and Zn. The presence of this last metal suggests that vitriol used to make these inks should have different provenances.

Furthermore Zn does not contribute to the color formation of the ink solution but possibly changes its chemical properties. Figure 4 presents a photograph of two regions of the manuscript under transmitted light showing the analyzed inks. As it has been verified throughout the manuscript, parchment was strongly attacked by a fungus exhibiting dark brownish stains.

However, whenever Zn based ink was employed (Figure 4 b), this biological alteration was not observed in its adjacent area. The presence of a light aureole around the written text may confirm the assumption that Zn inhibits the degradation process of the parchment [24]. In addition, the detection of Br in this manuscript suggests the use of a bromium-based insecticide in the past. In fact the use of methyl bromide was one of the most popular fumigants used in museums until recently [28, 29].

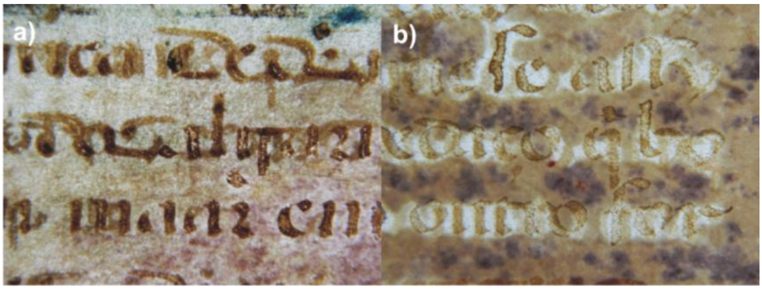

Figure 4. Picture under transmitted light taken from the foral charter of *Sintra* showing Fe based ink a) Fe and Zn based ink b).

Pigments

Every color in the illumination was analyzed by EDXRF and, when micro-samples were available, by Raman spectroscopy and SEM-EDS. Due to the great detail in the manuscript design and the fact that almost all of the colored features were covered with white highlights or arabesques (and exceptionally with golden interlaces), some colors could not be resolved independently given the X-ray beam size. Hence, some contamination of different pigments could be seen in many colors, especially from adjacent ones.

White

The only available white pigment at the beginning of the 16th century was the basic lead carbonate also known as white lead. EDXRF spectra of this color, in all studied charters, are consistent with the presence of this pigment, revealing very intense Pb peaks as can be seen in Figure 5. The white lead is found almost ubiquitously in all charters and throughout all of the illumination, either combined with the other pigments, to get lighter shades, or in arabesques drawn over most of the features in the heraldic design.

This fact, coupled to the X-ray beam spot size, leads to the presence of the characteristic lead peaks in the EDXRF spectra in almost every pigment. Raman analyses on this pigment demonstrated that different compounds of lead were put in evidence, from basic lead carbonates to neutral lead carbonate, present alone or in mixtures, including the lead oxide carbonate $2PbCO_3.Pb(OH)_2$, designated as hydrocerussite or more generically lead white (detected in most of the charters), the lead oxide carbonate hydroxide $Pb_5O(OH)_2(CO_3)_3$, known as plumbonacrite (found in the foral of *Teixedo*) and the lead carbonate $PbCO_3$ called cerussite (the unique phase found in the foral of *Sintra*). In the pigment lead white artificially produced since early historical time, the presence of one or more phases can be traced back to the manufacture process, evolving to place lead sheets over pots filled with vinegar and surrounded by dung and left during three or four months, depending on the more or less complete reaction [30].

It was generally accepted, due to the lack of control during the fermentation process, that there would be a wide variation in the amount and purity of the lead phases formed, leading to different chemical and physical properties of the white pigment used. Hydrocerussite is regarded as the fine quality pigment, intentionally used in the illuminations for its high refraction and opacity, and cerussite, as the phase having the lowest binding-power.

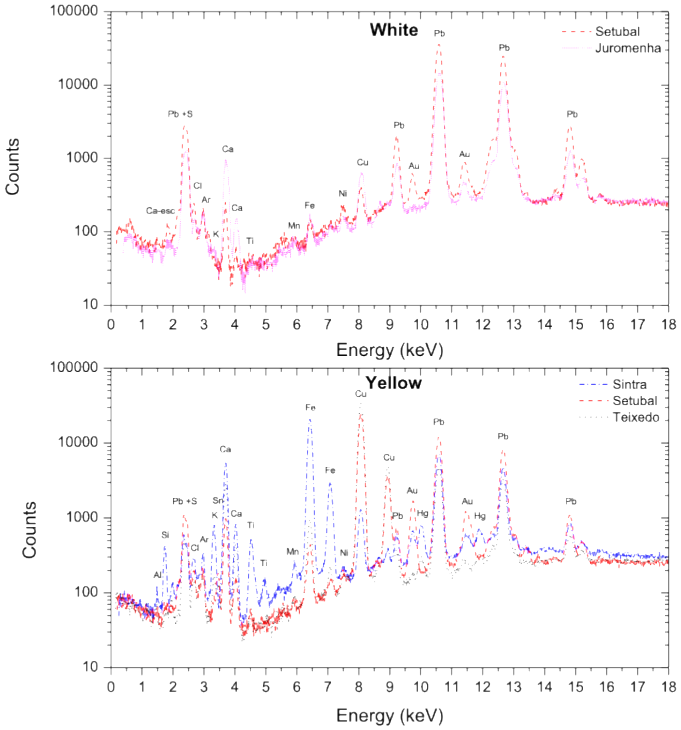

Figure 5. XRF spectra of the white and yellow colors of some of the studied foral charters.

Irrespective of the phases identified in the charters, lead white demonstrated a high record for permanence over five hundred years.

Although lead white is theoretically incompatible with sulfide pigments, and should form black lead sulfide in contact with them, this situation was not verified in the foral of *Sintra*, where lead white was tinted with very low amount of red mercuric sulfide (vermilion HgS).

Yellow

XRF spectra of yellow pigments used in the decorations of the frontispiece of some of the studied charters show the presence of Al, Si, Fe, Ti, Mn, Sn and Pb. At first sight the coloration of the yellow pigment suggests the use of goethite ($Fe_2O_3H_2O$) which was later confirmed by Raman spectroscopy. The identification of this pigment through Raman spectroscopy was quite difficult due to the background fluorescence.

Hence, it was decided that the laser source power should be increased by 10 times, which would result in the sample being burnt. However, the analysis in the burnt area revealed peaks corresponding to red ochre. The molecular transformation from yellow to red ochre has been particularly useful for enhancing the identification of the base raw material as being, in fact, yellow ochre [31].

Regarding the other elements observed in the EDXRF spectra, it should be noted that ochre materials are rich in Al and K from phyllosilicates minerals, titanium essentially in the form TiO_2 and manganese oxide which gives the yellow color a brownish hue. It is finally noteworthy that ochres from sulfide ores are enriched in minor elements such as Cu, Zn, As and Pb [32].

Red

Through visual analysis of the studied foral charters (see Figure 2), we observe a wide range of red colors in the frontispieces. The difference in shades suggested that the charters have been subject to one (or more) of the following conditions: different red pigments have been used in each charters, different state of conservation of the tint might alter the color over time, a mixture of several pigments have been used or an organic dye might have been employed. The EDXRF spectra of the red color (see Figure 6) in all charters, indicate that at least two different pigments and probably an organic dye have been used. The pigment most in usage is the vermillion or cinnabar (HgS), a very expensive pigment at the time, detected through the very intense Hg and S peaks in the spectra of all foral charters except that of *Setúbal*. Although the terms cinnabar and vermilion were used interchangeably in the technical sources to describe either the natural or manufactured pigment, it is believed that at the early 16th century, the pigment was deliberately produced by combining quicksilver, that is mercury, with virgin sulfur as described in many medieval Books of recipes [33].

In the charter of *Setúbal*, however, the red color has an almost orange shade and the EDXRF spectrum does not contain the characteristic Hg peaks that all other charters do. This charter reveals a strong presence of Pb in this color, which is compatible to another pigment used in that age, the red lead also known as minium (Pb_3O_4). The presence of small amounts of Fe seems rather related to the use of iron gall ink in the frontispiece than to the addition of iron oxide-based pigments employed for their red dominant color, usually recorded as ’ochers’.

The dark red found in the vertical stripes of the foral charters of *Castanheira e Povos* and *Juromenha* might have been obtained from an organic dye. Several red dyes are referred in medieval texts and might have been used.

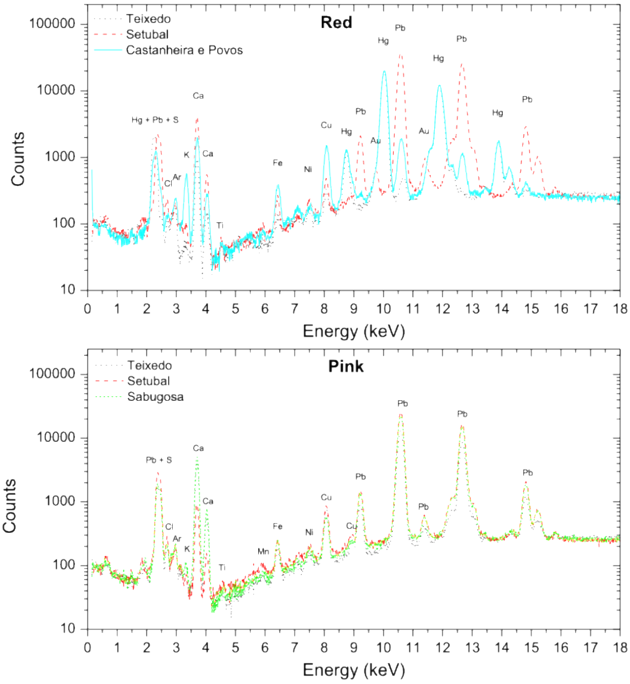

Figure 6. EDXRF spectra of the red and pink colors of some of the studied foral charters.

Among them, the most quoted are the Tyrian purple (extracted from marine gastropods mollusks), [34] turnsole (extracted from the plant Crozophora tinctoria), [35] archil (obtained from the lichen Rocella tinctoria), [34] the juice of pressed poppy flowers [34], carmine or crimson (sourced from the insect Kermes vermilio or extracted from ’deveined woad leaves’) [36], lac-dye (sourced from the insect Kerria Lacca), Brazil-wood (from trees of the family Caesalpinia), and madder (from the plants of the family Rubiaceae) [33]. As the foral charters are of Portuguese production, special attention should perhaps be paid to the use of Brazilwood, a raw material very much available in Portugal in the early 16th century, and specially quoted in the 15th century Portuguese manuscript: *O libro de komo se fazen as kores das tintas todas* [33].

Pink

The pink color is used throughout the frontispieces either in the initial of the King’s name or in the borders depicting flower motifs. Because of the homogeneity and fluidity of the pink color, it is likely that a combination of a red organic dye with lead white has been used to obtain such bright pink. The EDXRF spectra of the pink regions in all charters show high concentrations of Pb, and no other elements except the ones present in the parchment. From Raman spectroscopy, despite the high fluorescence, basic lead carbonate was detected very often. One of the red dyes enumerated above could in principle have been used to make the pink color. At this point, it cannot be asserted with certainty which of the recipes was employed to produce the pink color [33].

Green

Most of the green motifs are very small and in almost all the figures, the miniaturist sought to obtain different shades of green which were combined to give a three dimensional effect. The painted leaves in the marginalia were outlined with iron-gall ink, thus the presence of Fe is expected in the EDXRF spectra. In Figure 7, it can be readily seen that the tint is copper based. Peaks of gold in the charter of *Setúbal* appeared because of the proximity of the measurement to the gilded areas, and Hg and Pb in the foral of *Teixedo* because of the red and white used in the initial, close to the green color. However, only by means of EDXRF technique, it was impossible to establish whether the green layers contained verdigris, one of the most common synthesized green pigments, or malachite, a mineral in usage in its natural form. It should be mentioned that verdigris by its own is a collective term for copper acetates of different chemical composition which range in color from green, via green-blue and blue-green, to blue: basic verdigris (for example $Cu(CH_3COO)_2[Cu(OH)_2]_32H_2O$, of a green shade) and neutral verdigris (for example $Cu(CH_3COO_2)_2H_2O$, of a blue-green shade). At least, eight copper acetates compounds are currently recognized [37]. Regarding malachite, this term could also refer to a number of pigments, including material derived from the natural mineral. Malachite is a green basic copper carbonate with composition $Cu_2CO_3(OH)_2$, which may be found with azurite, chrysocolla, and cuprite; hence, these may be present as impurities in malachite pigments [38]. Noteworthy is the fact that crysocolla was also used historically as a term for malachite in classical and medieval literature such as the texts by Theophrastus (c. 315 BC), Vitruvius (1st century BC) and Pliny (77 AD), while chrysocolla is a soft and fragile copper silicate hydroxide hydrate mineral with chemical composition $(Cu,Al)_2H_2Si_2O_5(OH)_4n(H_2O)$. With respect to cuprite, it is a cubic red neutral copper oxide mineral, with chemical formula Cu_2O, but it may also be found as an alteration product of copper carbonate pigments such as azurite and malachite. Whatever be the pigments, peaks of Cu in the EDXRF spectra were not sufficient to duly identify the green colorant used in the foral charters, and Raman analyses were crucial to determine that in all cases, malachite ($Cu_2CO_3(OH)_2$) was the favorite pigment.

In the charters of *Sintra* and *Teixedo*, bright blue particles of azurite (an hydrated copper carbonate mineral of composition $Cu_3(CO_3)_2(OH)_2$) were also well differentiated by Raman in the color green, perhaps originated from contamination of adjacent areas in the former case, and likely deriving from the mineral ore deposits in the latter case. Not surprisingly, particles of calcium carbonate were also found in both charters, since this inert material could be used as extender [38].

Blue

The deep blue color applied in the frontispiece of all charters, and their coarsely ground particles, allowed their immediate visual identification as having been executed with azurite. Analyses performed by EDXRF confirmed this assumption, essentially through the intensity of the Cu peaks in the spectra, as can be observed in Figure 7. The Au, Hg and Pb peaks are correlated to the gold, red and white pigments which surround the blue areas. Azurite was one of the most expensive pigments, after lazurite (natural ultramarine blue), in the 16th century. Its use was in line with the Kings demands on using the best materials for such an important task, reinforcing the Kings power and influence.

Although the typical color of the naturally occurring mineral did not leave any doubt on the composition of the tint, it was verified, by cross-checking the EDXRF and Raman data, that iron was originating from the iron-gall ink, and lead from the white underlines highlighting the several blue motifs.

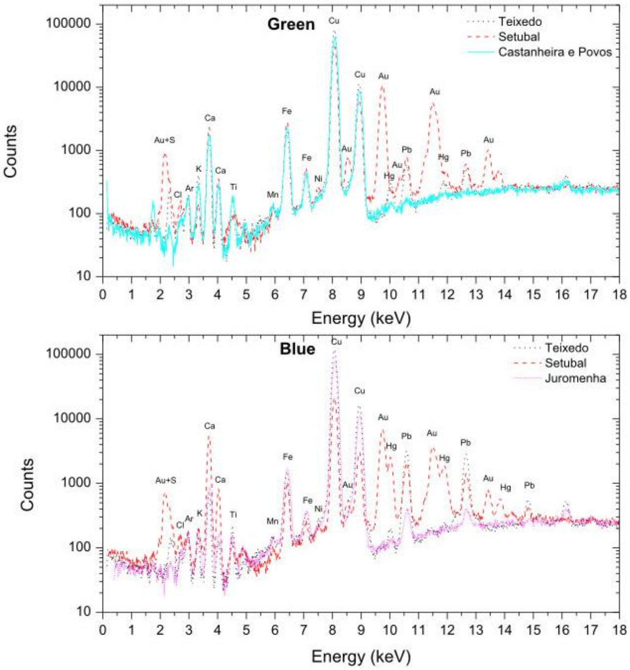

Figure 7. EDXRF spectra of the blue and green pigments of some of the studied foral charters.

Gilding and Silvering

Gold and silver were ubiquitously used in the illumination of medieval manuscripts in order to obtain the desired bright. In all the studied charters, gold and silver available in the form of hand-beaten leaf were ground prior to their application, thus matching with the so called ’shell gold’ and ’shell silver’. In all cases, they were laid directly on the parchment as paints, without no preparatory layers to increase their adhesion or modify their appearance (texture and color). Records by Optical imaging and BSE records by SEM imaging were obtained for the parchment (Figure 8 a), and the gilded (Figure 8 b) and silvered (Figure 8 c) areas as well, which illustrates some data of the illuminated frontispiece of the foral charter of *Castanheira e Povos*. The qualitative and semi-quantitative results demonstrated that, regarding gilding applied to the motifs in the border, particles of two different batches of hand-beaten gold leaf were used: a binary alloy containing (by weight) an average of 96% of Au and 4% of Ag; which matches with a 23 carat gold alloy, considered to be of a high grade in the 16th century [39]; and another gold-silver alloy containing less than 37,5% of Au, thus matching with a 9 carat gold alloy. Although this latter reading indicated the use of a very low-grade metal, the association between both gold alloys should not be regarded as a poor-quality coating but rather as a judicious way to obtain a different shade of yellow from the one applied to the other gilded areas of the coat of arms (crown and castles). Pure silver alloy was put in evidence in the escutcheon of the coat of arms, since no Cu was found. Sulfur was detected instead, referring to oxidized silver whose tarnishing in the form of sulfide is about 10% (in weight); which represents, at least on the surface of the coating performed by the EDS analysis, a corrosion of about 30%, in accordance with the stoichiometry of each particular element (Ag and S) needed for the chemical reaction to occur (to form Ag_2S). Figure 9 shows that the elemental composition in the gilded areas of the charters is very similar. The high content of Fe and the presence of Zn in the charter of *Castanheira e Povos* is due to the use of iron gall ink in outlining the gilded areas. The small Pb peaks are related to the white motifs inserted in the golden crown.

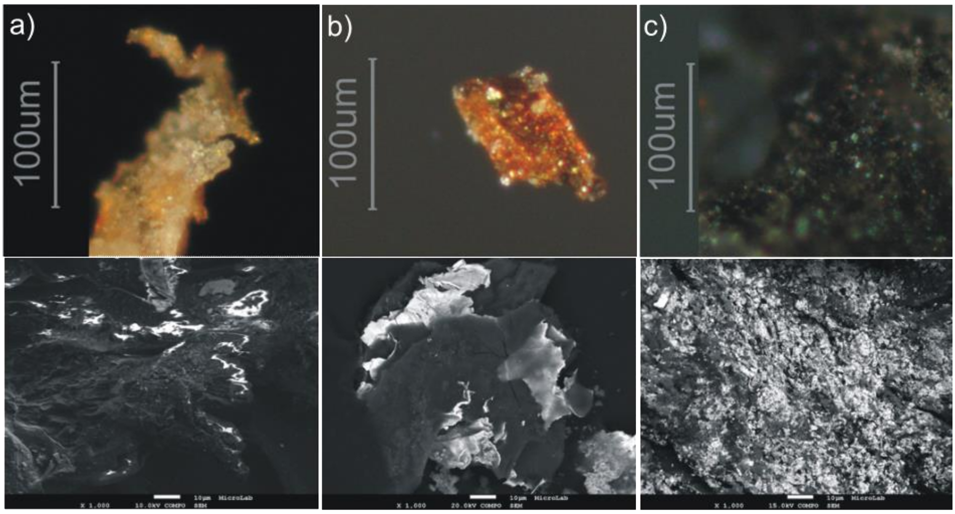

Figure 8. SEM images of the a) parchment, b) gold and c) silver metallic coatings of the foral charter of *Castanheira e Povos*.

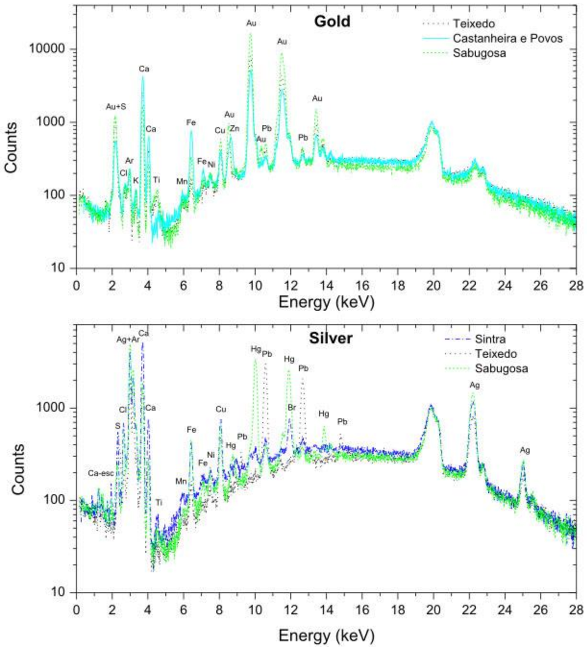

Figure 9. EDXRF spectra of the gold and silver coatings of some of the studied foral charters.

Regarding silvering, the EDXRF spectra show the presence of Hg and Pb in high quantities, apart from the expected Ag peaks. This is due to the fact that in the charter of *Sabugosa*, the measurement was performed in the shield, and hence very close to the red area giving rise to the observed Hg peaks. In the foral of *Teixedo*, the EDXRF measurement was performed in the area surrounding the initial, which is covered with white arabesques, hence resulting in the detection of lead. In the charter of *Sintra*, the presence of bromine, which is also detected in the parchment (see Figure 3), is noteworthy. Once again, Fe and Cu can appear due to the fact that all design outlinings were made with iron gall ink.

Oxidizing Agents

The silver coating in all forals, except those of *Sabugosa* and *Setúbal* which have very bright metallic coatings, present a tarnished brown or black color and, to some extent, can only be identified as silver through EDXRF. The silvered surfaces of the Manueline foral charters seem to have received no protective layer, which is surprising at a time when illuminators were well aware of risks of corrosion, and which, in fact, did not prevent silver from tarnishing. In pure silver materials, the main products formed by atmospheric corrosion are sulfide (Ag_2S), chloride (AgCl) and oxide (Ag_2O). The chloride and sulfide formation are the most critical ones, especially in places where the pollution is higher, like urban areas, where most of the silver artifacts are found. Due to the importance of sulfidation and chlorination in silver corrosion, these processes have been extensively studied [40-42]. However, as explained in Section (*Parchment Fabrication*), the parchment support is produced through an extensive set of physical and chemical reactions, such as liming, salting, pumicing and every other drying process, which results in the support having a high concentration of Ca, Cl, K and S ions.

This is probably the reason why the silver coatings in charters of *Castanheira e Povos*, *Teixedo* and *Juromenha* have become so dark. Thanks to the mapping of the elements and the presence of bromine in *Sintra* charter, we may explain the much stronger oxidation of the silvered areas since silver bromide is extremely photosensitive [43]. Bromine, which was also detected in other foral areas, though in lower intensity, might reflect the use of a bromine-based fumigant which was a common practice in the conservation of ancient manuscripts. The excellent metallic coating conservation state of the charters of *Sabugosa* and *Setúbal* is somewhat of a puzzle specially when no known interventions have been performed on the manuscripts.

CONCLUSION

This work highlights the role of non destructive analytical techniques in the study of cultural heritage. We show that a better understanding of the implemented materials and techniques regarding the illumination of ancient manuscripts, such as the Manueline foral charters, is possible with X-ray fluorescence spectrometry and complementary techniques. With this information, the restoration and conservation of these precious manuscripts can be undertaken with a raised awareness, especially in what regards the materials and the construction techniques. The richness of the foral charters can be inferred by the high quality of the metal coatings and pigments and also by the attention to the fine details in the illumination. The conservation of the paints and metal coatings greatly varies from charter to charter, and some of the degradation processes could be identified through EDXRF spectra. The ability of the miniaturist in combining fine quality materials to obtain rich palettes of colors and well executed paint layers, whatever the size of the motifs to be depicted, show that every aspect of the illumination process was taken into consideration to bring the charters to the latest fashion. The extensive production of the renewed codices suggests a network of well organized workshops throughout the country.

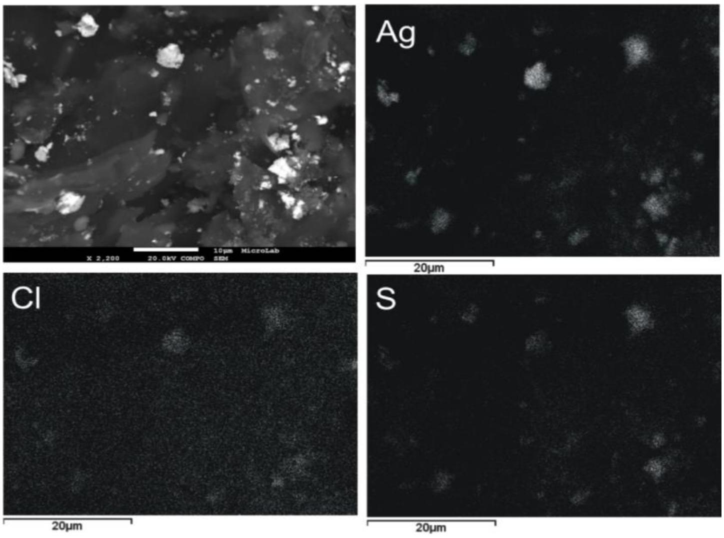

Figure 10. SEM-EDS elemental mapping of the silver metallic coating of the foral charter of Teixedo.

Bearing in mind such organization, it should be noted that the use of different pigments, especially in the red and pink colors, suggests that different individuals have performed the illumination of the charters. The elemental composition of the iron gall inks further indicates that the provenance of the raw materials, such as vitriol, might have been obtained from different mines. We also show that, contrary to ancient treatises, the metallic coatings do not present a protective layer, which results in the tarnishing of the silvered areas. The tarnishing in the charter of *Sintra* is even more dramatic since a bromine-based fumicide appears to have been used in the conservation of the foral. This fumicide, however, was not effective in protecting the charter which presents dark stains caused by a fungus. Nevertheless, this fungus allowed us to discover that this particular fungus growth was inhibited by the presence of Zn in the iron gall ink. Further studies are needed to assess the mechanism of this inhibiting process.

ACKNOWLEDGMENTS

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Chapter 10

PREVENTIVE CONSERVATION OF CULTURAL HERITAGE: AN INTEGRATED SYSTEM OF BIOLOGICAL AND MICROCLIMATE MONITORING

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ABSTRACT

Cultural heritage preserved in indoor environments (museums, libraries, archives, etc.) is subject to *biodeterioration* caused by specific groups of biological agents called *biodeteriogens*. Several factors may affect the process of biodeterioration, depending on the chemical and physical characteristics of the materials, the state of conservation of the artefacts, the environmental conditions and the nutritional needs of biological agents.

The biological components of air (bioaerosol) can be a potential biodeteriogen for cultural property. In the case of artefacts made using organic materials, they can be identified in a specific fungal and bacterial microflora. Once deposited on the surface of cultural objects, these microorganisms can find favorable nutritional and environmental conditions, thus becoming biodeteriogens. Certain classes of airborne particles contain allergens or toxins, and can pose a risk to the health of operators and visitors. The prevention of biological risks is based on a thorough knowledge of aerobiological particles and the factors that affect their circulation, survival and growth in a specific

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environment, associated with careful control of microclimatic parameters. Such an integrated system of biological (air and surfaces) and microclimatic monitoring, based on a methodological model, represents the basis for studying the "environment-artefact-man" complex in order to understand, assess and prevent biological risks. The proposed approach relies on the analysis of: 1) airborne microorganisms with active and passive methods; 2) the surface of cultural objects with non-destructive and non-invasive techniques based on nitrocellulose membrane filters; 3) fungal spores with a spore trap (Hirst type) and microscope; 4) surface and airborne allergens with immunoenzymatic assays; 5) airborne particles, with a laser particle counter; 6) indoor microclimatic conditions: air temperature, relative humidity, air velocity and distribution, light, temperature of surfaces, related to the conservation of cultural property and the risk of contamination by biological agents, are also analyzed. The effect of ventilation strategies on the microclimate can be evaluated using computational fluid-dynamics (CFD) tools. A multiphysics approach combined with CFD is used to assess air ventilation and microclimate. Transient simulations based on experimental data, run on three-dimensional models of the studied environment, which helps to define preservation and maintenance criteria. CFD plays an important role in the prediction of damage and risk, as it helps to evaluate the efficiency, adequacy and reliability of any Heating, Ventilation and Air Conditioning (HVAC) system and its maintenance criteria, thus providing critical indications for indoor air quality control and energy savings. Studying both the biological and microclimatic quality of cultural heritage environments is fundamental to define adequate conservation methods and standards, and to protect the health of operators and visitors. This methodology is also a useful tool for managing cultural heritage sites and for choosing the best environmental control strategy when retrofitting buildings, especially in all those cases where a historical building is modified to become a museum, library or archive.

1. INTRODUCTION

Indoor environments such as museums, libraries and archives host a wide variety of cultural objects, both organic and inorganic. These precious artefacts are vulnerable to many types of deterioration by physical, chemical and biological agents. The interest in biological deterioration, also called *biodeterioration*, showed a strong increase over the last few decades. The term biodeterioration, which was introduced in 1968 during the first International Biodeterioration Symposium in Southampton, UK, denotes "any undesirable change in the properties of a material caused by vital organisms" [1]. *Biodeteriogens*, that is biological agents responsible for alterations, are divided into autotrophic and heterotrophic based on their nutritional needs and ability to use substrata for growth and reproduction. Several factors affect biodeterioration processes, which vary according to the type of materials and their biodegradability, the ability of biological agents to use cultural property as a source of food, and environmental conditions. Some conditions can allow the development of potentially biodeteriogenic agents, which in turn can lead to serious damages and significant cultural and economic losses. It has been shown that in indoor environments the biological component of air, collectively known as *bioaerosol*, may be a potential cause of deterioration for artefacts and may have an important role in the etiology of several diseases in operators and visitors. To better understand the relationship between aerobiological particles, the biodeterioration of artefacts and the risks associated with the conservation and restoration of cultural property, *aerobiology* has been introduced into the field of cultural heritage [2-5]. Aerobiology is a discipline that studies biological airborne particles, their origin, their movements in the air and their effects on the environment (outdoor and indoor) as well as on humans, animals, plants and artefacts. Aerobiology has therefore become one of the fundamental scientific disciplines for developing prevention and conservation strategies for cultural property. The goal of an aerobiological investigation is to estimate the biological risk for artefacts and humans (operators and visitors) by sampling air and surfaces. The information collected will reveal the quality of air and provide an evaluation of the contamination of cultural objects and microclimatic conditions. In this context, we have developed an integrated system of biological and microclimate monitoring to analyze the biological risks for organic materials and people. The application of this system, which is described below, allows for a quantitative and qualitative study of the biological agents associated with biodeterioration and can be used to process forecasting models of biological risk. This information is important to devise appropriate corrective actions and is a prerequisite for an adequate preventive conservation of cultural heritage.

2. CHARACTERISTICS OF INDOOR BIOLOGICAL PARTICLES

In indoor environments, most of biological particles (bioaerosol) are microorganisms such as bacteria, fungi and their spores, viruses, algae and protozoa, but also spores of Bryophyta, Pteridophyta, lichen propagules, algal cells, pollen grains and Protozoan cysts may be present. Microorganisms are often found aggregated to or incorporated in other solid particles (dust from minerals, plants and animals, or resulting from the drying of saliva and secretions) or liquid particles (droplets of Flügge) that protect them from environmental stress and allow them to survive for a long time. Their size ranges from 10 µm to 100 µm for pollen grains, 1 µm to 1 mm for algae, 1 µm to 100 µm for bryophytes, 10 µm to 1 µm for lichen propagules, 2 µm to 50 µm for fungal spores, 0.1 µm to 10 µm for bacteria and 1 nm to 850 nm for viruses [2]. Bioaerosol can come from a variety of indoor and outdoor environmental sources, such as contaminated materials and objects, badly functioning ventilation systems, and modifications or renovations of buildings, where dust and debris are inevitably produced and the number of airborne microorganisms increases, especially fungal spores. Every building has its own microbial ecology, depending on its structure, finish and furnishing materials. In indoor environments, people represent one of the primary sources of microbial air contamination. Microorganisms are introduced into the environment through droplets that are emitted by the human respiratory system when talking, coughing or sneezing. Hair and skin are natural sources of microorganisms, due to the continuous process of desquamation.

For organic cultural property, fungi and their spores play a crucial role. The transport and dispersal of fungal spores is a complex phenomenon: they remain suspended in the air until their falling speed, which is proportional to the square of their radius, becomes smaller than the speed of the air movements that keep them suspended. There are several physical factors that contribute to the movement and deposition of fungal aerospores, and they may be endogenous (size, shape, roughness, density and electric charge of the spore) or exogenous (environmental parameters such as air currents, viscosity, temperature and relative humidity) [2].

Germination and development of fungal spores may be influenced by a number of environmental factors (physical, chemical or biological) that may limit or promote biological growth [6-8]. The most important environmental factors are water, temperature, light and nutrients. The presence of water, in particular, is crucial, since biological agents cannot grow and develop without a minimum amount of water, which is essential for their metabolic processes. Indoor relative humidity, air temperature and surface temperature of cultural objects are the main factors determining how much water is available to microorganisms [4, 8-9].

The principal biological agents that attack the organic materials, such as paper, wood, texiles, parchment, etc., are specific groups of fungi and some categories of bacteria, including *Actinomycetes.* The type and amount of biodeterioration on artefacts depend on how it occurs: physical or mechanical processes cause disintegration and irreversible transformations, while chemical processes, caused by metabolic mechanisms, cause the deterioration or decomposition of materials and external damages associated with the production of pigments (various types of stains, foxing, etc.) [2, 3]. The deteriorated artefacts show specific morphological characteristics depending on the microbial species involved, their physiologic conditions, the nature of the material and microclimatic conditions. Many factors are involved in the process of biodeterioration in indoor environments [2, 6-7]. In order to fully understand the causes and the mechanisms underlying this phenomenon, it is necessary to take into account the systemic action of several connected factors. These factors are, schematically:

- viable biological particles, classified according to their characteristics, their potential danger and the type of alterations caused;
- artefacts, classified according to their composition and chemo-physical characteristics and degree of biodegradability;
- environmental conditions, in particular microclimatic parameters promoting the development of biodeteriogens.

Currently there are no specific recommendations for biological monitoring of air and surfaces and no threshold values for the different types of artefacts and the different classes of environments. The variety of methods and sampling techniques used do not allow us to compare data [10-21].

The Italian Ministry of Cultural Heritage has included in its Guidelines on technical and scientific criteria, and operating and development standards for museums (*Atto di indirizzo sui criteri tecnico-scientifici e sugli standard di funzionamento e sviluppo dei musei*) a section on biological contaminants and biological risk assessment for artefacts [22]. As for the prevention of risks to human health deriving from bioaerosol (infections, allergies and other toxic effects) [23-25], the Italian act n. 81/2008 *Attuazione dell'articolo 1 della legge 3 agosto 2007, n. 123, in materia di tutela della salute e della sicurezza nei luoghi di lavoro* prescribes that risk assessments for biological agents be carried out in all work environments, including those dealing with the conservation and restoration of cultural property.

3. MICROCLIMATE CONTROL AND INDOOR QUALITY ANALYSIS

The degradation of works of art stored in indoor environments and the degradation of materials in historical buildings that have been turned into museums, libraries or other types of structures mainly depends on indoor microclimatic conditions [26]. At present the Italian standards [27-31] are the only official method for evaluating environmental stress levels and the degradation process of the spaces for conservation and of the objects exhibited. These standards refer to an official document concerning parameters for surveying and monitoring procedures [28-30, 32]. The measurement of indoor climate in heritage buildings is a fundamental technique to evaluate environmental damage and degradation processes, to support the protection, conservation and preservation of works of art, by improving the quality of indoor environments. This is particularly important when old buildings have special architectural and historical value. In most cases, buildings themselves are works of art and at the same time preserve various precious objects [33, 34]. The stability requirements of microclimatic conditions play a key role in the deterioration processes. It is necessary to reduce variations in thermo-physical parameters because they are as damaging as their absolute values, ensuring a sufficient comfort level for users [32, 35, 36]. Monitoring campaigns connected to CFD modelling and transient simulations are necessary in order to assess if the building can be used for a purpose, such as a museum, and if it is possible to reactivate passive systems (lighting, cooling, natural ventilation) [35, 36]. Several studies are based on experimental monitoring campaigns consisting of non-invasive in situ analysis, whose results provide a characterization of works of art and the environment where they are exhibited. Monitoring campaigns need lengthy processing and high costs. Furthermore, non-invasive techniques using sophisticated instruments are very expensive. Microclimate control is based on the measurements of the air temperature, air velocity and air humidity, but also on the analysis of the main thermo-physical properties and performances of building materials. The indoor air quality and the number of air changes should also be controlled, especially where the presence of people cause high and latent heat loads and can be a significant source of pollution. At present there is no single protocol accepted at the international level. Guidelines and recommendations only set basic criteria and provide guidance on recommended levels for the main environmental parameters for conservation (internal air temperature, relative humidity, lighting levels, ultraviolet and infrared components filtering).

A recent work [37], belonging to non-invasive techniques, proposes a method based on the implementation of the current standard UNI EN ISO 13786 [38], to study the heat transfer to and from a single thermal zone (one of the exhibition rooms) of a museum. The proposed method [37] can provide useful support in decision making regarding the most suitable environmental control strategies such as passive control, controlled ventilation, shading and added insulation of building, modular and movable heating/cooling plant systems. It also assists in the estimation of the time-course of the temperature on the internal surface of the walls, which is an important factor for optimally arranging the paintings inside the exposition rooms [37]. To evaluate the effects of management policies, including the possible installation of a HVAC system, microclimate risk assessment for preservation and maintenance of cultural heritage numerical simulations performed using computational fluid dynamics CFD, combined with a multiphysics approach, improves the information obtained from experimental measurements [35, 36]. However, microclimatic measurements do not provide complete information, because they neglect the important synergetic effects of different parameters. The assessment of such complicated situations by easy-to-handle and low-cost techniques can be achieved using Multiphysic-CFD simulations [35]. CFD simulations provide important results for defining preservation and maintenance criteria but also the necessity of a correct ventilation system [35, 36]. Suitable conditioning plant design is only one aspect of a wide problem that concerns the thermo-physics of a building connected to the stability requirements (air temperature, velocity and relative humidity into a specific bandwidth) of the internal ambient.

4. INTEGRATED SYSTEM FOR BIOLOGICAL AND MICROCLIMATE MONITORING

The development of an integrated system of biological (air and surfaces) and microclimatic monitoring, based on a methodological model and non-destructive and non-invasive techniques, represents the starting point for studying the *environment-artefact-man* complex so that we can understand, assess and prevent biological risks (Figure 1).

The importance of simultaneously assessing the biological environmental components (air and surfaces) and microclimate derives from the close relationship between the concentration of microorganisms, their type and their circulation, which are strongly associated with the microclimatic conditions and the movements of air. The integrated system provides a global view of biological contamination and microclimatic parameters from the static and dynamic points of view. Data gathered and analyzed through provisional models allow us to detect situations of risk for both artefacts and humans.

The integrated system relies on the analysis of: 1) airborne microorganisms with active and passive methods; 2) the surface of cultural objects with non-destructive and non-invasive methods based on nitrocellulose membrane filters; 3) fungal spores with a spore trap (Hirst type) and microscope; 4) surface and airborne allergens with immunoenzymatic assays; 5) airborne particles, with a laser particle counter. Microbiological environmental pollutants are identified by means of direct culture and molecular biology techniques. Indoor microclimate conditions rely on the analysis of: air temperature, relative humidity, air velocity and distribution, and surface temperature. A multiphysics approach based on CFD simulations is used to evaluate air ventilation and microclimate. In order to obtain reliable information on the fluid-dynamic and thermal fields, the simulations, performed using experimental data, are carried out during microclimate measurement campaigns. Transient simulations are applied to three-dimensional models of the studied environment, helping to define preservation and maintenance criteria. The integrated system plays an important role in preventive conservation of cultural heritage and in the prediction of damage and risk, as it helps evaluate the efficiency, adequacy and reliability of any plant and its maintenance criteria, thus providing critical indications for indoor air quality control and energy savings.

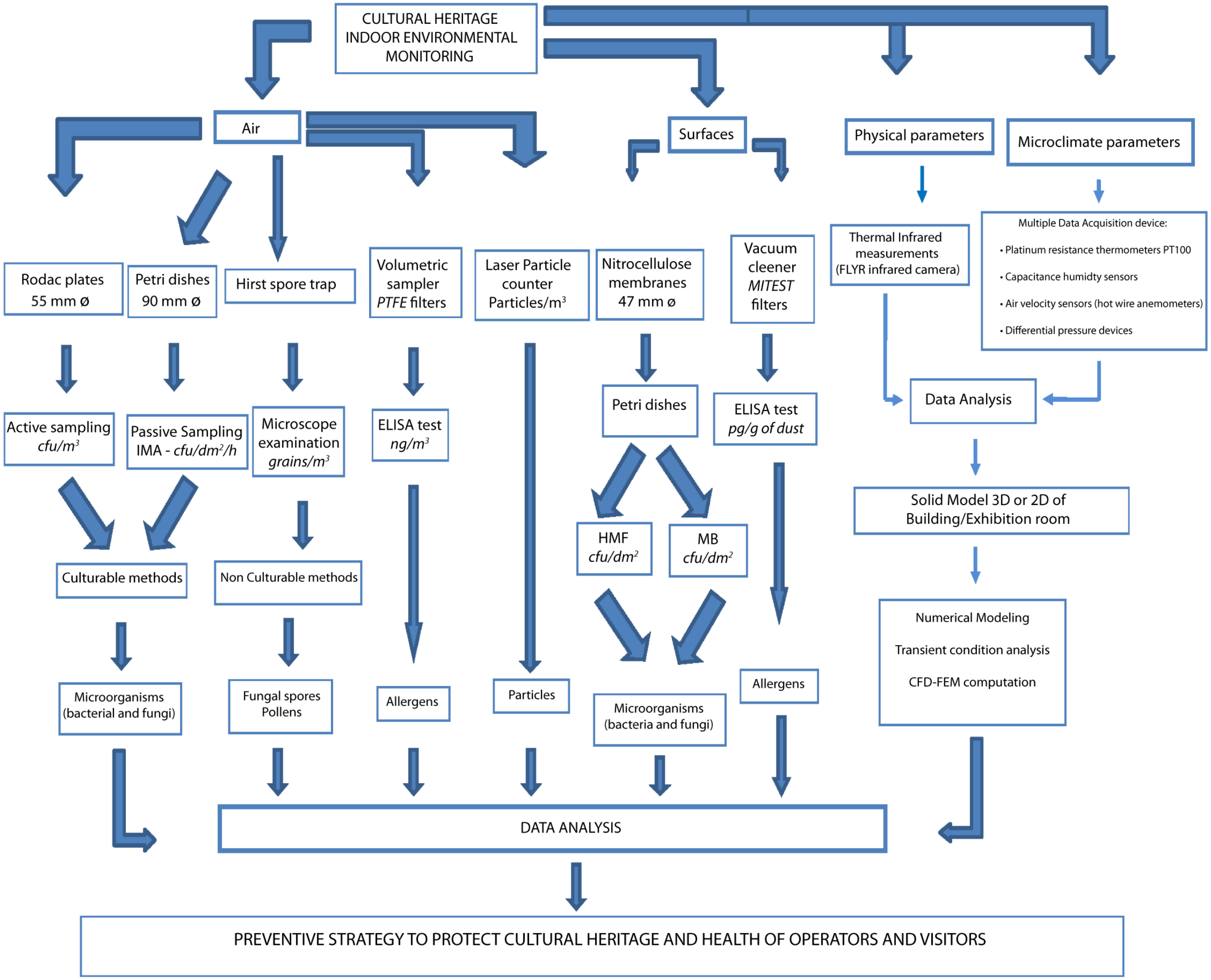

Figure 1. Flowchart of the integrated system of microbiological and microclimate monitoring.

4.1. Air Microbial Sampling

For air monitoring, both active and passive samplings are used (Figure 2) [39,40]. Active sampling measures the concentration of viable particles in the air, while passive sampling measures the rate at which particles settle on surfaces. For active sampling, however, there are many different types of samplers on the market, each based on a different design. As a consequence, different active samplers may give different results. We decided to use a DUO SAS 360 impactor (Surface Air Sampler) (International PBI, Milan, Italy), with a flow rate of 180 litres per minute (L/min), mainly for the following reasons: 1) it allowed us to simultaneously test two media (for example, one for bacteria and the other one for fungi); 2), it is certified to collect particles larger than 1.5 µm; and 3) it allows isokinetic sampling. The sampler is usually placed in the monitored room one meter above the floor and about one meter away from any physical obstacle. Tryptone Soy Agar (TSA) is used for bacteria isolation and Sabouraud Dextrose Agar (SDA) + chloramphenicol for fungi isolation. The results are expressed as colony forming units per cubic meter (CFU/m^3). Petri dishes are used for passive sampling to determine the Index of Microbial Air Contamination (IMA) [41]. This value corresponds to the number of CFUs counted on a Petri dish that is left open to the air for one hour (one meter above the floor and one meter away from walls or any major obstacle). Different heights and exposure times may also be used. Results expressed as IMA can also be expressed as CFU per square decimeter per hour (CFU/dm^2/h).

Figure 2. Equipment for air sampling. a) Active sampler; b) Passive sampler; c) Hirst spore trap; d) and e) Two rooms of the Magnani Rocca Foundation during air monitoring.

Figure 3. Surfaces sampling at Magnani Rocca Foundation. a) and b) Microbial Buildup (MB); c) and d) Hourly Microbial Fallout (HMF).

A Hirst spore trap with a flow rate of 10 L/min with a microscope is used to directly detect viable and non-viable fungal spores and to evaluate the temporal distribution of particulate. The count is performed according to the methods defined in UNI 11108/04 [42]. The Hirst spore trap is also used to identify pollens. The presence of pollens in an artificially ventilated environment can indicate an improperly controlled airflow between the outside and the inside (for example, if windows are opened when they shouldn't be).

4.2. Air Particle Sampling

A particle count is carried out using a laser particle counter to determine the number and size of different-diameter particles in a given volume of air, typically one cubic meter, without discrimination between viable and non-viable. Particle counters are commonly used to classify environments according to their contamination risk, for example in the pharmaceutical and electronics industries [43].

4.3. Surface Microbial Sampling

The sampling is carried out in a non-destructive way using nitrocellulose membrane filters (Sartorius AG, Goettingen, Germany) that measure the Microbial Buildup (MB) and Hourly Microbial Fallout (HMF) (Figure 3) [44, 45]. The MB indicates how many microorganisms are accumulated on a given surface during an indefinite period of time prior to the sampling. By pressing a nitrocellulose membrane onto the surface the data is collected by the operator's fingertips, which are protected by sterile gloves. The HMF corresponds to the number of microorganisms that fall on a given surface during a one-hour period. Samples are collected leaving a nitrocellulose membrane on the tested surface for one hour. After samples are collected, nitrocellulose membranes are transferred to Petri dishes. The results for MB and HMF are expressed as CFU/dm^2, as suggested in ISO 14698-1 [39].

4.4. Air and Dust Allergen Sampling

The sampling of allergens in air and dust is performed using a volumetric sampler fitted with PTFE and a vacuum cleaner fitted with MITEST filters. An immunoenzymatic assay is performed to determine the concentration of the different allergens that can be found inside libraries, such as mites Der p1 (*Dermatophagoides pteronyssinus*) and Der f1 (*Dermatophagoides farinae*), animals Fel d1 (cat), Bla g2 (cockroach), Rat n1 (rat), Mus n1 (mouse), and fungi Asp f1 (*Aspergillus* spp.), Alt a1 (*Alternaria* spp.) [46].

4.5. Indoor Microclimate Measurements

The experimental tests are usually carried out in each single thermal zone of a museum or historical building. It is also important to collect general data about the location, the local climate, the orientation of the building, but in particular, thermo-physical characteristics of all the building materials. Data concerning the existing plant system (the cooling and heating plant and also the artificial lighting system) hours of opening and temporal presence of visitors and their heat and moisture released to the ambient must be collected. Measurements are performed using a multiple data acquisition device (Babuc-ABC, LSI-Lastem instrument) with a multi-data logger by cordless data acquisition. The acquisition process is carried out every 5 minutes with hourly data and daily data processing. The sensors system is composed of: platinum resistance thermometers PT100, for ambient temperature measurement (range -20-60°C); accuracy 0.1%; resolution 0.001%); capacitance humidity sensors for the relative air humidity measurement (range (0 ÷100)%; accuracy 2%); one black globe thermometer with a 150 mm diameter, internal temperature sensors PT100 and probes BST131 (range -40 ÷ +80°C; accuracy 0.15 ÷0.35%; 20 minutes response time); hot wire anemometers (range 0÷20 m/s; accuracy 0 ÷ 0.5 m/s, ±5 cm, 0.5 ±1.5 m/s, ±10 cm/s, >1.5 m/s ±4%); differential pressure devices. The sensors are located avoiding any interference with visitors and museum technicians.

4.6. The Computational Fluid Dynamics Application

The use of numerical simulation methods for the Cultural Heritage is of increasing importance for the analysis, conservation, restoration and appreciation of works of art. This is particularly important when preservation and planned maintenance are the primary aim. Today museums, and particularly historical buildings that are turned into museums, should be considered as places where precious artefacts should have first-rate protection and conservation. It is a question of solving the compromise between protection, conservation and comfort for workers and visitors, with the consequence that preservation and planned maintenance criteria must prevail over use requirements. The aim of this project is the application of CFD in the Cultural Heritage field, specifically oriented to conservation and preservation of works of art. Airflow patterns prediction is also of great importance.

This approach is particularly useful for all old buildings and especially for those not usually provided with mechanical systems for the control of indoor air conditions. For these buildings the problems are related to the proper design and installation of HVAC systems, and to real difficulties, times and costs for carrying out a direct monitoring campaign. The methodological approach based on the combined use of some basic data (building, materials and external climate) and transient simulations using thermo-fluid-dynamic modeling of the building presents a real efficacy due to the fact that, when experimental data are not available, results can be carried out just using data provided by literature evidences, historical references and standards. This method can be a useful tool for exhibition planning and management solutions. It can help in defining preservation, maintenance and plant intervention. In particular, the knowledge of indoor climate conditions in the different zones of a building, connected to the dynamic thermal performance of the walls, is a non-invasive technique, which permits identification of the best solution for the arrangement of the various works of art.

Multiple data acquisition devices or multi-data loggers are used in indoor environments to measure key physical parameters (temperature and relative humidity of air and surfaces, lighting levels, speed and direction of air movements). Data of monitoring campaigns and indoor air pollution are fundamental for CFD simulation and models validation. The variety and complexity of the objects that make up cultural heritage, however, is so great that the present research has not been able to establish conclusive results. In this scenario, monitoring campaigns and indoor air quality controls can be difficult. The degradation of graphic collections is caused mainly by microclimatic conditions in combination with the characteristics of heritage materials and the presence of bioaerosol. Analyses of indoor temperature, relative humidity and vapour concentration distribution are carried out with dedicated transient CFD simulations, which take into account the thermo-physical behavior of building components and associate it with the thermal performance of the building detected by IR measurements. The 3D modelling and CFD simulations are applied to all those situations where there is a clear interaction between external climate variations, building structure and fluid flow domains associated with indoor microclimatic conditions. Results are crucial in order to devise measures that allow the preservation of artworks, and to understand deterioration processes and develop new preservation techniques and strategies. It is necessary to define a solid 3D model of the historical building and/or museum investigated and monitored. The meshing technique used for the 3D model must be checked and validated comparing experimental measurement data. The mesh used for CFD simulation must be checked for resolution and accuracy, comparing simulation results with experimental data. The simulations in transient conditions carried out using CFD dedicated software based on the finite element method (FEM), required the following steps:

- using assembly for the 3D drawing of the complex geometry of building and exhibition rooms;
- mesh definition with different accuracy levels utilization;
- computational domain and sub-domain definition and setting;
- thermo-physical properties assignment to the different building materials;
- boundary conditions definition;
- heat transfer analysis; turbulence flow analysis using Reynolds Averaged Navier-Stokes equations (RANS) and k-ε model used to describe the motion of fluid flow, with logarithmic wall functions; convection and diffusion analysis.

CFD simulations show that for the building structure and exhibition rooms, from a thermodynamic point of view, the compromise between protection of works of art and the museum ambient is necessary. Control of thermal, hygrometric and pollutant loads from people and various activities, as well as thermal loads from the lighting system, are necessary to obtain and guarantee the fundamental indoor microclimatic conditions for the museum and its contents. This procedure does not require too much computational time and is not difficult to use in a practical situation when considering historical building refurbishment, conservation and maintenance criteria.

5. CASE STUDIES

The integrated system we describe has been applied, at least for the biological monitoring, to several cultural heritage environments in Parma (at the Pilotta Palace during the Correggio exhibition [47], at the Palatina Library [48] and at the Magnani Rocca Foundation, which is the case described below). In Florence, inside the Salone dei Cinquecento hall in Palazzo Vecchio, a CFD transient simulation was carried out with experimental data on microclimate, indoor airflow, thermal, and air velocity (Figure 4). Thanks to a funding by Cariparma Foundation, the integrated system in its entirety has been applied at the Palatina Library in Parma. Results are currently being analyzed and prepared for publication.

5.1. The environmental microbial monitoring at the Magnani Rocca Foundation

The Magnani Rocca Foundation was created in 1977, following the wish of Luigi Magnani (1906-1984), with the aim of promoting and developing cultural activities, specifically art, music and literature. Luigi Magnani donated a villa to the Foundation, in Mamiano, near Parma, which was converted into a museum in 1990. Today the villa hosts an art collection which includes, among others, works by Gentile da Fabriano, Filippo Lippi, Carpaccio, Dürer, Titian, Rubens, Van Dyck, Goya and contemporary artists such as Monet, Renoir, Cézanne, De Chirico, De Pisis, Morandi, Burri, in addition to sculptures by Canova and Bartolini. The famous painting *The Family of the Infante Don Luis,* a masterpiece by Francisco Goya, is the emblem of a collection characterized by an extremely high quality. Valuable furniture items from the Napoleonic Empire period can be found, among which are a large malachite cup by Thomire, a gift from Czar Alexander I to Napoleon, and furniture by Jacob. The restoration and transformation works that turned the villa into a museum followed the most advanced methods to guarantee a perfect preservation of the artworks. Today the museum is an ideal place to hold high-level temporary art exhibitions.

Microbial Monitoring of Air and Surfaces

Environmental microbial monitoring was carried out in five rooms of the museum, on two different days. The first monitoring was carried out when the museum was closed to the public, while the second monitoring was performed during normal opening hours.

Microbial air samplings were performed with active and passive techniques to assess bacterial and fungal contamination (Figure 2). Active sampling was performed with a DUO-SAS 360, with an aspiration volume of 500 L; results were expressed in colony forming units per cubic meter (CFU/m^3). In addition, a Hirst spore trap (Burkard sampler) was used to measure fungal spores over a period of one week. Passive sampling was performed using Petri dishes to determine the Index of Microbial Air Contamination (IMA). This value corresponds to the number of CFUs counted on a Petri dish that is left open to the air for one hour, one meter above the floor and about one meter away from walls or any major obstacle.

Surface samplings to determine MB and HMF were performed on three surfaces: the painting of Saint Sebastian by Lorenzo Costa, the statue of Tersicore by Antonio Canova and the surface of an item of furniture (Figure 3).

Results

Table 1 shows the mean, standard deviation (SD) and median microbial contamination values recorded in the different rooms of the museum.

Results show a low bacterial contamination but higher fungal values. Unexpectedly, microbial contamination decreased while the museum was open to visitors. Observation at the microscope of the slides from the Burkard sampler shows a high level of *Cladosporium* spp. and inert particles from 10 to 11 p.m. on Monday, Friday and Sunday and from 3 to 4 p.m. on Thursday. On Monday the museum is closed to both visitors and operators. MB values increased during opening hours: without visitors ranged from 0 to 0.06 CFU/cm^2, with visitors from 0 to 0.35 CFU/cm^2. HMF values varied between 0 and 0.12 CFU/cm^2 both with and without visitors. Unfortunately there are no reference values that can help to interpret these results, so this study represents a contribution towards the definition of a standardized microbial sampling method and corresponding threshold values.

Table 1. Microbial air contamination

	Without visitors						With visitors					
	IMA			CFU/m^3			IMA			CFU/m^3		
	B	**F**	**T**	**B**	**F**	**T**	**B**	**F**	**T**	**B**	**F**	**T**
Mean	4	5	9	55	159	232	2	2	6	25	134	159
SD	3	2	4	34	90	114	0.4	1	3	15	79	76
Median	3	5	7	76	154	175	2	2	5	21	150	181

IMA Index of microbial air contamination, *B* bacteria, *F* fungi, *T* total microbial charge

5.2. The Study of an Indoor Microclimate of a Museum Applying the Integrated Approach Based on CFD Combined with Experimental Measurements

The present research work based on the integrated proposed approach, was applied to a particular and important case study: the *Salone dei Cinquecento* of the Palazzo Vecchio in Florence. The *Hall* is the most important official venue in Florence: it is the seat of economic and functional activities, conferences, international meetings, ceremonies, concerts and also national funeral celebrations. In this work an appropriate transient 3D model by CFD software based on the FEM method was used. Variations and interaction between indoor and outdoor microclimatic conditions, the thermo-physical behavior of the building related to its lighting and air conditioning design, and visitor presence, were all considered (Figure 4).

Figure 4. a) External view of Palazzo Vecchio; b) Internal view of Five Hundred Hall (Il Salone dei Cinquecento)

Architectural and Functional Features of the Ambient Studied

The *Hall* located on the first floor in the central part of *Palazzo Vecchio* is a single volume with a trapezium base area of about 1000 m^2, 18 m high and a volume of 20 000 m^3. East wall is 62 m long and the West one 53 m. On the North-West and South-East walls there are respectively three, two and four wide arch windows. The side walls are frescoed and in the lower parts all the walls are covered with typical local stone and marble. Sixteen marble sculptures stand inside special niches. The floor is supported by the cross vaults of the *Dogana Court* of the Palace. The roof covering system of the building belongs to the so-called "architectural machine" of Giorgio Vasari of the 16th Century.

The Indoor Climate

Indoor climatic data were provided by a long experimental monitoring campaign conducted by the *Opificio delle Pietre Dure*, the leading restoration lab in Florence. The monitoring system used 27 sensors for temperature and relative humidity data was taken and recorded at a stratigraphic and planimetric level. From the experimental data analysis it can be noted that the air temperature variation from the floor to the coffered ceiling is between 8-30°C. The relative humidity ranging between 28-71% has the same temperature trend during the entire year. Yearly temperature variations obtained for all the lateral walls are quite limited; at different measuring points at the coffered ceiling higher variations were deduced. A particular case concerns the central zone of the *Hall*: the measured data analysis shows a reversal trend. In the upper part of the coffered ceiling the temperature values are lower with a higher relative humidity. This is probably due to the fact that this zone is not affected by solar radiation coming through the windows, but it is strongly affected by visitor presence. Data collected by sensors located at different heights of the North-East walls, near the windows, show a clear difference between temperature and humidity values measured in the lower and upper zones. Visitor numbers cause the presence of a high quantity of heat, vapour, dust and pollutants (CO, CO_2, O_3, NO, VOC). The indoor air temperature trend is a typical seasonal one with maximum values during the summer period (20-30°C) and relative humidity of 40-50%. Rarely, the relative humidity exceeds 60%. The stronger stresses for organic material (fittings, paintings, gilded ornaments) are due to the effects of the presence of large numbers of people during important events. Optimal condition maintenance for the coffered ceiling conservation and in particular for its gilded cornices, imposes very strong prescriptions and limits for thermo-hygrometric conditions that must be controlled and managed by a possible air conditioning system design. Temperature and/or humidity gradients even if reduced, between intrados and extrados of the ceiling, could be very damaging.

The Plant Solution Proposed

From some data provided by the Florence Museums Department on visitor numbers, the mean number was calculated for some months and a typical day of highest activity. The results on thermal power, CO_2 and vapour emission released to the ambient, indicate the great influence of visitor numbers and their comfort and indoor air quality. Traditional heating systems imply air temperature stratification with values increasing in the zone adjoining the ceiling. Taking into account that the upper zone of the ceiling is in direct contact with the external air, through the ventilation gratings, this would provide a strong temperature gradient between the intrados and extrados of the ceiling. A forced air change is very difficult because air extraction from the internal ambient will disfigure the architectural and the artistic system due to the very large crossing sections required to maintain low air velocity. Traditional low temperature floor radiant panel technology implies quite limited air convection motions and reduced thermal stratification in comparison with other plant systems, but it is an invasive plant. Plant design proposals should start from the minimum incidence on the structure and present conditions under which the “building has become stable” following seasonal climatic variations. The reversibility requirement of the intervention led us to a plant proposal with its structure placed on the existing ones and addressing only winter heating. This system is modular with a movable mounting structure, which allows characteristic adaptation and heat power supply for different needs.

CFD Modelling

The simulation was realized on the system defined by the building the *Hall,* and the proposed container and radiant platforms. An initial simulation concerned the analysis of the temperature gradient in the zone occupied by sittings, along the perimeter walls and in the coffered ceiling zone. A second simulation solved the study of the effects due to heat and vapour diffusion and also some pollutant diffusion, which were introduced into the ambient by 150 visitors. Transient simulation implied the following steps:

1. computational domain and sub-domain definition and setting;
2. thermo-physical property assignment to the different building materials;
3. boundary condition definition;
4. mesh definition with different accuracy levels;
5. heat transfer analysis, non-isothermal flow and convection analysis for temperature and heat flux (convection and total) streamline evaluation and velocity field evaluation.

An initial transient simulation of the internal ambient of the *Hall* was performed. Taking into account the transient regime of the plant (starting time), the heating radiant platforms were schematized with a constant heat flux on the upper surface function of a uniform superficial temperature value of 26°C, convection and radiation coefficient values were calculated using the literature expressions. Thermal power, vapour and CO_2 released into the ambient by 150 seated persons were taken into account using the reference literature values. Diffusion coefficient of water-vapour into the air at atmospheric conditions and those of the main air pollutants were calculated as a function of the air temperature using literature data. A transient simulation of the 3D model was also performed to control the distribution and trend of the air velocity field and the thermal gradient, particularly around the coffered ceiling zone (Figure 4).

Basic Results of CFD Analysis of the Plant Proposed

The plant proposed belongs to the recent solutions with thin floor radiant panels placed on an insulating material protected in the upper parts by a metal plate, to allow both the sitting positioning and people passing. No thermal stresses are induced by small structural changes and very low thermal inertia, if compared with a traditional system. A thermodynamic and fluid dynamic analysis of the system, to study air velocity and air temperature distribution, was made by a CFD simulation in transient conditions (Figure 5). Because the *Hall* is a single volume, for the numerical simulation a 3D model was used. Building mass and thermo-physical properties of different building materials were taken into account. For the external ambient the air temperature and humidity values and mean wind direction and velocity, correspond to those days of the experimental monitoring campaign; the indoor microclimatic conditions belong to experimental data.

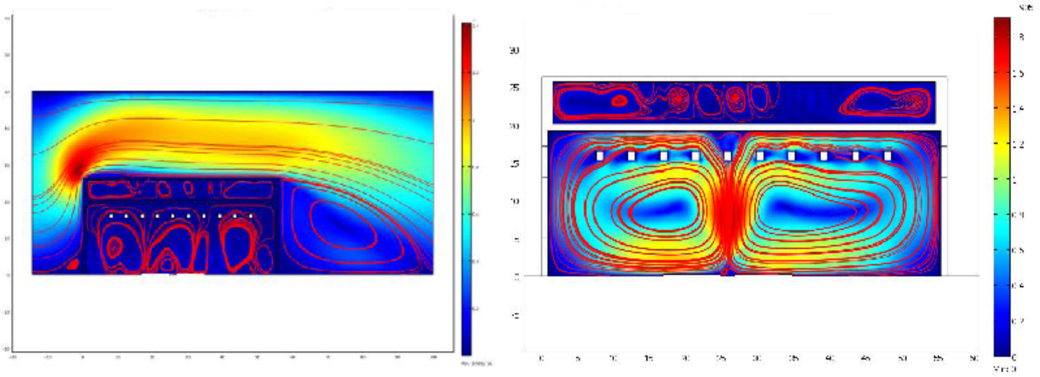

Figura 5 c) Velocity field and internal convection streamlines; internal ambient without radiant platforms (January, h:13 a.m.); d) Velocity field for the internal volume with radiant platforms (January, h:13 a.m.).

Discussion

Results show that indoor winter climatic conditions are often far from comfortable levels; this is less of a problem during summer. Comparison shows that the proposed heating and cooling plant does not imply important vertical temperature gradients, particularly at the ceiling. Analysing the velocity field, there are very wide laminar vortices not producing stagnation zones. This plant allows a micro-ambient with average constant air temperature around the radiant platforms, directly around the sittings zone: no appreciable temperature difference can be deduced from the base of the platform up to a height of about 3 m,. Results obtained, considering sensible and latent loads due to people presence, show that the global heat flux from the radiant platforms remains mainly in the microclimatic zone defined by the volume around them. This effect guarantees acceptable thermal conditions for people. A last transient simulation was performed considering the radiant platforms working, heat from people, and also their vapour and pollutant release. From the obtained result analysis it can be easily seen that the vapour concentration and the CO_2 pollutant load remains in proximity of the emission sources, whereas the water vapour rises to the ceiling due to partial pressure differences and temperature gradients. Vapour concentration calculated is not of particular importance for the coffered ceiling conservation and protection, in particular if it is compared with convection fluxes and total thermal flux which in this same area causes wide recirculation zones. Taking into account the same boundary conditions for the external and internal computational domains, used in the 2D simulation model, a transient simulation for the 3D model was also performed. In the 3D model pollutant loads due to people were disregarded. The plant system proposed allows winter conditioning for a limited zone of the *Hall*. Simulation results show that the system proposed is a solution for the necessary compromise between protection of artworks and the museum ambient, and indoor thermal conditions that can be satisfactory for visitors. This system does not guarantee total comfort for the occupants but the necessary indoor microclimatic conditions for the museum and its artwork protection. A modular and movable heating plant system was proposed for the *Hall* in Florence. This radiant platform system can be proposed for the historical buildings refurbishment, in particular when turned into museums. It was shown how a CFD analysis corresponds well to the experimental data and it can then be used to evaluate the plant's impact on the building structure. Experimental data of the indoor climatic conditions, collected by a wide measuring and monitoring campaign, were taken into account. The simulation results showed the minimum incidence of the radiant platform on temperature gradient and air velocity distribution, which provides the formation of a zone with a "microclimatic control" around the radiant system. This particular effect also happened when pollutant diffusion was considered. Even if the vapour diffusion, from people's presence, rose to the coffered ceiling, its concentration was not particularly risky or damaging. The results show that the heating plant proposed is totally compatible with the building structure and its uses. Variations of indoor microclimatic conditions, due to the thermo-physical behavior of the building relative to those of the external climate and to visitor presence, are not strongly modified by the radiant system collocation. This work is an important example of our integrated approach application based on CFD simulations combined with experimental data. This approach does not require too much computational time, it has no high costs and is not difficult to use for all those solutions oriented to historical building refurbishment, conservation and maintenance.

CONCLUSION

The methodological model used for the integrated system provides a range of information (assessment of biological contamination of air, artefacts, places of work of conservation and restoration) to be used by researchers, conservators and security managers for the development of preventive strategies or optimization or intervention. It is also a useful tool for choosing the most suitable cooling and heating plant for a building (e.g. passive control or controlled ventilation, modular and movable heating plant systems, humidification plant systems or, whenever possible, heating ventilation and air conditioning (HVAC) systems. CFD simulations, based on the FEM method in transient conditions, performed using experimental data, can provide reliable information on a room's dynamic and thermal fields, together with vapour, CO_2 and diffusion and concentration of several pollutants. Data collected on indoor microclimatic variations (due to the thermo-physical behaviour of the building), outdoor climatic variations and the presence of people, should be used for CFD transient simulations before renovating and retrofitting interventions in historical buildings, especially in the case of museums, archives and libraries. Experimental data on biological environmental contamination regarding different positions, different seasons, different extensions of time, different operational conditions, together with a study of microclimatic conditions using thermo-fluid-dynamic analysis based on CFD–FEM simulations, are necessary to assess the circulation and spread of microorganisms and to identify the baseline contamination of indoor heritage environments. CFD-FEM simulations are necessary to assess the circulation and spread of microorganisms and to identify the baseline contamination of indoor heritage environments. The described integrated system is a contribution toward the definition of standardized methods for assessing the biological and microclimatic quality of cultural heritage environments in order to preserve cultural property while also protecting the health of operators and visitors.

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Chapter 11

WHEN GRAFFITI IS NOT ART: THE DAMAGE OF ALKYD SPRAYS ON CALCAREOUS STONES EMPLOYED IN CULTURAL HERITAGE

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ABSTRACT

In order to evaluate the damage of alkyd sprays on calcareous monument stones, limestone and marble samples of renowned building materials and ornamental stones in the Portuguese architecture, *Lioz* and *Branco*, were submitted to artificial graffiti. The harmfulness was assessed in relation to the variation of water vapour permeability, static contact angle, water microdrop absorption, chromatic changes and surface contact roughness. For evaluation of the degree of the aerosol's penetration into the stone and the morphological surface changes, Scanning Electron Microscopy was used.

Apart from the aesthetics aspects, which threaten the historical significance of the monument, the current research has shown that alkyd sprays used in graffiti interact with the stone substrate by reducing the water vapour permeability of the studied stones and thus leading to water condensation just underneath the paint. Moreover a significant reduction of the roughness of the stone surfaces is generated by the application of these paintings, creating a smooth and uniform overcoat that modifies surface texture and the details intentionally left in the original work of art. The water repellency of the stone surfaces is also significant incremented.

An increase knowledge of the interaction of alkyd sprays with stone materials provides valuable insight and greater understanding of the vulnerability of stone to graffiti vandalism, namely to some Portuguese monument stones.

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1. INTRODUCTION

Most of the world's cultural heritage was built from natural stone, one of the most important materials in construction and ornamentation. Throughout history, historical monuments have suffered damage from environmental factors, the use of incompatible materials, inadequate maintenance or inappropriate conservation measures. Moreover the current condition of many historical monuments clearly reveals that graffiti is a threat to culturally valuable historical buildings and historical sites. Graffiti can be defined as an engraving, scratching, cutting or application of paint, ink or similar material onto the stone surface and is the result of vandalism [1-6]. Graffiti, as an act of vandalism, is undoubtedly a major, increasing danger to Cultural Heritage and a risk for the preservation of the historical and cultural legacy for future generations, i.e., their own sustainability. Graffiti can severely damage materials, accelerating their decay and lead to important materials losses and even to loss in value and significance [2, 3]. Decay associated to graffiti has inevitable negative economic impacts to stone cultural heritage due to the impossibility to enjoy it adequately, and also to the necessity of application corrective measures.

Graffiti, as a vandalism form, is usually not elaborated nor demonstrates any type of technical expertise. Most of the times is just a scratch or an individual mark having little or no aesthetical appeal, that mischaracterizes a monument or building. Graffiti meant to be appealing, quick to make and difficult to remove. So resistant materials, fast to dry and durable are used. Different types of materials are used to produce graffiti [1], however because graffitists want to produce their marks quickly, boldly and indelibly, they prefer to use aerosol spray paints of various compositions. Graffiti media includes nowadays paints applied by brushes (oils and synthetic resins such as vinyls, acrylics, acetates, methacrylates or alkyds) or aerosols (polyurethanes, lacquers and enamels), dyes, felt-tip markers (permanent and water-soluble), ball-point pens, wax and oil crayons and lipsticks, chalks, adhesive labels and posters and the physical scratching of surfaces [2, 3]. The range of materials adopted by graffitists continues to expand.

During the last years several research initiatives and international conferences and publication of brochures on the graffiti subject dealing with different aspects like vulnerability of historical buildings, to graffiti risk assessment methodologies, behavior of materials, protection of fabric, prevention of graffiti spread, detection and suppression requirements, training and management of staff were undertaken. As an example an European intergovernmental project for cooperation in the field of Scientific and Technical Research in this subject was established as part of the Sixth Framework Programme- the GRAFFITAGE Project [7].This project aimed at developing a new conservation product coating for protecting materials constituting immovable heritage against graffiti, through a multidisciplinary research and a totally novel chemical approach. Moreover renowned institutions such as The International Centre for the Study of the Preservation and Restoration of Cultural Property and Instituto Centrale del Restauro [8], the National Park Service of the US Department of the Interior [3], the English Heritage [1] have been working on this subject.

Monument stone damage by graffiti is a theme that has been mostly studied in terms of graffiti cleaning systems [9-20] and anti-graffiti protection/ barrier coatings intended to facilitate the removal of graffiti from the surfaces [12, 21-36].

Little detailed study has been made on the effects of aerosol paint graffiti on a range of building stones. So, and apart from the aesthetics aspects associated to graffiti, which threaten the historical significance of the monument, it is fundamental to study the interaction that aerosol paint graffiti may have with the stone substrate and that may deteriorate it. Therefore this chapter provides a synthesis of results of the scientific work done in the last years in Portugal. The research program concerned alkyd paint sprays induced modifications in calcareous stones when subjected to simulated graffiti situations in the laboratory and to assess their harmful effects.

An increased knowledge of this interaction provides valuable insight and greater understanding of the vulnerability of stone to graffiti vandalism, namely to some Portuguese monument stones.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Investigated Stones

Two different Portuguese calcareous stones commonly used in Portugal as building materials and ornamental stones were chosen: a cretaceous limestone- *Lioz* and a white marble-*Branco* (Figure 1). These materials have been widely used in monuments and are still used in the construction of modern buildings and sculptures.

Stone samples were obtained from quarries and latter cut into parallelepiped probes with 5 cm width, 7 cm length and 1.5 cm height using a circular diamond swan. Their surfaces were finished using carborundum 180 (silicium carbide) without any other surface finish.

Lioz is a coarse cream microcrystalline limestone, bioclastic and calciclastic. It is a biosparite-microsparite. The heterogeneous texture is defined by the widespread fossils debris, mainly from rudistes (120-2000µm size) formed by fibrous calcite. As the result of the partial recrystallization processes the sparry calcite (0.20-0.30mm grain sized) is abundant. It is a Middle Turonian (Middle Cretaceous) limestone. A detailed petrographical, chemical, physical and mechanical characterization of this limestone is presented by Figueiredo and Aires-Barros [37].

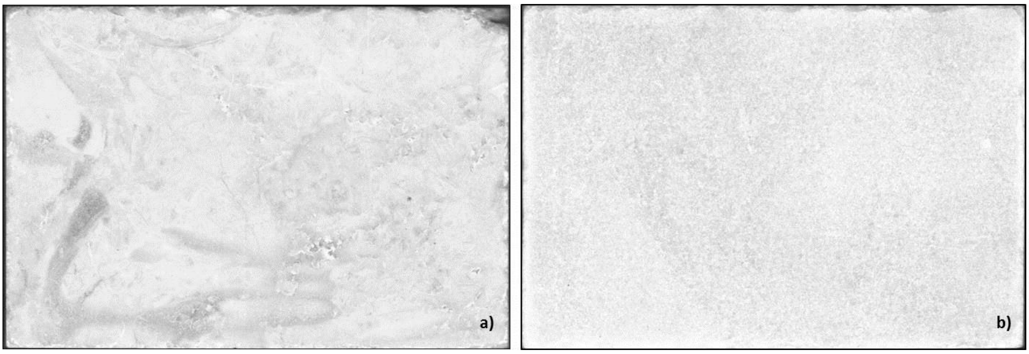

Figure 1. Investigated lithotypes: a) *Lioz* and b) *Branco*.

Branco is a crystalline calcite marble made up of roughly 98% calcite, with a granoblastic texture with medium-grained zones. This marble probably dates from the Cambrian to Upper Silurian geological period and is exploited in the Estremoz–Borba– Vila Viçosa anticlinorium [38]. A detailed petrographical, chemical, physical and mechanical characterization of this marble is presented by Lopes and Martins [39].

In spite of their different geological and petrographical characteristics, both lithotypes present very low porosity (<0.40%) and water absorption capacity (<0.15%); their uniaxial compressive and flexural strength can be considered medium to high (>1000 kg.cm^{-2} and >200 kg.cm^{-2}, respectively).

To understand possible influence of polluted environmental conditions on the damage of alkyd sprays, laboratory artificial ageing tests were performed on some samples after application of alkyd aerosol paints simulating urban environmental conditions (combining SO_2 (10 ppm) with different temperature and humidity cycles according to the European Standard Methods for Natural Stone EN13919 [40]. A climatic and corrosion chamber (Fitoclima 300 EDTU, ARALAB) was used.

2.1.2. Investigated Graffiti Alkyd Sprays

Alkyd sprays were chosen based on their low price and availability in non-specialized stores and graffiti were simulated using commercial alkyd resin aerosols from MOTIP HOME and HOBBYLACQUER® brand [41], identified by their RAL codes as gentian blue (RAL 5010), carmine red (RAL 3002) and jet black (RAL 9005).

To confirm the composition of the paints, FTIR spectra with diamond cell were performed with a Nicolet Nexus spectrophotometer coupled to a Continuμm FTIR microscope.

The graffiti was sprayed onto the stone for a couple of seconds at an average angle of 45° and from a distance of 30 cm, with environment conditions ranging between 18-25 ºC temperature and 60-70 % relative humidity. After painting, samples were left to air-dry in the laboratory during seven days.

To summarize, two different scenarios were considered: (i) alkyd aerosol-paint application on sound stone samples and (ii) artificial ageing of sound stone samples after alkyd aerosol-paint application.

2.2. Analytical Methods

In order to characterize the morphology, continuity, thickness and penetration depth of the paints, cross-sections of the stones surfaces painted with the three colours were studied with field emission scanning electron microscopy (FESEM) using a Jeol JSM-7001F microscope equipped with an Oxford EDS light elements detector. The samples were coated with a high conductance thin gold film. The harmfulness was assessed in relation to the variation of water vapour permeability, static contact angle, water absorption, surface contact roughness and chromatic changes measurements.

Water vapour permeability measurements were carried out using sample cells according to the wet cup ASTM E95-96 standard test method [42]. Containers, with a known volume of water, closed by a sample of 1 cm in thickness were used. The containers were submitted to a controlled temperature of 20±2 °C in an environment of 40±5 % relative humidity.The containers were weighed at suitable time intervals until the weight stabilized. Water vapour transmission rate was determined by the change in mass at the steady state of the system. The results are expressed as water vapour permeability in $kg.m^{-1}.s^{-1}.Pa^{-1}$.

For the evaluation of water repellency, the static contact angle (a reliable method to characterize the interaction between a liquid and a surface) and the microdrop absorption time were used. The static contact angle was measured under a microscope in a microdrop of 4 μl. This technique was adapted from existing methods [43]. Static contact angle gives an indication of condensed water repellency by a surface [44]. It is useful to remember that static contact angle is not necessarily “equilibrium” values; they generally correspond to metastable or stationary states. When one places a liquid drop on a surface, one effectively creates a process of advancing of the liquid meniscus on the solid surface [45]. According to Tsakalof et al. [44] the static contact angle is related to instantaneous (short-term) surface water repellence. The microdrop absorption time is the ratio (expressed as percentage) between the evaporation time of a microdrop placed onto the tested surface and a similar microdrop placed onto a rough glass surface. The use of a glass surface makes it possible to compare values obtained on different occasions wit different hygrometric and temperature conditions [43]. For both techniques (static contact angle and microdrop absorption time) each value is the mean of measurements performed on six individual microdrops.

The morphological changes of the sample surface were assessed by means of a surface roughness instrument (Surfecoder SE1200) that evaluated the parameters Ra, the arithmetic mean deviation of the roughness profile and Rz, the mean value of roughness depth of three consecutive sampling lengths. A scan length of 4 mm was used, measured in triplicate for each sample at three different sampling points.

A Minolta portable spectrophotometer (model CM508i) was used to measure the chromatic properties of the samples and any changes induced by application of the aerosol-painted graffiti. Colour characterization tests were carried out with an integrating sphere (diffuse illumination /8º viewing angle), featuring an 8 mm diameter area of measurement with diffuse illumination by means of xenon flash arc lamp and 10 nm diffuse bandwidth. In order to quantify colour, the CIELAB values (L, a*, b*) for D65 average daylight illuminant including ultraviolet radiation and CIE 2º Standard Observer following the ASTM-D2244-79/ D2244-85 standard method [46], was used. The L values refer to the luminosity which varies from 0 black to 100 white; while a* and b* are the chromaticity coordinates: +a* is red, -a* is green, +b* is yellow and –b* is blue. The colour differences can be determined as follows: $\Delta L^*=L^*_1 - L^*_0$; $\Delta a^*=a^*_1 - a^*_0$; $\Delta b^*=b^*_1 - b^*_0$, where L^*_1, a^*_1, b^*_1 are the final values, and L^*_0, a^*_0, b^*_0 are the original (sound) ones. The total colour difference is determined as follows: $\Delta E^*= (\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2}$

3. RESULTS AND DISCUSSION

3.1. Water Vapour Permeability

Figure 2 presents the values of water vapour permeability obtained in both lithotypes before and after the application of sprays and also after artificial ageing of stone samples with alkyd aerosol-paint. A significant reduction in the diffusion rate after alkyd aerosol-paint application occurred for both types of stones and values close to zero were obtained.

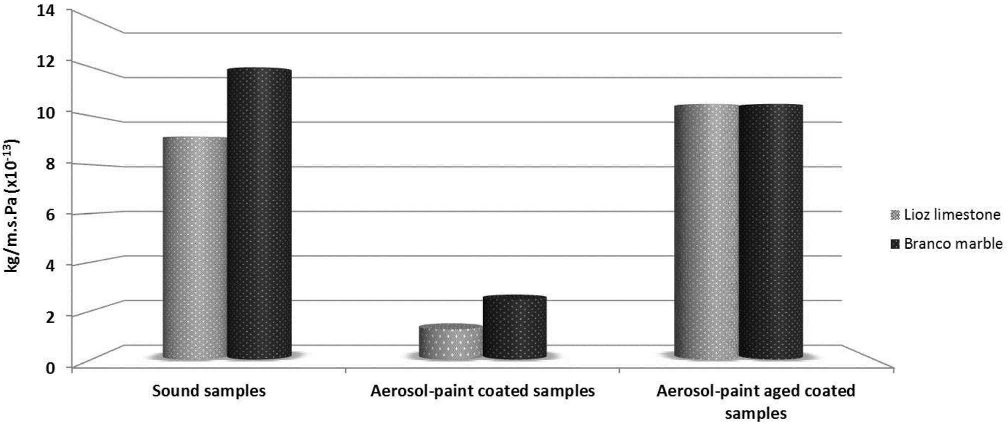

Figure 2. Water vapour permeability of sound stone samples, aerosol-paint coated samples and aerosol-paint artificial aged coated samples (average values).

The water vapour permeability of *Lioz* and *Branco* (without application of paints) is roughly seven and five times greater than after alkyd spray application, respectively. These results clearly demonstrate that alkyd sprays act as a barrier not allowing moisture transport inside the stone material and thus lead to moisture accumulation in the substrates or, under unfavourable circumstances, to delamination of the paint and stone set.

Although with artificial ageing these samples become more water vapour permeable (Figure 2). This fact can be associated to the experimental conditions: an environment rich in SO_2 and cycles of variation in air temperature and relative humidity, i.e., these conditions not only the stone became more permeable but also the alkyd paint used in these graffiti modified their polymeric structure with the formation of pores and fissures (as verified with FESEM, Figure 7d and e).

3.2. Static Contact Angle and Time of Microdrop Absorption

Before the application of aerosol-paints both lithotypes can be considered hydrophilic since they present values of contact angle (static) significantly lower than 90º (Figure 3). An increase in the hydrophobic behaviour of both lithotypes, without achieving surface hydrophobization (Figure 3), is obtained after the application of alkyd aerosol-paint: an increase of 19% and 20% of static contact angle is registered respectively for *Lioz* and for *Branco*.

This behaviour was also corroborated by the results of water microdrop absorption time (Figure 4) with an increase of 65% and 76% respectively for *Lioz* and for *Branco*, i.e., a significant reduction in the wetting aptitude of the surfaces is registered.

However the values of static contact angle, obtained either in *Lioz*, either in *Branco* for the red aerosol-paint are significantly higher than those obtained with the two other colours. Two different explanations can be proposed: (i) dye responsible for the red colour may have different hydrophobicity and (ii) the reticulation of this alkyd resin may not be completed when the test was performed [47].

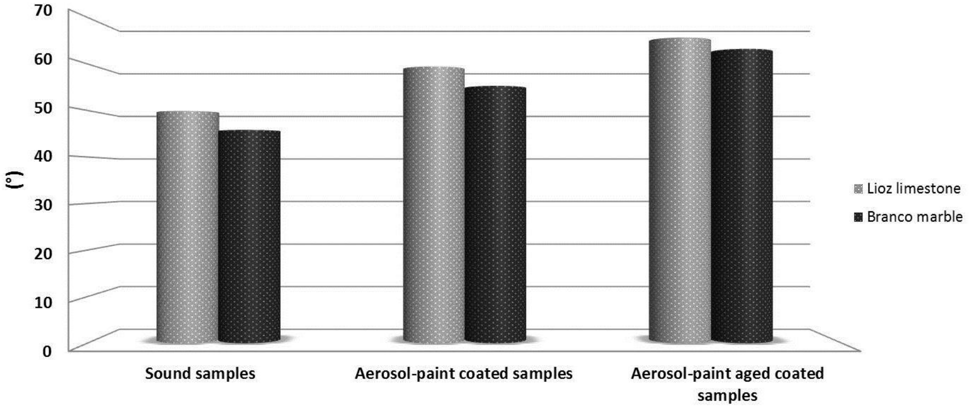

Figure 3. Static contact angle of sound, aerosol-paint coated samples and aerosol-paint aged coated samples (average values).

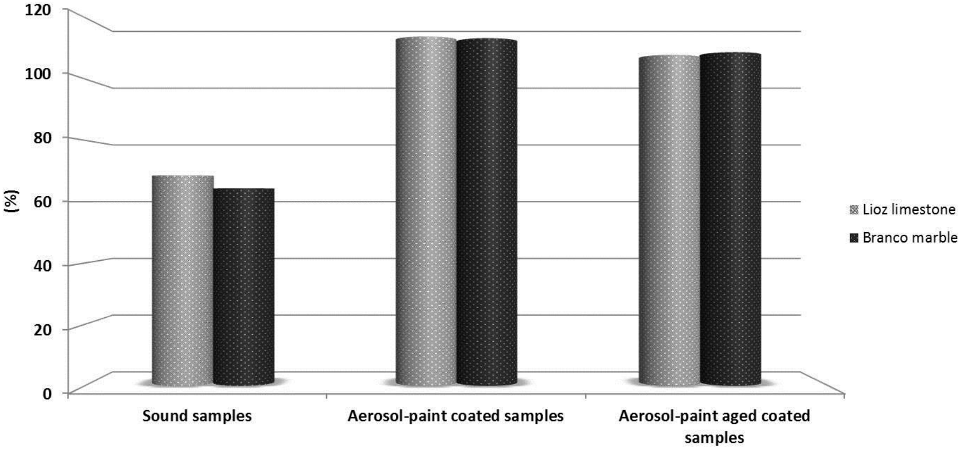

Figure 4. Microdrop absorption time of sound, aerosol-paint coated samples and aerosol-paint artificial aged coated samples (average values).

After artificial ageing in a SO_2 atmosphere, the black and blue aerosols showed a larger static contact angle (Figure 3), with an average increase of 19 % for *Lioz* and 22 % for *Branco*. This was not the case for the red aerosol although the obtained value is still higher than that for the other colours, corroborating the fact that it contains a hydrophobic dye.

The average microdrop absorption time after ageing of the graffiti applied on *Lioz* and *Branco*, were, 107.79 % and 108.69 %, respectively (Figure 4). Consequently, this parameter fell slightly when comparing with aerosol-paint applied to sound samples. This decrease could be attributed to the aerosol ink reticulation process being completed.

3.3. Surface Contact Roughness

Roughness evaluations confirm that *Lioz* is significantly rougher than *Branco* (Figure 5), before the application of alkyd aerosol-paints.

Rz values are approximately six times higher than Ra values, for both lithotypes. After applying the aerosols the surfaces of both calcareous stones became smoother (Figure 5) but still maintaining the same ratio Ra/Rz. These values approach 1 μm in Ra, and 5 μm in Rz. The aerosols filled in surface irregularities, creating a smooth and uniform overcoat, as confirmed in the FESEM images (Figure 7a, b and c). After artificial ageing of stone samples after alkyd aerosol-paint application, and contrary to the previous mentioned parameters no major differences were detected in relation to contact roughness (Figure 5).

3.4. Chromatic Measurements

As expected, applying the aerosols caused a dramatic change in CIELAB values (Figure 6). The average total colour difference (ΔE) was 37.79 for *Lioz* and 36.54 for *Branco*. As well as for contact roughness no major differences were detected after artificial ageing in an SO2 atmosphere The ΔE average values obtained for *Lioz* and *Branco* were 38.48 and 36.00, respectively.

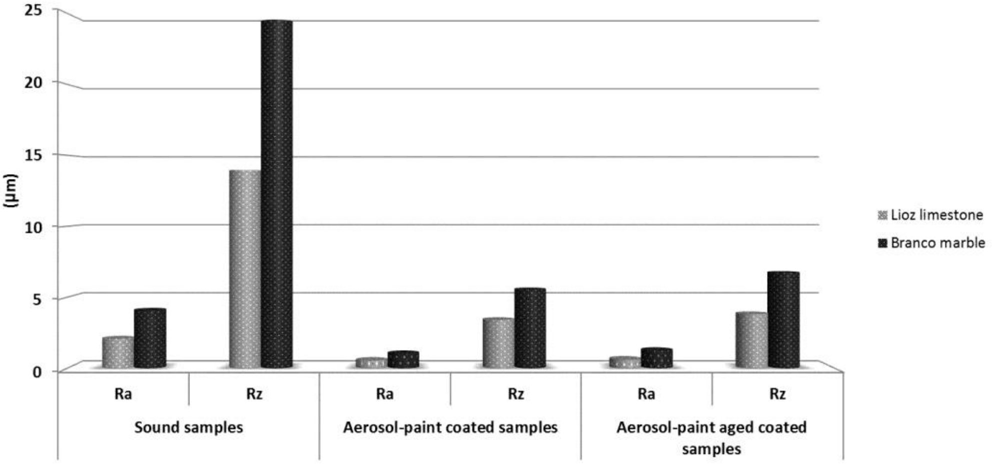

Figure 5. Ra and Rz roughness parameters (average values) of sound, aerosol-paint coated samples and aerosol-paint artificial aged coated samples.

3.5. Morphology, Continuity, Thickness and Penetration Depth of the Paints

FESEM analysis showed that both stones were covered with a layer about 10 μm thick (Figure 7a, b and c), creating a smooth, uniform and dense overcoat and filling in surface irregularities (Figure 7b and c). These paints form superficial coats with a clear distinction between the aerosol-paint and the stone material (Figure 7b and c). The low penetration is in agreement with the low values of porosity and capillarity exhibited by the studied lithotypes.

After artificial ageing of sound stone samples after alkyd aerosol-paint application it was possible to observe cracking of the surface of the aerosol (Figure 7d and e) and the formation of holes in it (Figure 7e).

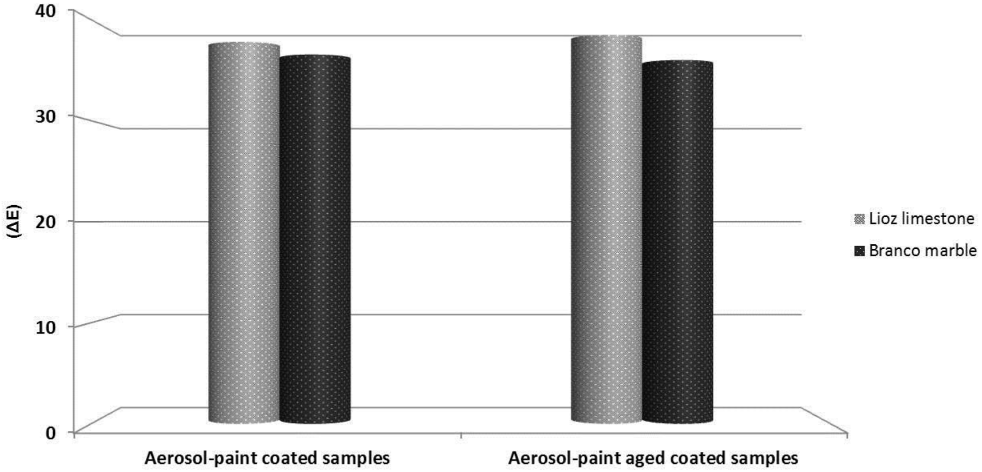

Figure 6. E average variation values for aerosol-paint coated samples and aerosol-paint artificial aged coated samples.

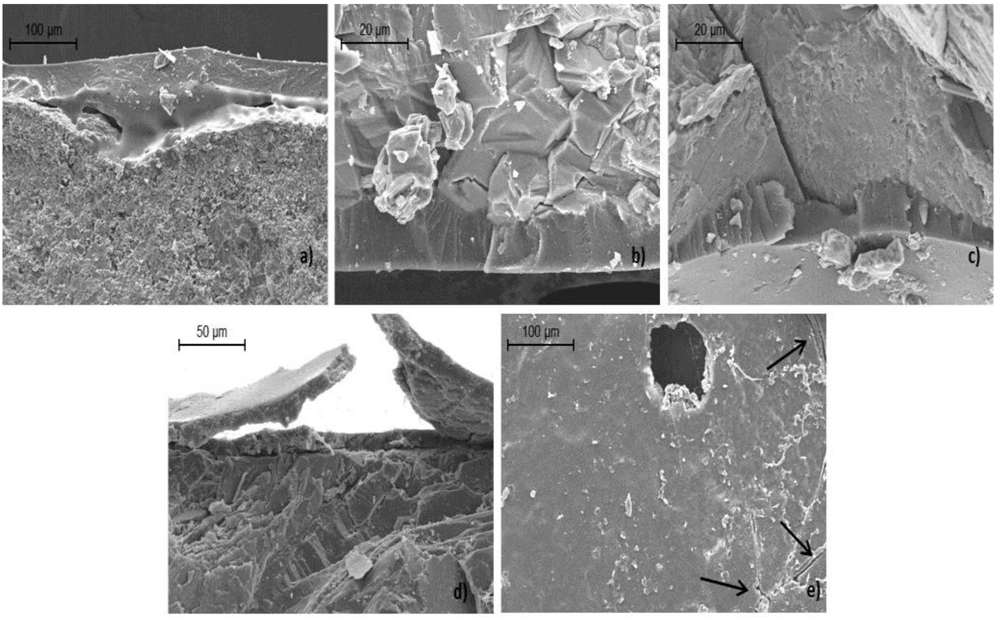

Figure 7. FESEM images of aerosol-paint coated samples and aerosol-paint aged coated samples: (a) cross-section perpendicular to the impregnated surface of *Branco* showing the overcoat of the paint; (b, c) cross-section perpendicular to the impregnated surface of *Lioz* showing the smooth and uniform overcoat of the paint; (d) cross-section perpendicular to the impregnated surface of aerosol-paint aged coated sample of *Lioz* showing the cracking of the surface of the aerosol; (e) image of the surface of an aerosol-paint aged coated sample of *Branco* showing the formation of holes.

Moreover oxidation of metallic ions that are found in aerosol inks was also possible to observe. The wear, erosion and also the formation of surface deposits in the alkyd paint can be attributed to the distribution of SO_2 in the polymeric structure of the paint [48].

CONCLUSION

The research carried out has shown that stone materials can be seriously affected by graffiti alkyd sprays. According to the laboratory study performed it was possible to establish that alkyd sprays interact with the stone substrate modifying not only the colour, bright and morphology of the stone surfaces, but also introducing significant changes in water vapour permeability and water repellence.

To summarise according to the results obtained with the present samples, alkyd aerosol paints induce, in addition to visible colour changes: (1) significant reduction in water vapour permeability of the stones, keeping the stone from interacting with its surrounding environment and thus leading to water condensation just underneath the paint; (2) significant increment of the water repellency of the stone surfaces; and (3) significant reduction of the roughness of the stone surfaces, creating a smooth and uniform overcoat and thus modifying surface texture and details intentionally left in the original work of art by the artist.

On the other hand the results presented in this chapter suggest that alkyd sprays with different colours can affect differently stone hydrophobicity. This may be related to the dye responsible for the spray colour which may have different hydrophobicity.

The results obtained within this chapter also serve to alert the general public to the problems of graffiti (apart for aesthetical considerations) and to guide those who are responsible for cultural heritage to promote more adequate graffiti cleaning interventions.

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Chapter 12

CLIMATE CHANGE AND ITS IMPACT ON *TANGIBLE* CULTURAL HERITAGE: CHALLENGES AND PROSPECTS FOR SMALL ISLAND NATIONS

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ABSTRACT

There has been little discussion on the threat posed by global warming, rising seas, and coastal erosion to archaeological, historical, and other types of *tangible* cultural heritage sites located along the world's coastlines. It is a well-known fact that for the smaller oceanic islands, most notably on low-lying atolls, sea-level rise is of immediate concern as present-day inhabitants have few options in relocating to higher ground. Unlike people who might consider moving off island, cultural heritage sites cannot easily be relocated to safer areas. Moreover, the strong "sense of place" experienced by Pacific island societies, and no doubt other insular communities, which includes overlapping cultural and natural assets of the land- and seascape, highlights the need to preserve and protect these sites. Using a case study from Micronesia (Kiribati), it is argued that *tangible* cultural heritage should not limited to strengthening cultural identity in a rapidly globalized world, but could also serve as a benchmark in providing long-term perspectives on environmental change, integrate itself with biodiversity conservation, create local opportunities for heritage tourism, as well as articulate with the use of traditional material culture and skills in modern-day contexts.

INTRODUCTION

Climate change is now considered one of the world's most pressing environmental issues. The projected rise in mean annual temperature and the dire predictions of sea-level rise on the

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order of up to 1.0 m by 2100 do not augur well for coastal dwellers worldwide. Within the Pacific Island region, several communities face displacement as intensified storm surges and the creeping effects of global warming pose an increasing threat to sustainable livelihoods. While experts and politicians can still debate the short- and long-term scenarios, there is no denying that climate change has strong implications for policy formulation at the social and cultural levels.

Pacific Island communities faced environmental crises long before contact with the West, but they were generally successful in adapting to change. In some cases, they migrated to other islands or took advantage of close family ties elsewhere to avert food shortages and other calamities. They also modified their settlement patterns and food production systems. This is not to say that they were always able to return to their ancestral land. Tidal waves and volcanic eruptions for example, on occasion badly damaged the land- and surrounding seascape.

Today's concerns differ in that climate change is taking place more rapidly than in the past, and the impacts are truly global. Urban centers with large concentrations of people pose an additional challenge when there is talk of relocation. Land ownership might preclude resettlement schemes, and thus some regional governments are seeking migration outlets to places like Australia and New Zealand.

Assuming that foreign governments agree to take on large numbers of environmental refugees, how would these displacements affect people's economic, cultural, and psychological well-being? Individuals can adjust and even prosper in new settings, but culture by its very definition is a shared human experience that includes, but is not limited, to a common language. The Polynesian Diaspora has shown resilience among migrant communities. However, what would happen if the home island ceases to support permanent habitation? Would diasporic communities continue to thrive knowing that their "cultural hearth" has literally been submerged beneath the waves? Although this is unlikely scenario in most cases, for atoll dwellers especially, the prospect of having to abandon an islet village because of the encroaching sea is very real.

There has been little discussion on the threat posed by global warming, sea-level rise, and coastal erosion to archaeological, historical, and other types of *tangible* cultural assets along the world's coastlines. For small island nations, most notably those comprised of low-lying coral islets, sea-level rise is of immediate concern as present-day inhabitants have few options in relocating to higher ground to pursue sustainable livelihoods. Regardless of their location, cultural heritage sites on these islets are at risk.

Unlike people, these sites cannot easily be relocated to safer areas. Moreover, the strong "sense of place" experienced by Pacific Island societies, which includes overlapping cultural and natural assets of the land- and seascape, highlights the need to preserve and protect these sites. Heritage practitioners might devise complex and expensive preservation and management plans. However, much can be accomplished by local communities provided members who own the sites take on a leading role in protecting them. This could be partly accomplished by assisting them through appropriate education initiatives that highlight the "tangible" (economic) and "intangible" (cultural pride) benefits of heritage management. For example, the Kiribati Adaptation Project [1] emphasized that this island nation is one of the most vulnerable countries in the world to the effects of climate change. As part of the Project's Community Adaptation Investments, some communities' adaptation initiatives, such as mangrove replantation and water and coral conservation, would benefit heritage site preservation efforts by maintaining natural barriers against the encroaching sea. In turn, these could provide opportunities in assisting the country’s fledging tourist sector.

While these endeavors might not be sufficient to avert the destruction of heritage sites, they do demonstrate the capacity of communities to devise local adaptive strategies in preserving both their past and living cultures, which are ultimately tied to their island home and surrounding waters.

HERITAGE AND CLIMATE CHANGE

As indicated above, climate change discourse has not been generally framed in terms of impacts on *tangible* cultural heritage [2, 3], although there are frequent references to the threat of global warming on the cultural fabric of small island nations, notably those classified as “developing states”. A clear expression of this threat is the growing crisis that might lead to mass human migrations; “climate change refugees” and attendant cultural loss with the added stress of potential conflict between relocated and resident communities [4- 7]. On the other hand, small island communities are said to exhibit certain characteristics (e.g., tight kinship networks, a strong sense of identity) that would enable them to deal effectively with environmental and social change [8]. Yet, it has become clear that several communities in the Pacific most threatened by sea-level rise have expressed concern that with the loss of land, local culture itself would be lost as well. It is not only the “living” culture that is being assaulted, but ancestral connections through natural and built environments [9, 10].

THE REPUBLIC OF KIRIBATI, MICRONESIA

The Republic of Kiribati, a Micronesian nation of around 100,000 people, consists of 32 atolls and table reefs and one raised coral island spread over an area exceeding 3 million km² of ocean. The total land area, however, only slightly exceeds 800 km². As islands formed by biogenic agents (unconsolidated carbonate sediments deposited by waves on reef platforms) atolls and table reefs or low coral islands without lagoons can be regarded as especially constraining habitats for human communities. The challenges people face include low soil fertility, absence of perennial fresh water and extreme vulnerability to flooding by storm surge because of low elevation of the highly fragmented landmass, only a few meters above mean sea level. Contemporary challenges are not much different from those encountered in the past. Population growth and consequent pressure on resources and infrastructure, as well as climate change, have exacerbated an already precarious balance between people and their environment [11, Figure 1].

The islands of modern Kiribati cluster into three island groups: the Gilbert, Phoenix, and Line Islands. Archaeological evidence indicates human settlement of the Gilberts about 2,000 years ago when dropping sea-level allowed the atolls to become emergent and habitable [12, 13], while the Phoenix and Line Islands appear to have been settled much later, by about AD 1200. By the time Europeans re-discovered the latter two island groups, no indigenous communities were encountered, having become extinct or migrated elsewhere [14, 15].

Photo F. Thomas.

Figure 1. Flooded landscape.

Photo F. Thomas.

Figure 2. Traditional shrine.

Heritage Background

Kiribati possesses a rich cultural heritage that is closely related to oral traditions, the arts, indigenous epistemologies, material culture and – more recently – historical sites from interactions with the outside world. Some efforts have been made to collect information on oral traditions (16 - 19], performance arts [20, 21] and language [22, 23]. Attempts have also been made to document cultural and historical sites and objects [24, 25], as well as history and development in general [26, 27, 28]. However, proper management, which includes preservation and dissemination of information on historical and cultural sites, remains largely unattended to.

Some cultural and historical sites have fallen into disuse and others have been used for other purposes like the old *Mwaneaba ni Maungatabu* (house of parliament) being used as a marketplace for local production. Still others have been modified and many more, like *bangota* -traditional shrines (Figure 2), have been neglected and destroyed. The majority of traditional utilitarian objects are stored in metropolitan museums overseas. Contrastingly. Most World War II relics are exposed to the natural elements. As such, some of these require more urgent attention than others. It is important to point out that these are not “stand-alone” objects; each has a story that connects it to the people. Such stories and connections have helped to shape the history, character, and culture of the *I-Kiribati* (people of Kiribati).

Unlike “American Micronesia” [29], there is no historic preservation legislation in place in Kiribati. However, Kiribati is a state party to the UNESCO World Heritage Convention. The Phoenix Islands Protected Area, one of the largest marine protected areas in the world, was inscribed on the World Heritage List in 2010 [30]. Traditionally, many significant cultural objects, sites, and the land upon which they stand, belong to specific clans and not the country as a whole. This makes it difficult for the government as well as local island councils to formulate and implement appropriate legislation.

The absence of a regulatory body to provide for the preservation of the cultural and historic heritage puts that heritage at risk, but without mechanisms for enforcing laws, this becomes a moot point. Elsewhere in Micronesia, while heritage preservation follows the American model closely [31], there have been attempts to accommodate the specific context of Pacific Island societies in drafting local legislation, particularly in light of issues surrounding land ownership [32]. Some heritage practitioners advocate education rather than legislation as a means of encouraging the preservation of the *tangible* cultural heritage [33]. Moreover, while Pacific Islanders are linked in certain aspects of their history with the Western world and some Asian countries, especially Japan, the legacy of colonialism expressed though visible and potentially preservable sites, may not necessarily appeal to local communities [34, 35]. For that reason, heritage preservation efforts in the Pacific are increasingly engaging local practices of preservation [36]. Similar to recent academic practices that allow for the re-emergence of more local histories in the region [37], local preservation initiatives call attention to what is important to the community.

The Kiribati National Cultural Centre and Museum / *te Umwanibong* (Figure 3), is part of the Culture Division of the Ministry of Internal and Socials Affairs. Since 2005, it has been surveying most of the outer islands primarily to collect oral traditions and also to photograph and map cultural sites, including old and recently renovated structures such as *mwaneaba* (traditional meeting houses). Recently, it completed the first “Endangered Heritage Mapping” exercise on Tabiteuea North, an atoll in the Southern Gilbert Islands [38]. The site, referred to as *Nnabakana* and described below, highlights the threat posed by climate change and sea-level rise on a nationally significant cultural heritage landmark

Photo F. Thomas.

Figure 3. Interior of Kiribati National Cultural Centre and Museum.

Cultural Identity

Kiribati, more than any other Micronesian country, has held onto traditional values and customs. Culture and environmental change is taking place, however, as is the case throughout the Pacific region and indeed the word. Rapid, extensive urbanization on Tarawa, the main atoll and administrative center, has discouraged a satisfactory maintenance of the indigenous subsistence economy and the related retention of traditional knowledge of resource utilization and conservation. Global warming may also alter patterns of traditional resource utilization on the outer islands. Through a combination of sea-level rise and expansion of human activities associated with population growth, a range of cultural sites located near the present-day shoreline are threatened by accelerated erosion and other destructive processes. This is readily observable for several of the Japanese World War II fortifications on South Tarawa.

Ethic or cultural pride, an excellent educational tool for preservation, may not work well in Kiribati as it does in other places. Unlike other regions of the world where there are indigenous groups struggling for the protection of their land from those they perceive as “outsiders”, this situation does not occur in Kiribati. The vast majority of the residents are indigenous Micronesians, and since foreigners are legally prohibited from owning land, the *I-Kiribati* do not perceive that foreigners are destroying their cultural heritage in a direct way, although a growing number of citizens understand that the release of green-house gases by the outside world is a direct threat to their livelihood and ultimately their sense of identity [39]. Sites are also being threatened from within, as noted above, as the people of Kiribati, especially on Tarawa, face declining access to land, partly as a result of uncontrolled urban growth.

Environmental Change

In recent years, historical ecology has emerged as one of the most useful and comprehensive approaches to understanding how environments and landscapes were affected by climate change, early human settlement, historical interactions, and modern development and industrialization [40, 41]. This approach, which combines the natural and social sciences using paleoecology, archaeology, land use history, and long-term ecological research, has great potential for examining natural and cultural phenomena behind changes to island ecosystems [42, 43, 44].

Compared to “high” volcanic islands, atolls and table reefs have received scant attention from archaeologists focusing on historical ecology. More specifically, little is known about paleoclimatology, the introduction history of exotic fauna, the extent of human-induced environmental impacts, and social transformations on low coral islands prior to Western contact [45 - 50]. Given the unique environmental challenges posed by coral islands, it is all the more surprising that pre-European ecological research has been largely neglected. By contrast, the last twenty years have witnessed a host of environmental studies, from sea-level rise to contemporary human impact on terrestrial and marine resources [51].

Photo F. Thomas.

Figure 4. Japanese gun, South Tarawa.

Photo F. Thomas

Figure 5. Japanese bunker and encroaching sea.

Shell remains are a case in point. Empty shells, which are ubiquitous near present-day dwellings in Kiribati, are likely to occur among deposits from the more distant past as well. As demonstrated elsewhere, shell remains at archaeological sites can be used to measure changes in human exploitation patterns, as well as the influence of environmental factors, including climate change [52, 53, 54]. The localized effects of recent sea-level change can be assessed by monitoring traditional sites and historic structures such as the Japanese shoreline fortifications on Tarawa, similar to shipwrecks and airplane wrecks whose date of sinking or construction is known, when they were coral free at the time of submergence (Figure 4, Figure 5).

The Culture Division of the Ministry of Internal and Social Affairs recently organized a workshop on the Safeguarding of Intangible Cultural Heritage to discuss a safeguarding strategy in cooperation with the UNESCO Office in Apia, Samoa, with financial support from the Japanese Government. As in many other Pacific Island communities, *tangible* and *intangible* cultural heritage exist side-by-side in a living environment. A good example of this indigenous heritage is represented by a well-known site known as *Nnabakana* on Tabiteuea Atoll, whose history has been documented by oral traditions. The site consists of large coral slabs stacked to resemble *I-Kiribati* warriors (31 in all) associated with a famous battle in the 17th century between warriors from the islands of Beru and Nikunau against the Tabiteueans. The research by the Cultural Centre and Museum, with financial assistance from the European Union, highlighted the need to protect the site from winds, waves, and rising sea-level, as evidenced by several cracked and toppled pillars. It was noted that the current legal framework of the island council did not have provisions for the protection of this and other cultural sites and that it appeared the community did not recognize the importance and value of cultural sites. The work aimed to organize consultations with elders of communities and to formulate a long-term management plan. It further highlighted the need to document (publish) different versions of the story. In Kiribati, as elsewhere in the region, there are sometimes different versions of a story or variations around a theme that reflect differences between island communities and even between clans on the same atoll.

Biodiversity Conservation

Kiribati, like all atoll nations, is described as a biodiversity "cool spot", with threatened floras and faunas [55]. Even the comparatively rich marine ecosystem has been modified to some extent by direct human harvesting of resources and shoreline development against the background of changing environments [56,57]. A better understanding of extant biodiversity can be comprehended through a temporal perspective. Adding an archaeological dimension significantly expands the concept of biodiversity by generating a long-term perspective on the impact of natural processes and people on terrestrial and marine ecosystems. An understanding of ecological complexity over time is an important step in the process of identifying the causes of environmental change and devising realistic methods for managing and conserving resources [58, 59]. There is also a growing appreciation among cultural heritage practitioners of the linkages between cultural and natural resource management via the concept of biocultural diversity and land- and seascape, and the need for active participation by local communities to ensure success in these preservation goals [60].

Heritage Tourism

The visitor industry in Kiribati is small scale compared to other Pacific destinations. Cruise ships make stopovers in the Line Islands and sports fishermen and bird watchers travel by air from Honolulu to Christmas Island, and although their numbers are relatively small, they bring in much needed income. Most Pacific Island countries seem able to showcase their natural heritage and "living" culture better than evidence from the past, and Kiribati is not an exception. With a few exceptions, museums in the region are either diminutive or non-existent. They are chronically underfunded, and therefore handicapped in properly managing their collections. The same applies to the maintenance of sites, especially when there is a lack of community involvement. Features that stand out are usually the recent colonial past, including those associated with World War II and subsequent nuclear tests, such as those that took placed on Christmas Island.

War relics have been subjected to illegal trade and the sale of scrap metal. In places where governments are more actively involved in preserving the more recent past, most visitors are veterans of the war and their descendants. With the passing away of this generation of soldiers, it is expected that memories will fade. Even with low levels of economic development on most islands, sites dating from this period are threatened by coastal erosion or the deteriorating effects of the humid tropical environment [61].

On South Tarawa, the vast majority of Japanese fortifications are in a poor state of preservation. Many have been deliberately defaced due to either pressure for more land or lack of appreciation of the historical significance of these relics. Most elders view the Battle of Tarawa as a conflict between two external powers in which they found themselves in between. There are no active efforts to preserve these highly visible sites, primarily because of a lack of funding and the low numbers of foreign visitors, who in turn provide little incentive to restore and maintain the sites. “Red Beach”, one of the US Marines’ landing areas during the Battle of Tarawa in 1943, on Betio Islet for example, has become a rubbish dump of the local community. While heritage tourism in Kiribati offers several prospects, particularly in regards to contemporary practices (e.g. dance), the *tangible* cultural heritage remains a much harder sell. For traditional indigenous heritage, one incentive for preservation could be to more strongly relate the *tangible* and *intangible* aspects associated with these sites, particularly for those that feature different local narratives. As for recent sites, notably those dating from World War II, the focus could be to document and represent more personal and local histories [62].

Traditional Material Culture and Skills

Coral islands present cases of both sustainable living as well as instances where societies did not survive. It may be that success of some communities rested partly on greater awareness of resource limitations, and thus the need to conserve and manage resources [63]. Today, atoll countries like Kiribati face several new social and environmental challenges linked to growing population. Modernization, and global warming, but the past and traditional knowledge and values can still be a source of inspiration to navigate the uncharted seas that lead into the future [64]

The documentation of traditional material culture and skills is becoming an increasingly important component of cultural heritage management in the Pacific Islands region. For decades the traditional skills and technologies used by indigenous groups were perceived by governments, the media, and consultants to be outdated and inferior to those of the West. Gradually, however, attitudes began to change. The former Institute of Pacific Studies at the University of the South Pacific has played an active role in encouraging the preservation of Pacific peoples’ knowledge, including skills in sailing technology, fishing, gardening, and medicine for future generations [65, 66, 67]. Likewise, the Institute of Education, School of Education, and the Re-thinking Pacific Education by Pacific Peoples Initiative have been at the forefront of efforts to conduct research into indigenous epistemologies with a view to grounding contemporary educational practices on Pacific worldviews and values [68].

With the rising costs of fossil fuels and the health risks faced by many Pacific Islanders who are neglecting their traditional diet in favor of less nutritious imports, enhancing self-sufficiency is an achievable goal if local communities, cultural heritage practitioners, and other concerned parties turn to the maintenance or restoration of traditional knowledge, together with selected and judicious application of Western science. Hybrid knowledge of this sort should provide a workable template as contemporary communities work toward sustainability [69].

CONCLUSION

Cultural sites and their content have pragmatic value: politically, for purposes of national pride and partisan advantage; economically, for display to tourists, museum goers, magazine readers and television-program watchers; scientifically, as research material for scholars pursuing academic careers; and in the case of artifacts, as merchandise for dealers in antiquities. The indigenous notion of place is important because places and people are given their character by their specific histories [70]. Viewed from this angle, the land, sea, and stories that accompany particular events, features, and sites in the *I-Kiribati*'s relationships with the environment are essential characteristics of the *I-Kiribati*'s sense of being and identity – albeit one that is always in a state of becoming.

Conflicting interests and expectations often complicate the management of cultural heritage, similar to the management of natural heritage areas [71]. It is argued that both the *tangible* and *intangible* elements of cultural heritage, channeled through appropriate public education initiatives, can serve multiple functions among Pacific Island communities in this era of expanding globalization [72]. The success of cultural heritage management in Kiribati and elsewhere will depend largely on local community support, in partnership with museums, various government organizations, and external stakeholders [73]. The participation of those who own the sites and knowledge is essential. Modern threats to knowing the past are offset by the education, process, and the results of doing cultural heritage training, and given present-day concerns about cultural diversity, cultural identity, and global modernity's impact on cultural maintenance, cultural heritage management seems ever more essential.

The increase in population on small islands like Kiribati will bring about pressures on the physical environment, thereby threatening the existence of a large number of archaeological, historical, and traditional sites. Inventorization and possibly conservation of such sites is needed, the sooner the better, in light of both human-induced environmental change and natural processes.

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