Detecting Past Attempts To Restore Two Important Works of Art

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ABSTRACT
Chemistry plays a fundamental role in the preservation of our heritage. Artistic and archaeological materials deteriorate over time due to their interaction with the environment, and human intervention can trigger unexpected deterioration pathways. Previous intervention can also sometimes obscure information regarding the original techniques or the materials used to execute the artwork. Our studies of past intervention and attempts to conserve the *lunette* of the church of Santa Maria la Vetere in Militello Val di Catania (Italy) and Donatello's carved marble panels of the pulpit of the Duomo of Prato (Italy) are discussed as two examples of how chemistry can provide guidance for conservators and fill gaps in the known life of works of art.

1. Introduction

Chemistry has been involved in the study of works of art and archaeological objects since the 18th century, when renowned scientists puzzled over how to solve a variety of restoration and conservation problems. However, a direct link between chemistry and conservation was established only in the 19th century as a consequence of an increase in the number and variety of collections exhibited in Europe's museums. Most of these collections included excavated material in a state of advanced deterioration, which required a new approach to conservation based on scientific methods. The opening in 1888 of the first laboratory devoted to scientific conservation at the Königlichen Museen in Berlin was an important step in establishing this new approach. Unfortunately, research in this laboratory ceased in 1927, and the leading research laboratory established at the British Museum in 1920 has since been acknowledged by most as the oldest surviving laboratory devoted to scientific conservation.[1] Later, alongside other museum-based laboratories, a variety of university and national laboratories began to contribute to the development of the field by applying many of the tools that chemistry had developed throughout the century.[2] Today, the role played by chemistry in the conservation and the restoration of objects of artistic or archaeological value is fully established. Chemistry is used both to characterize the materials constituting the objects and to identify the technique used in their production. In addi-

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tion, chemical methods and techniques enable us to understand the mechanisms that cause the objects to degrade in order to set up procedures aimed at stabilizing decay and preventing further deterioration. Chemists also intervene to find the best way to restore ancient objects.

It is also worth remembering that chemistry is sometimes asked to solve unexpected problems arising when artworks come into contact with the real world around them. Acts of vandalism on important pieces of art such as the Roman mosaics of the Villa del Casale in Piazza Armerina (Italy) or on the painting "Bathtub" by the father of Pop Art, Andy Warhol, are two striking examples of this. In the former case, vandals poured dark brown paint over several of the Villa mosaics — the finest still in situ anywhere in the Roman world.[3] In the latter, a misguided fan left a kiss-shaped imprint of red lipstick on the painting exhibited at the Pittsburgh Andy Warhol Museum.[4] These problems and many more have been dealt with thanks to the continuous collaboration of chemists and those in charge of the restoration and conservation of archaeological and artistic material. Their efforts have prompted effective interdisciplinary teamwork in which chemists are often called upon to find solutions for a variety of complex questions and challenges.

This Account will present some of the work involving the identification of past intervention and attempts to conserve two important works of art that has recently been reported from our laboratory. The aim is to show two examples of how chemistry may be employed to gain an understanding of the role played by past restoration treatments on the final state of works of art and to aid restorers when deciding actions to be taken. In both of the studies discussed, a microdestructive approach was maintained thanks to the use of spatially resolved analytical techniques.

2. What Are the Problems of Past Intervention?

When identifying procedures for restoring an ancient object or work of art and preserving it from further degradation, the first step is to gain as much information as possible on its constituent materials and on the products formed as a consequence of both degradation processes and past attempts at restoration and conservation. Treatments carried out with no previous knowledge of the chemical and physical modifications that may have occurred in the sample matrix may generate new forms of degradation or favor degradation pathways that accelerate damage. Previous intervention may also make it difficult to identify the original techniques or the materials used to execute the artwork. The restorers of the past lacked an understanding of the chemical and physical processes induced by the treatments they used. Moreover, since most of their experience was based on a hands-on practical approach, past restorers often used procedures that were highly unsuitable for the unusual techniques

or materials used in the creation of the work of art being treated.

The restoration of important works of art is usually preceded by accurate historiographical studies that explore the life of the object on a documental basis. Unfortunately, gaps in documental reconstructions are very common, and scientific investigations are often required to identify undocumented treatments undergone by the object and to confirm the documental findings. Information drawn from scientific investigations is used when deciding on the course of restoration, for example, in deciding whether to remove nonoriginal elements introduced by successive intervention, or how to select and set up the most appropriate chemical and physical procedures to be used. Our study of the lunette of the church of Santa Maria la Vetere in Militello Val di Catania (Italy) had an aim of this kind.[5]

3. The Lunette Case Study

The progressive construction of the church of Santa Maria la Vetere began around 1100 A.D. The most important steps in its construction were carried out in the 15th century when the portal and the bell tower were built. The portal includes a lunette, dated 1506, showing a bas-relief of the Virgin Mary and the infant Jesus adored by two angels. It is attributed to Antonello Gagini (1478–1536), believed to be the greatest Sicilian sculptor of the 15th century. At the time of our studies, the brightly colored beauty of the original lunette reliefs was almost completely imperceptible, this being due to the presence of a 500–1000-μm-thick yellow-brown patina, the result of a layer of plaster being indiscriminately applied over the entire area of the lunette. A study of the composition of the different strata constituting the samples taken from the lunette provided information that was useful in showing what had been performed in previous intervention. Spatially resolved SEM-EDX analyses carried out on 5 samples taken from angel hair areas (Figure 1) were particularly useful. Four samples were about 1–2 mm × 1–2 mm in dimension while the fifth sample (shown in Figure 2) was about 3 mm × 5 mm. Information regarding the elemental composition of the different layers allowed us to discover that the original gilding had been touched up by the simple overlapping of a new gold sheet. Our study also revealed that different techniques had been used to lay down the original and successive gold foils. As will be familiar to those working in the field of art conservation, *gilding* is the term used for the process whereby a thin gold sheet is laid onto the surface to create the illusion that the whole object has been crafted in precious metal. Gold sheets are called gold *foil* or gold *leaf* if they are thicker or thinner than 1 μm, respectively.

Techniques used to lay down gold sheets on a variety of objects were established as early as the Bronze Age (~3000 B.C.)[6] From that time on, gilding was used to decorate various metallic objects,[6] manuscripts,[7] and painted surfaces, and descriptions of techniques used to lay gold sheets onto stone substrates can be found in

FIGURE 1. Detail of the lunette of the church of Santa Maria la Vetere in Militello Val di Catania (Italy), dated 1506. The red color of the angel hair is due to the Armenian bole used as the substrate for gilding.

several Medieval manuals.[8] One of the most common techniques used to gild stone substrates involved using a mineral called *Armenian bole*, composed mainly of red iron oxide and hydrous silicates of aluminum. The bole was mixed with a water solution of partially denatured collagen (gelatin), obtained by treating animal or fish bones or cartilages with warm water.[9] The solution acted as an adhesive and was called *animal glue*. The sticky red mixture was applied onto the stone substrate that had been previously treated with a mixture of gypsum (CaSO$_4$·2H$_2$O) and animal glue. Armenian bole was preferred as the substrate upon which gold sheet was applied since it was available in the form of a very thin powder, thus making it possible to polish the gold sheet to a mirrorlike finish. This polishing procedure was called *burnishing*. Unfortunately, changes in relative humidity, coupled with external chemical and microbiological attacks, significantly deteriorate the adhesive properties of the glue.[10] Deterioration, thus, accelerates on gilt surfaces that are exposed to the elements, as seen in the case of the lunette.

An alternative technique used for gilding employed linseed oil as the adhesive. This technique is known as "*a missione*" (i.e., a "mixture") because of the adhesive mixture used. Linseed oil is made from the seeds of the flax plant (*Linum usitutissimum*) and is typically composed of triglycerides of unsaturated fatty acids, such as oleic acid (14–24%, 9-octadecenoic acid), linoleic acid (14–19%, 9,12-octadecadienoic acid), and linolenic acid (48–60%, 9,12,15-octadecatrienoic acid), and of triglyc-
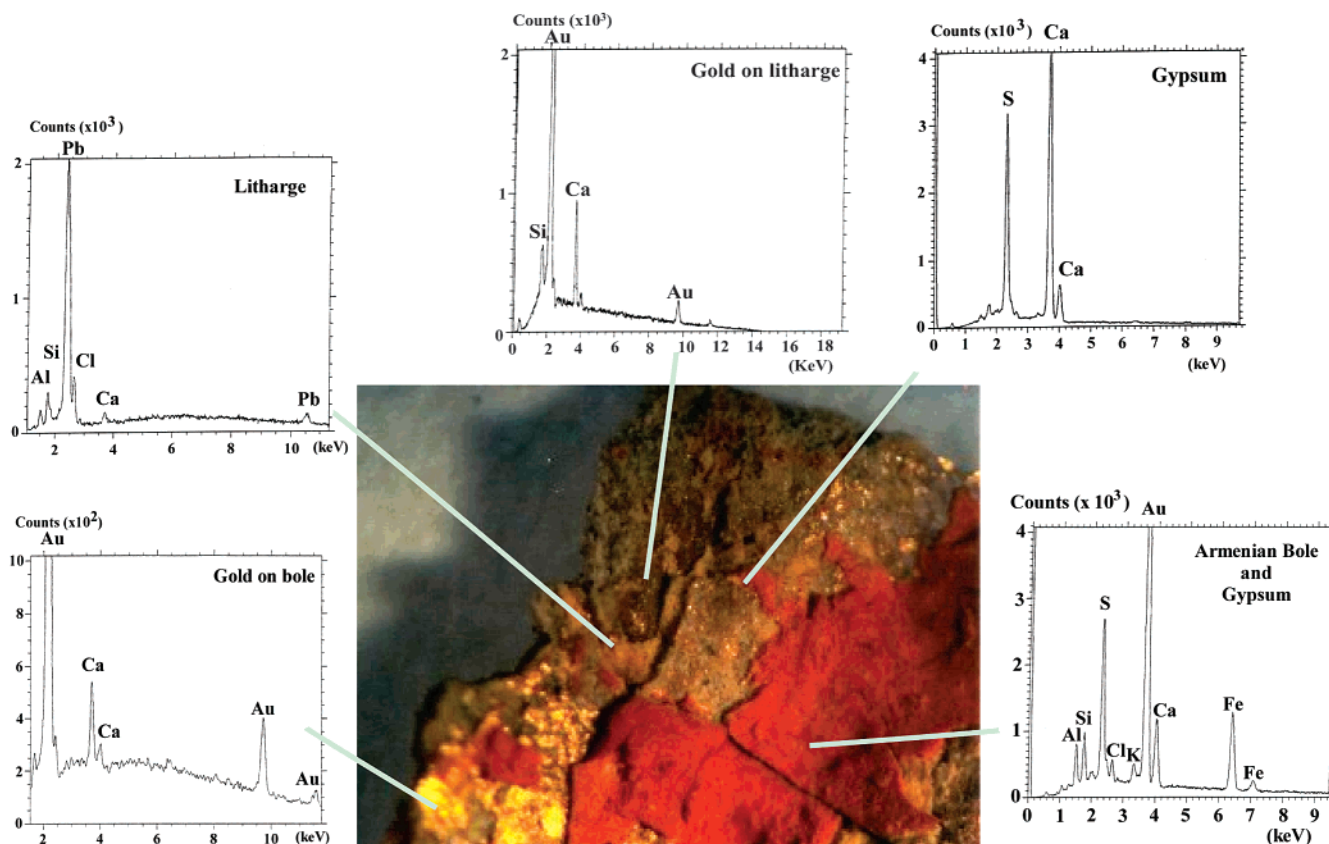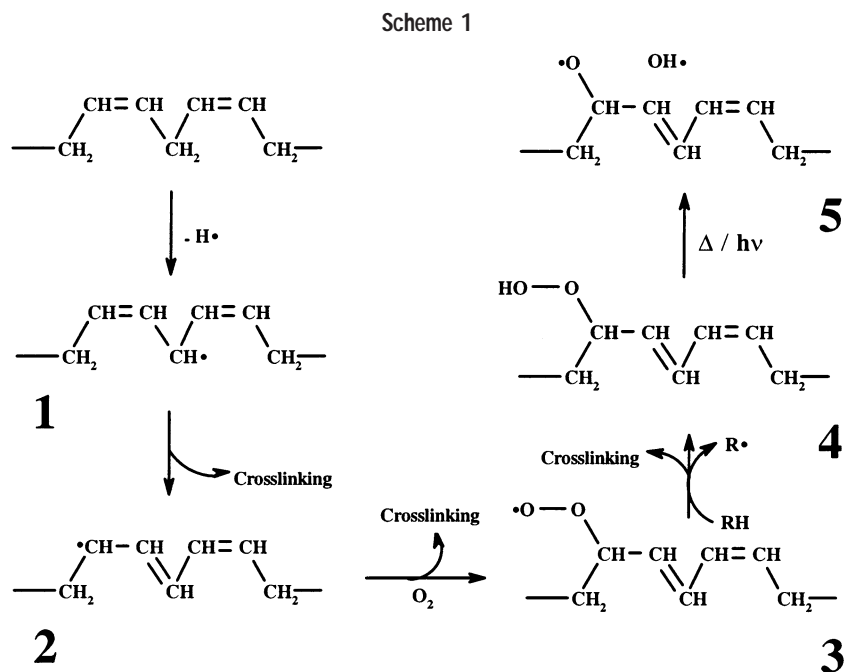
FIGURE 2. Optical image (×26) of a sample taken from the hair region of the angel shown in Figure 1. The sample, shown in reverse, allows the identification of the different strata whose elemental composition was obtained by SEM/EDX analysis. The spectra of relevance for the different strata are also shown.

Scheme 1

erides of saturated fatty acids (9–13%).[11] This oil has been widely used both as an adhesive and as a binding medium for painting[12] by virtue of the ability of the unsaturated fatty acid chains to polymerize and form a semisolid film.[11] The polymerization process is perceived as a "drying" of the oil. For this reason, linseed oil and other oils, mostly

composed of tri-esters of glycerol and unsaturated fatty acids, are also called *drying* or *siccative oils*. The mechanism by which linseed oil hardens has been studied extensively, but it is still far from being completely understood.[11,13] It is based on a free radical chain reaction (Scheme 1) that is induced by the loss of a hydrogen atom
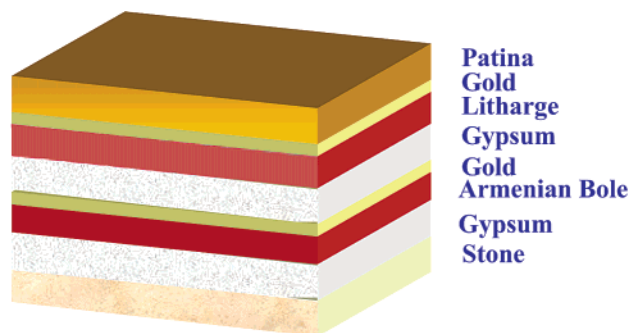
FIGURE 3. Stratification scheme of the layers constituting the angel hair region of the lunette.

in the allylic position, **1**. The transformation of cis bonds to trans, **2**, in the starting radical is followed by the formation of a mixture of peroxy radicals, **3**, after a reaction with oxygen. Hydroperoxides, **4**, then form and may further decompose into alkoxy radicals, **5**, which are involved in various chemical processes that permit polymerization. However, colored or volatile products are also formed and may induce the degradation of the chain.

Reactions such as these are catalyzed by metal ions.[13c,14] Metal ions such as Co^{2+}, Mn^{2+}, Ce^{3+}, V^{3+}, and Fe^{2+} are called primary driers and catalyze the hydroperoxide decomposition. Metal ions such as Pb^{2+}, Zr^{4+}, and Al^{3+} are called secondary driers and are active for polymerization, whereas ions such as Ca^{2+}, K^+, Li^+, and Zn^{2+} act as auxiliary driers by modifying the activity of primary driers. The artists of the past were certainly aware of the fact that certain inorganic pigments caused the accelerating drying of linseed oil. For this reason, they mixed linseed oil with the lead oxide-based red-orange pigment *litharge* (PbO), or else boiled the oil in lead pots.[15] The presence of lead under a gold sheet is thus a clear indication of the use of linseed oil as an adhesive.

The SEM/EDX analyses of the different layers constituting the samples taken from area around the angel hair in the lunette (Figure 2) showed that the composition of the layers closely resembled the stratification scheme reported in Figure 3. This indicates that a missione gilding was carried out on top of the preexisting gold layer laid down using the Armenian bole technique, probably because the original gilt effect had deteriorated. The presence of Pb (M_α, L_α), in the layer beneath the top gold sheet and signals due to Al (K_α), Si (K_α), and Fe (K_α, K_β) from the red layer below are clear proof of the two different methods used for gilding. These conclusions were also supported by SEM-EDX evidence showing that the gold sheet overlapped substrates with the elemental composition of the Armenian bole or of the litharge, respectively (Figure 4). Our conclusions led the people in charge of the restoration to modify their actions. In fact, in their initial inappropriate approach, it had been decided to remove the thick yellow-brown patina from the angel hair areas before a systematic scientific study had been carried out. The red color of a large area of the hair of one of the adoring angels (see Figure 1) is the irreversible consequence of an inappropriate restoration approach.[16]
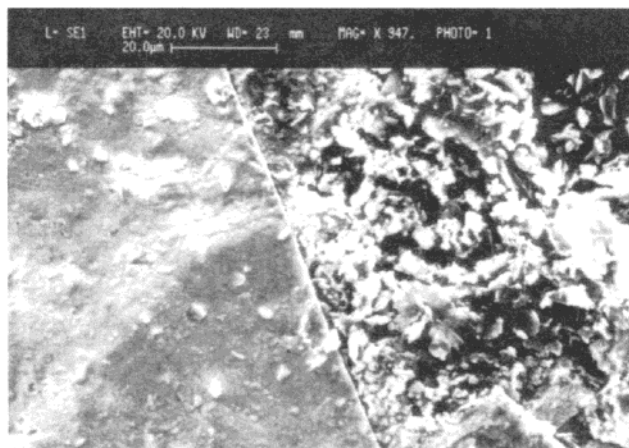

FIGURE 4. Secondary electron image of a gold sheet fragment laid onto the Armenian bole substrate.

4. The Donatello Pulpit

Donatello (1386−1466) was one of the greatest sculptors of all time.[17] The artist lived in the Florence area, where he left spectacular examples of his ability to innovate upon existing sculpting techniques. Donatello boasted the best combination in Renaissance art of mastery of composition and design as well as technical skill.[18] Among the many other technical innovations he introduced in sculpture, the "*schiacciato*" technique ("flattened out") is the best known. The technique involved extremely shallow carving and led the sculptor to model the shapes in such a way as to catch the light in a pictorial manner. The seven carved marble panels of the open-air pulpit in the Duomo of Prato are prime examples of his innovative work. They were commissioned from Donatello and Michelozzo in 1428 by the local town authorities of Prato. Michelozzo was responsible for the architectural design and also helped to make the bronze castings for parts of the pulpit. However, it was only six years later, after signing a new contract, that Donatello carved the first panel. The seven carved panels were placed in their final position in 1438 and show groups of angels intertwined in a surprising variety of poses (Figure 5). Unfortunately, the outdoor location of the pulpit significantly contributed to its accelerated degradation, as testified by the first known intervention dated 1598.[19] The pulpit's corner position (Figure 5) also caused it to be more easily susceptible to thermal stresses and weathering. Photographs of the pulpit (the earliest dating from 1876) show that the condition of the panels on the exposed side of the pulpit is considerably worse than those positioned closer to the building, thus pointing to the effect the unusual arrangement of the pulpit has had on its degradation. The central panel (the fourth from the right in Figure 5), that is, the panel most highly exposed to atmospheric agents, was seen to be in the worst condition of deterioration. Thermal stresses facilitate deterioration of the marble as a result of the extremely anisotropic coefficient of thermal expansion (CTE) of calcite, calcite being the form of the $CaCO_3$ present in the marble.[20] A CTE of +25 ppm/°C is observed along the *c* axis of the calcite, whereas a CTE of −6 ppm/
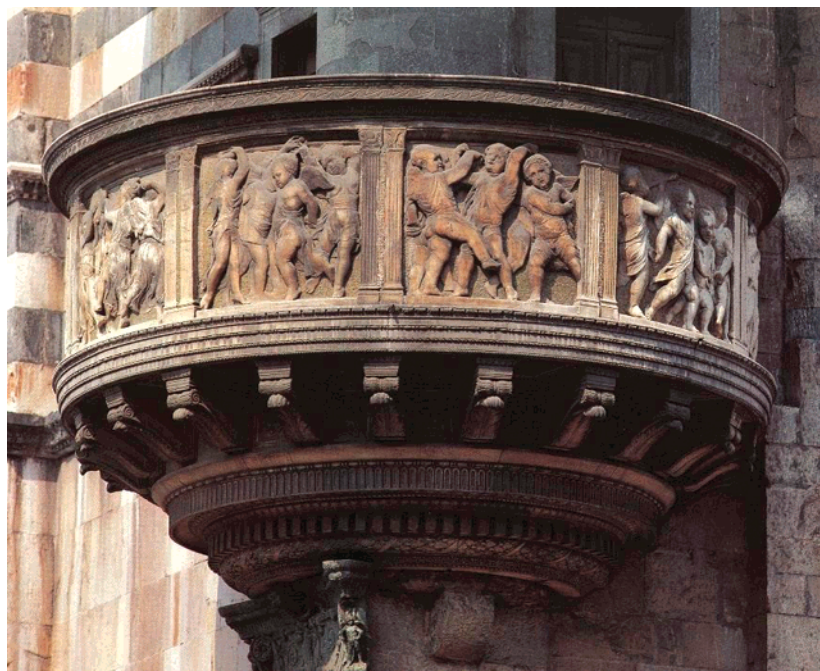
FIGURE 5. The pulpit of the Duomo of Prato (Italy). The original panels are now stored in the Opera del Duomo Museum of Prato.
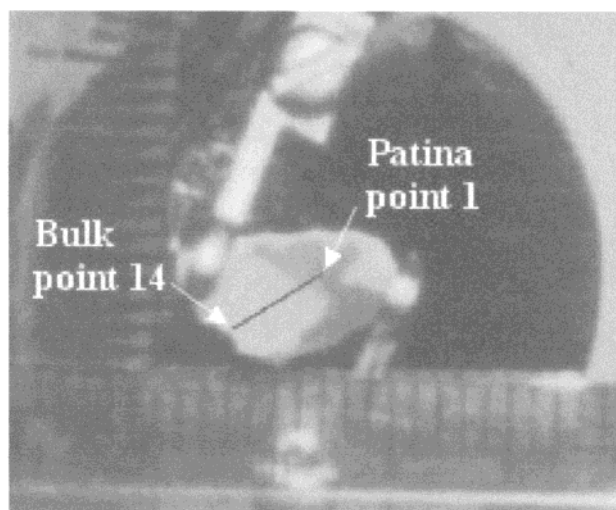

FIGURE 6. Sample taken from the Donatello pulpit panels. The line along which a series of 14 XPS point analyses were carried out is highlighted.

FIGURE 7. Ca/Si, Ca/F, and Si/F atomic ratios obtained from the 14 XPS point analyses carried out along the line shown in Figure 4. The reported values are the mean of three series of analyses.

°C is observed moving in the *a* direction.[20a] Changes in outside temperature induce internal stresses that cause micro-cracks to develop in the marble matrix and promote its physical weathering.

The deterioration of the marble panels prompted a variety of different methods to be tried throughout the last four centuries in order to preserve Donatello's masterpiece from further degradation. These treatments greatly altered the near-surface composition of the panels, which is known to comprise a mixture of residues from early restoration attempts and products formed from the chemical degradation of the exposed marble.[21] Because of the gradual worsening of their condition, in 1970, the panels were removed from their original position and replaced by copies. The original pulpit has been housed in the Opera del Du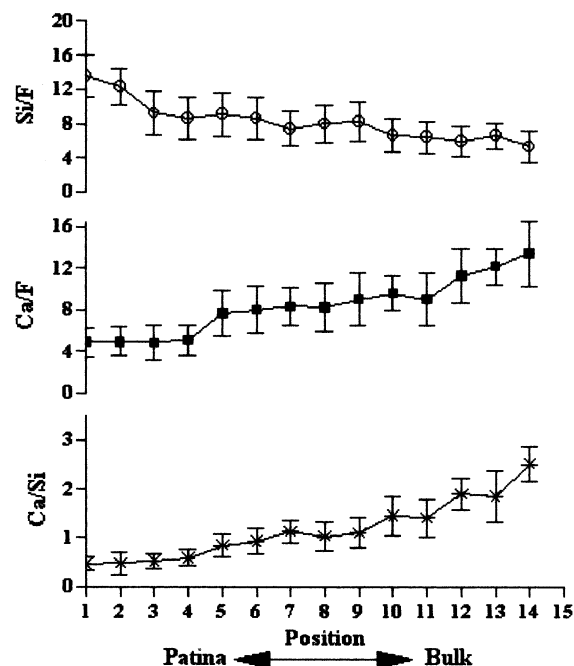omo Museum in Prato since 1976 and underwent extensive restoration work undertaken by the Opificio delle Pietre Dure of Florence between 1990 and 1999.[22]

The mixture of residues and degradation products has commonly been held to be the reason the panels were in such an awful state of repair with deep cracks appearing almost everywhere. The scientific debate over the exact consequences of the architect Pietro Sanpaolesi's treatment of the panels with a mixture of $ZnSiF_6$ and $MgSiF_6$ in 1941 is a case in point. At the end of the 1970s, some scientists began to suspect that this fluorosilicate treat-
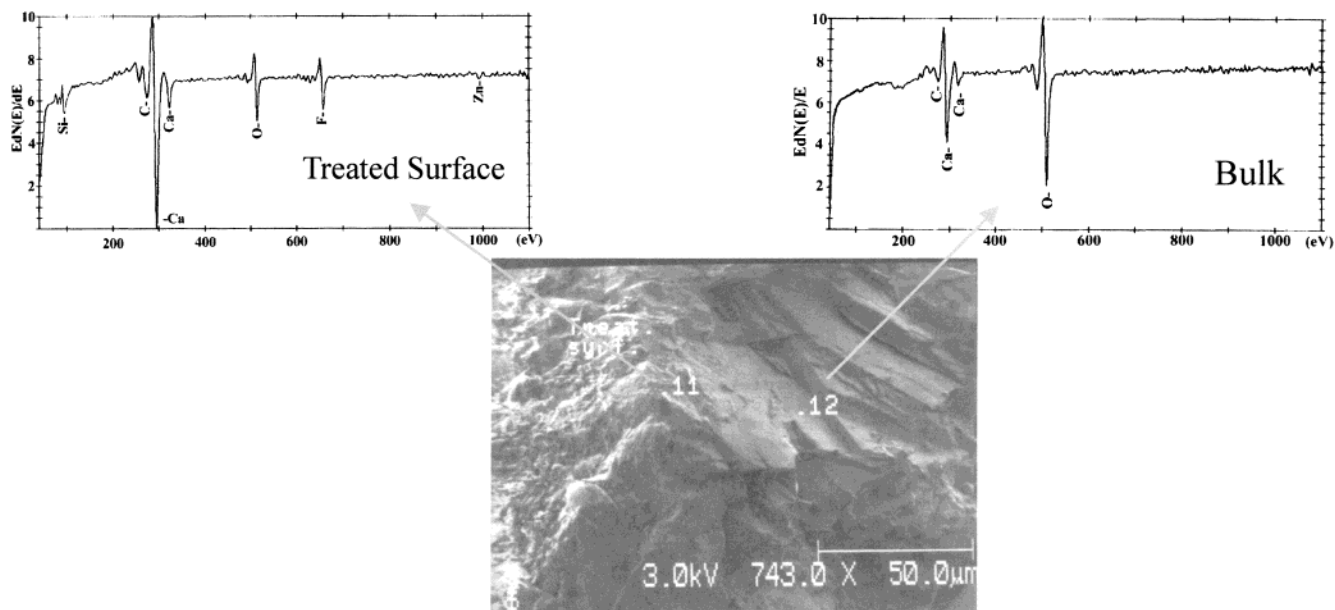
FIGURE 8. Secondary electron image of a fractured Carrara marble sample after 5 h of treatment with a $ZnSiF_6$ (0.7 M) solution. The AES point spectra of the treated surface and the fractured surface are also shown. The fluorine (KLL) and the silicon (LMM) signals from the products of the treatment disappear from regions 50 μm beneath the external surface.

ment was in fact the cause of the deep cracks. Others, however, have opposed this hypothesis.[21b,23] What Sanpaolesi had aimed to do was consolidate the deteriorated surface of the marble through the coherent layer of ZnF_2, MgF_2, and silica gel that had formed on its surface as a result of a water solution of fluorosilicates reacting with the $CaCO_3$ of the marble. The CaF_2 also formed as a reaction product is not believed to act as a binding agent.[24] This method was also effective in waterproofing the deteriorated surface, as the products formed are able to block the pores present in the stone. Modern restoration principles, however, tend to exclude procedures of this kind, since they are based on reactive chemical attacks on the deteriorated surfaces. Moreover, modern restoration relies on procedures which have been appropriately tested, especially as regards aging properties, and published in peer-reviewed literature.[16] Sanpaolesi operated in the 1940s when such an approach was far from being affirmed.

An X-ray photoelectron spectroscopy (XPS) study of the penetration depth of the products formed after fluorosilicate treatment in the marble matrix of the pulpit showed that both the fluoride- and silicon-containing compounds introduced by Sanpaolesi's treatment enrich the most external layers of the marble.[25] Two small fragments, about 1.0 × 0.5 cm wide and <0.5 cm thick, were studied from a chemical point of view and replaced in their original position after the study in an attempt to minimize any damage or alterations to the work-of-art as a whole. Figure 6 shows the line along which a series of 14 XPS point analyses were carried out on a pulpit sample. The lateral edge went from the surface down to about 2 mm into the marble at an angle of about 30°. A lateral resolution of ~150 mm was used for the XPS analyses. Moving from the external patina towards the innermost

point analyzed (i.e., ~2 mm deep into the marble) (Figure 7), the Ca/Si quantitative ratio increased from 0.5 ± 0.1 to 2.5 ± 0.4. The Ca/F quantitative ratios along the edge also increased from 4.9 ± 1.4 to 13.5 ± 3.1. To fully understand the significance of these data, it is necessary to consider that the calcium detected comes from the $CaCO_3$ of the marble. By comparing the amount of calcium with the amount of silicon and fluorine, it is thus possible identify the areas where the $CaCO_3$ was transformed into CaF_2 and silica gel was formed. The increase in the ratio values indicates that this area is essentially located in the first 1−2 mm of the pulpit marble. Thus, Sanpaolesi's treatment cannot be held solely responsible for the formation of the deep cracks. Moreover, the binding energy of the Si 2p XPS peaks observed at 102.5 ± 0.1 eV excludes silica gel as being the main silicon-containing compound in the pulpit. Silica gel generates a Si 2p signal centered at ~103.4 eV.[26] The silicon detected on the marble surface comes from residues of silicone elastomers used in 1971 to make the moulds of the replacement panels.[21b] The study of the Si/F quantitative ratio trend, which ranges from 13.6 ± 2.5 to 5.4 ± 1.8, shows that the most superficial modification was in fact introduced by these silicone elastomers rather than by Sanpaolesi's treatment.

The conclusions drawn from the XPS study of the samples taken from the Donatello pulpit were also supported by experiments carried out in our laboratory whereby Carrara marble test samples were treated with a $ZnSiF_6$ solution (0.7 M). The samples were left in the solution for 5, 10, and 25 h and then analyzed by XPS. The treated samples were also fractured under vacuum and analyzed by auger electron spectroscopy (AES). The XPS spectra confirmed the production of silica gel as a result of the reaction between the $ZnSiF_6$ and the $CaCO_3$

by providing a Si 2p signal centered at 103.3 ±0.1 eV.[26] AES confirmed the near-surface confinement of the reaction products (Figure 8). In fact, spot AES analyses carried out at increasing depths along the fractured edges showed the F KLL and the Si LMM signals[27] to disappear beyond 600 μm from the surface samples that were treated for 25 h.

The study of the Donatello pulpit further demonstrated that the best intentions can generate the worst results, and that an in-depth knowledge of the chemical and physical processes activated by restoration procedures must be obtained before restoration can be carried out.

5. Concluding Remarks

The last four decades have seen a tremendous evolution in the ability of chemistry to provide those in charge of the restoration and conservation of works of art and archaeological material with answers to a great variety of questions. This has been possible thanks to the continuous cooperation and collaboration of chemists and restorers, which has provided a greater understanding of how even the most sophisticated tools available to chemists can be applied to investigate the complex materials that often constitute artworks or archaeological remains. The examples in our laboratory experience discussed show just two ways in which a microdestructive chemical approach can support conservators' decisions by revealing previous interventions and by identifying the chemical evidence of treatments carried out in the past. For their part, chemists need to continue to interact and collaborate with other conservation professionals as it becomes increasingly necessary to compare their own chemical findings with historiographical data.

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