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Multidisciplinary scientific analysis on restoration of a renaissance masterpiece: Verrocchio's "L'Incredulità di san tommaso", outdoor bronze group of Orsammichele Church in Florence. A case history[☆]

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Abstract

Outdoor bronzes present special alteration dynamics leading to stratification of the degraded surface; the more the surface interacts with the environment, the more the stratification develops. So, alterations diversify according to longer or shorter exposure to weather agents in highly polluted urban areas.

"L'incrudulità di S. Tommaso" (the doubt of St. Thomas) by Verrocchio is, from all aspects, a truly interesting case. Over the centuries, it was jutting out of a niche in the wall of Orsammichele Church in Florence and just this partially sheltered position led to such diverse alterations that multidisciplinary diagnosis and analysis proved to be necessary. Thus, different scientists and institutes with different scientific instruments worked together to resolve many analytical problems and questions.

The alloy and the presence of different metal phases were the first object of metallurgical tests, followed by the elemental, structural and crystallographic characterisation of both soluble and insoluble patinas. Correlation hypotheses relevant to patinas and to alteration processes producing them were then formulated.

Only the meeting of such different sectors and experience, aiming at strict result correlation, enabled the successful restoration of such a famous renaissance bronze masterpiece.

Keywords: Bronze restoration; FTIR; Ion exchange chromatography; L'incrudulità di San Tommaso; Metallurgy; Microscopy; Patina; Renaissance statue; X-ray diffraction

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1. Introduction

The replacement of restored works of art is one of the most important decision to be taken by conservators.

Owing to the almost exponential trend of environmental pollution, especially in urban areas, there is strong suspicion that different factors, such as accumulation and different kind of aerosol, the increasing presence of traces of heavy metals with strong catalytic properties in lower air layers – residues from modern vehicle technology, the increase of highly reactive and oxidising substance concentrations, such as non-metallic oxides and ozone, contribute to make the unidentified decay mechanisms of outdoor works of arts, especially bronzes more complex and more varied.

This explains the increasing number of masterpieces that must be shielded from polluted urban atmosphere and so withdrawn from public admiration. It is a consequence of the necessity to protect works of art in more easily controllable places, such as museums where the environmental conditions can be under strict control, that the restored works must be substituted by copies.

The restored surfaces of several artifacts, even if cleaned and protected, have been shown to be more vulnerable to decay processes and also more reactive to new alteration; when the altered and defacing crusts and patinas are removed; a dumping layer, that acts as a protective shield and prevents certain kinds of alteration, is also eliminated.

2. Case history: Verrocchio's "The doubt of St. Thomas"

Recently the Opificio delle Pietre Dure di Firenze (OPD) took care of "The Doubt of St. Thomas", a bronze group whose sculptor, Andrea del Verrocchio, is considered to be Leonardo's maestro. This sculpture stood on the eastern front of Orsammichele Church in Florence, in the "Tabernacolo della Mercanzia" since 1483. Even considering the extraordinary importance of the masterpiece, the studies have been exceptional, and a remarkable group of scientists, institutes, technical and scientific means united in a unique effort of analytical, technological and rheological investigation.

The researches were organised into three phases. The first was devoted to understanding the materials and execution techniques, the alteration products and their origin, and the possible reaction processes and the genesis of some decay compounds. The second phase dealt with the choice of the patinas to be removed during the restoration and then with the analytical monitoring of several ionic species. The last, not covered here, was carried out on bronze specimens treated with many measures for protecting metals and aged in a climatic cabinet under thermohygro-metric cycles to enable the choice of the best protective layer, with a view to future copies and place of conservation.

First of all, the different degree of decay of the two statues was taken in account. They were positioned in a niche: the figure of Christ was more sheltered while St. Thomas jutted outwards, so different distributions and types of alteration had resulted (Fig. 1).



Fig. 1. Alteration map of statues: darker areas correspond to more damage.

3. Alloy composition: metallurgical and elemental characterisation by SEM/energy-dispersive spectrometry (EDS)/wavelength-dispersive spectrometry (WDS) and optical microscopy

A statistical determination of alloy composition enables useful information about manufacturers and execution techniques to be obtained. Metallurgical analysis of alloys, by both optical and scanning electron microscopy (SEM) with microprobe, were carried out on samples of bulk metal taken from the rear of the bronzes with a micro core tool in the Laboratory of Europa Metalli-LMI in Fornaci di Barga (LU) [1]. The results confirmed that alloys of the past are not a true solid solution, but contained particles of pure metallic Pb and regions of different percentage composition in Cu/Sn ratio, caused by differences in the solubility of Sn in the fused alloy resulting from different cooling speeds, according to metallic plate thickness, so inducing a segregation phenomenon. (Fig. 2).

It is interesting to note that the cast was carried out in a single step, instead of the ancient methods in artistic bronze in which statues were cast in separate parts which were then brazed together.

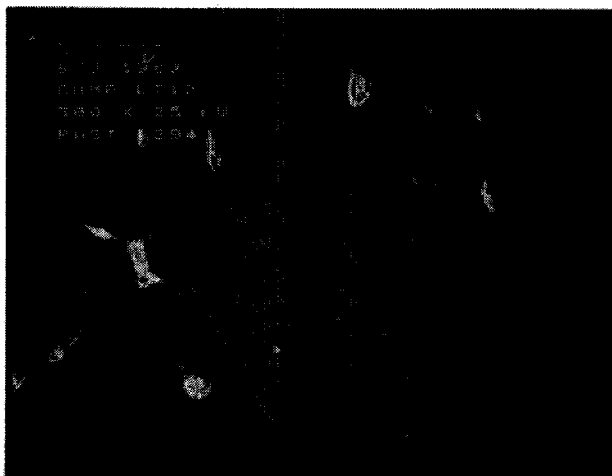


Fig. 2. SEM–BSE image of bulk alloy with Pb and Cu inclusion Europa Metalli–La Metalli Iratiana.

The percentage composition of characteristic alloy components, copper excluded, are listed in Table 1.

Data and direct observations allowed such an expert as Prof. Massimo Leoni [2] to give evidence of significant differences between the two bronzes; that they are two kinds of cast is indicated by the different amounts of Pb.

In Christ's bronze, the first to be cast, the amount of Pb is greater than that of Sn; this increases castability and is typical of an older technology. In St. Thomas's bronze, the opposite is true, i.e. the percentage of Sn is higher than that of Pb; that indicates a better bronze with good metallurgical properties, the so-called 'gun bronze' or 'bronze 90/10'. This difference seems to prove the work of two manufacturers, the first following the ancient metallurgy, the second mastering his own art in a typical post-renaissance fashion. The two compositions, as well as weather exposure, determine the origin of alterations and decay products.

4. Alterations: element characterisation by SEM/EDS/WDS

Decay products are many and very different; their genesis is not simple because alteration dynamics involve the bulk metal interphase, the stratification crusts of

Table 1
Composition of alloy components in statues

Statue	Sn%	Pb%	Sb%	Notes
Christ (cast between 1470–1476)	5	10	0.8–1.5	Higher percent Pb = better castability
St. Thomas (cast in 1479)	6–7	2	0.5–0.7	Better quality bronze

atmospheric deposits and particles and a medium layer composed of reaction products of both. The presence of fusion grounds on the rear of the statues increases the number of compounds present in alteration layers.

The analyses were carried out by SEM, EDS and WDS in CNR “Centro di minerogenesi geochimica dei sedimenti” in Florence [3] and confirm the non-homogeneity of alloys.

This kind of analysis is useful for determining alteration hypotheses, because it can give the possibility of positioning the elements in their own layers. Thus, samples had to be taken from the rear of the statues with micro scalpels and micro-milling tools, with the maximum care that only the scientific personnel of OPD could guarantee, in full respect due to this masterpiece.

The graphic reconstruction (Fig. 3), obtained from comparison between SEM back-scattered electrons (BSE), EDS, WDS and optical microscopy images using reflected and polarised light (parallels Nicol), shows four distinct zones, from bottom to top: a bulk metal with metallic inclusions, different phases of alloy and the interface where the corrosion initiator is dynamically active; a first red layer of corrosion products; a second greenish-greyish layer of more stable compounds; and the upper crusty layer of deposited dust and particles.

The element most responsible for dynamic corrosion in bulk alloy is chlorine, as is well illustrated by the SEM/BSE image and the EDS element map (Figs. 4a and 4b). An interesting result was the precise detection of the position of the chlorine; it is found

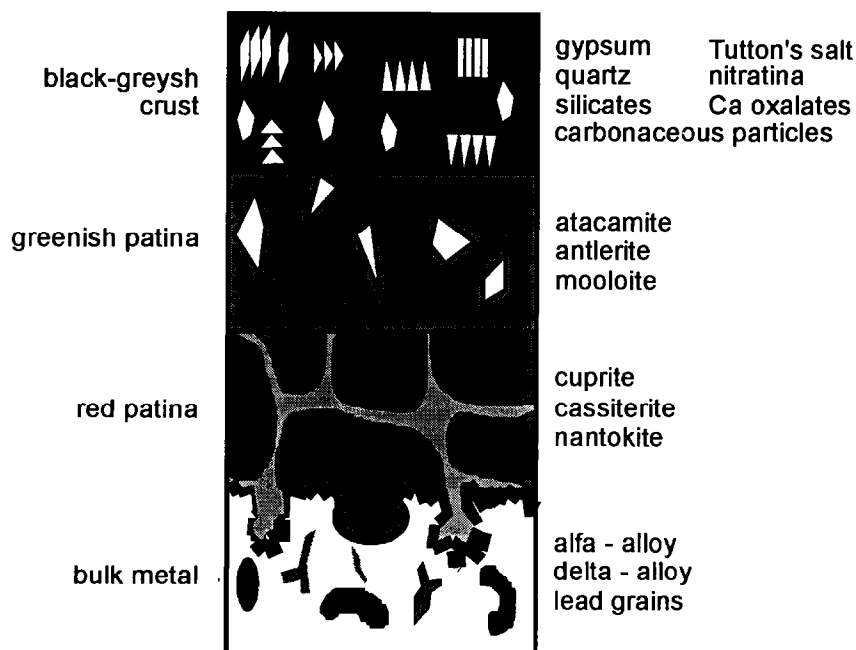


Fig. 3. Alteration layers: graphic reconstruction of compound position.

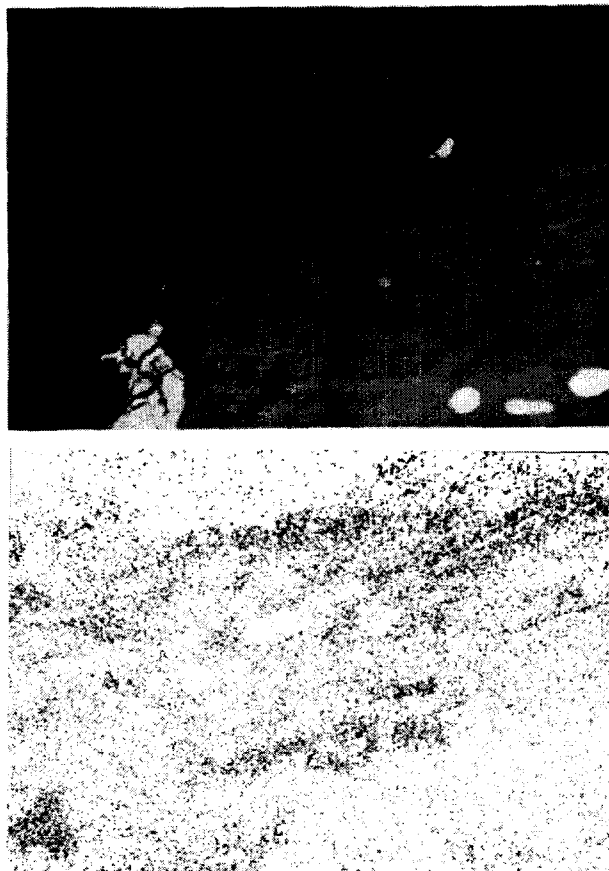


Fig. 4. (a) SEM–BSE image of alteration layers: crusts and patinas (CNR); (b) chlorine EDS map of the same area as (a) (CNR).

both in the alteration products of upper layers, as anion of salts, and in the Sn-rich zones of the alloy surface, such as corrosive agents. This agrees with recent literature [4], which refers to many chemical and physical parameters and confirms Cu corrosion proportional to the amount of Sn.

5. Alterations: mineralogical characterisation by XRD and FTIR

In order to define the different kinds of compound in each layer, it was necessary to apply qualitative analytical techniques. X-ray diffraction (XRD) [5] and fast Fourier transform infrared spectrophotometry (FTIR) [6] were used because of their respective capability of resolution of binary compounds and amorphous or deliquescent salts.

A special sampling method using a micro-milling tool was developed in OPD [7] allowing the progressive and controlled taking of ground material from crusts and patinas. It consists in a micro-mill mounted on a manual micrometer stage allowing the collection of dusty ground material, via vacuum pump, on a Teflon filter disk. In that

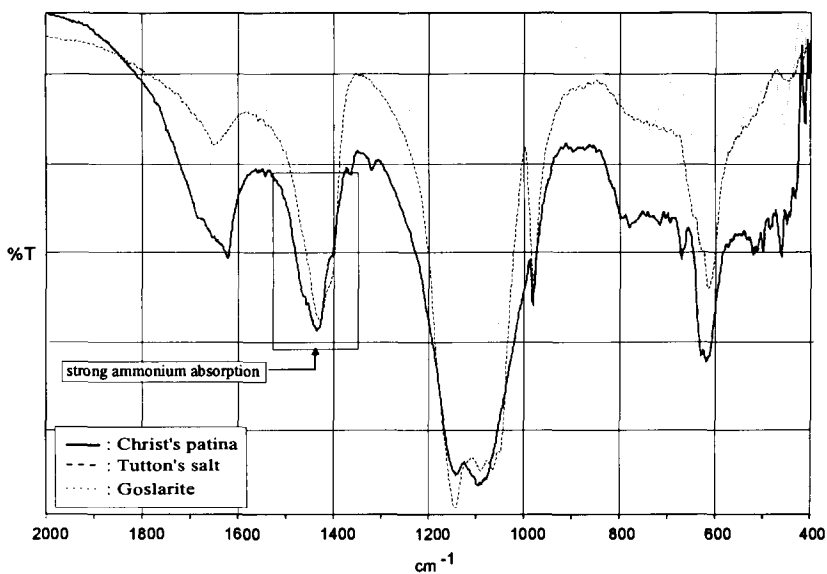


Fig. 5. Comparison of FTIR spectra of patina and reference standards.

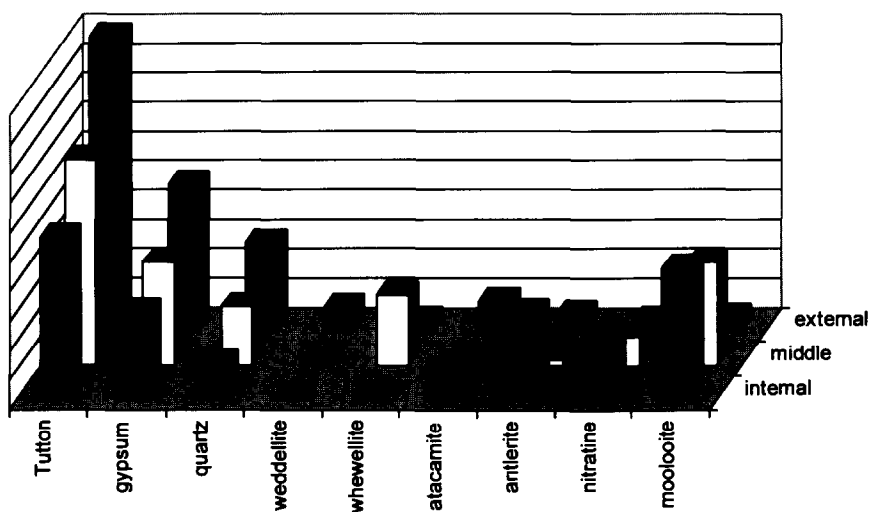


Fig. 6. Composition of St. Thomas patina at different depths.

way, we are able to obtain directly samples for XRD which afterwards can be analysed also by FTIR, thus giving the composition of each layer.

Sample taking from known positions necessitates reading the succession of layers, discerned by microscopic observation of samples of embedded metal and patina cross sections. Evaluation of layer colour also helps in selecting samples in the most precise way.

A very interesting result is the detection of a new salt in external patinas – ammonium copper sulphate hexahydrate belonging to the family of Tutton's salts. Because of the strong interference from signals from other compounds, detection by XRD was uncertain, but the high presence of ammonium ion, detected and quantified

Table 2
Components identified by IEC

Metal phases

Copper Cu

Phase δ $\text{Cu}_{31}\text{Sn}_8$

Phase η Cu_6Sn_5

Sulphides

Chalcocite Cu_2S

Chlorides

Atacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$

Paratacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$

Nantokite CuCl

Oxides

Cuprite Cu_2O

Tenorite CuO

Cassiterite SnO_2

Minium Pb_3O_4

Carbonates

Malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$

Nitrates

Nitratine NaNO_3

Silicates

Quartz SiO_2

Phyllosilicates (mica, chlorite)

Gypsum CaSO_4

Antlerite $\text{Cu}_3(\text{OH})_4\text{SO}_4$

Brochantite $\text{Cu}_4(\text{OH})_6\text{SO}_4$

Anglesite PbSO_4

Goslarite $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

Tutton's salt $(\text{NH}_4)_2\text{Cu}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$

Oxalates

Mooloite $\text{Cu}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$

Weddellite $\text{Ca}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$

Whewellite $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$

by ion exchange chromatography (IEC), suggested the formation of the salt, and comparison of the salt's FTIR spectrum with spectra of patina samples collected from zones of interest revealed by XRD. Comparison of patina and Tutton's salt spectra show characteristic peaks of ammonium salts, well revealed by IEC. The spectra of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Goslarite) is also reported for evaluation of superimposition of bands (Fig. 5).

Special care was given to studies on propagation and presence of different salts and compounds deep in patinas [8]; thanks to accurate sampling we can evaluate the distribution gradient of different salts (Fig. 6); the use of both techniques and data from IEC resulted in the identification of the compounds reported in Table 2.

A very remarkable result, also confirming what was said about the partially sheltered position of statues in the niche, is the comparison of the quantity of the compounds found in surface crusts and patinas of the same statues (Fig. 7).

Tutton's salt is present in a greater quantity on the Christ bronze surface than on that of St. Thomas, whereas quartz, accumulated from dust particles, is present at a higher percentage on St. Thomas. The rears of both statues contain a diffuse, low amount of basic sulphates like Autlerite and Brocantite. [Figs. 8a and 8b.]

6. Alterations: chemical and element characterisation of soluble salts by atomic absorption spectrometry, electrical conductivity and ion-exchange chromatography

The study of soluble portion of crusts and patinas had great importance to the correct conduct of the restoration. The relationship between corrosion product and

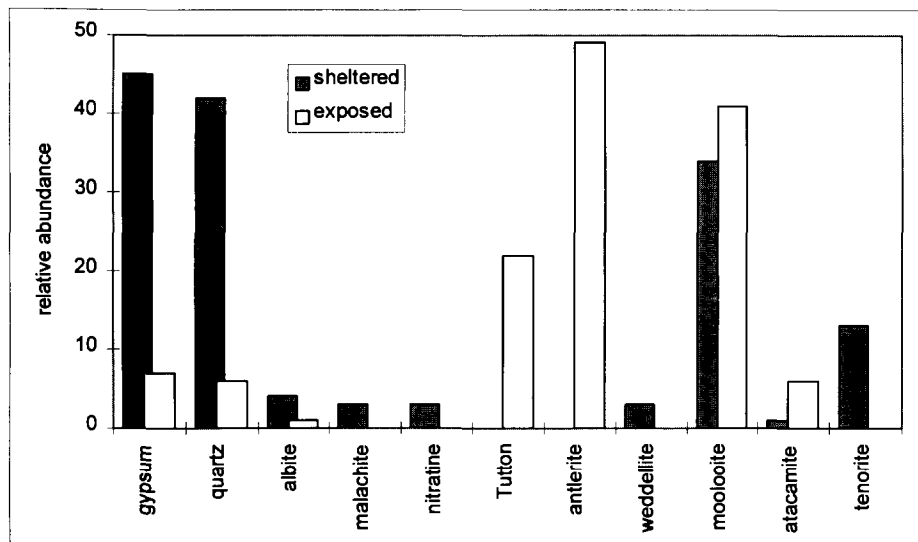


Fig. 7. Composition of patinas from different positions on the same statue: St. Thomas.

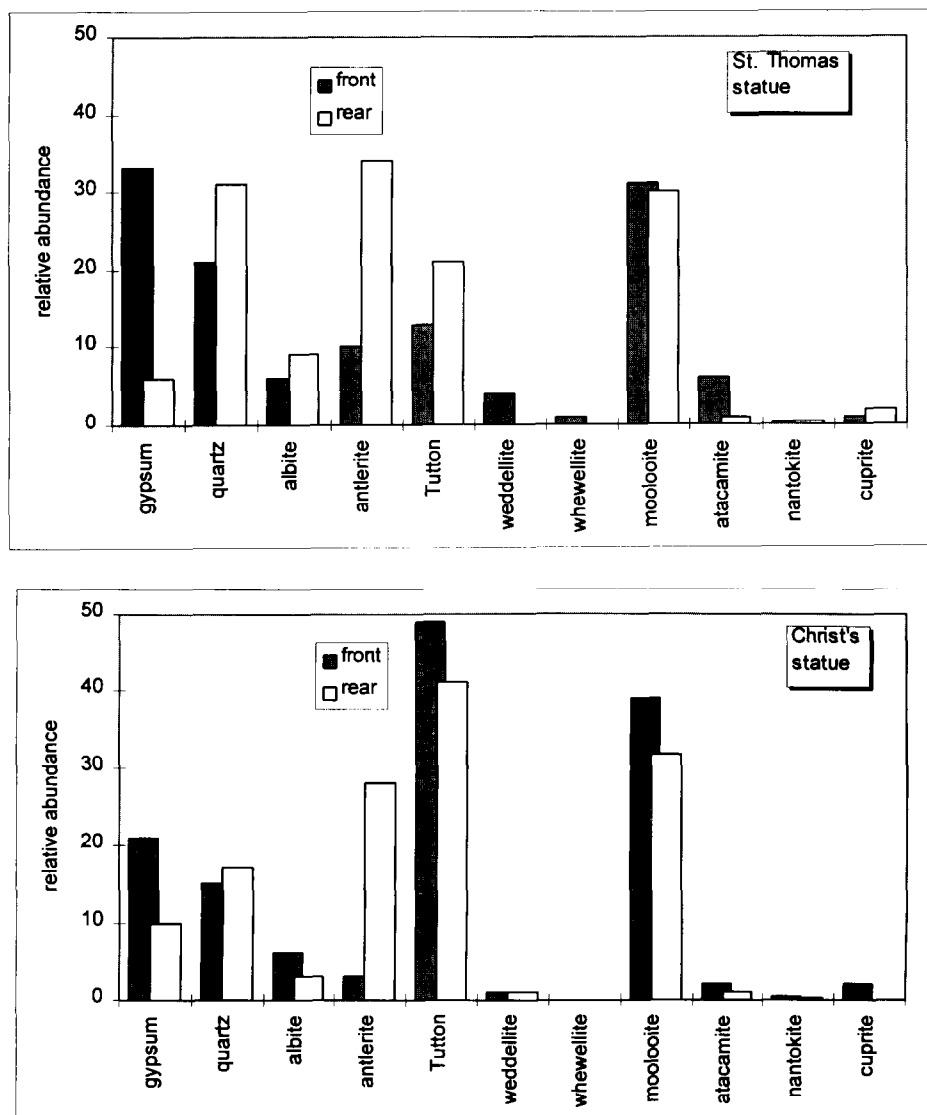


Fig. 8. Comparison of front and rear patinas from (a) St. Thomas bronze and (b) Christ bronze.

genesis of patinas has a large influence on the future stability of the restored masterpiece, which is why it is so important to identify soluble compounds to guide the cleaning of the bronzes. In fact, mechanical cleaning of superficial crusts, one of the restoration steps obviously performed carefully, removes the hard and concretionate

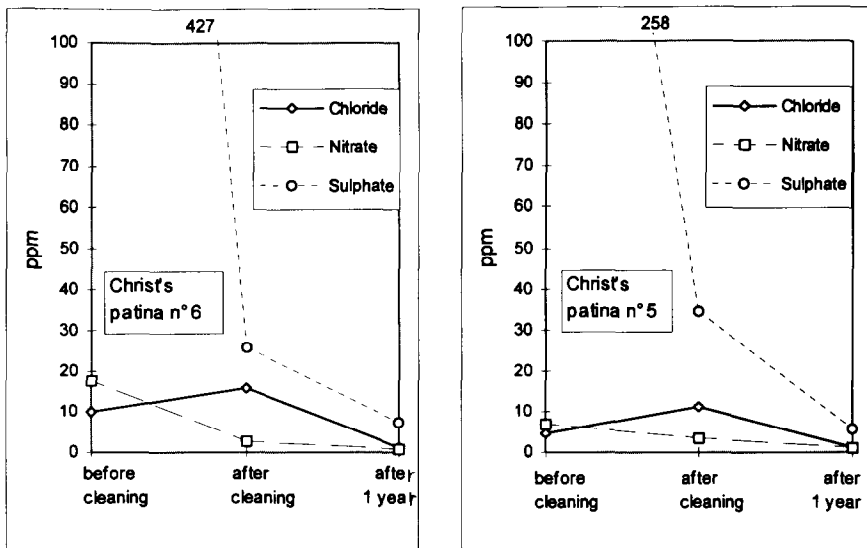


Fig. 9. Monitoring of soluble salts during and after the cleaning of Christ bronze.

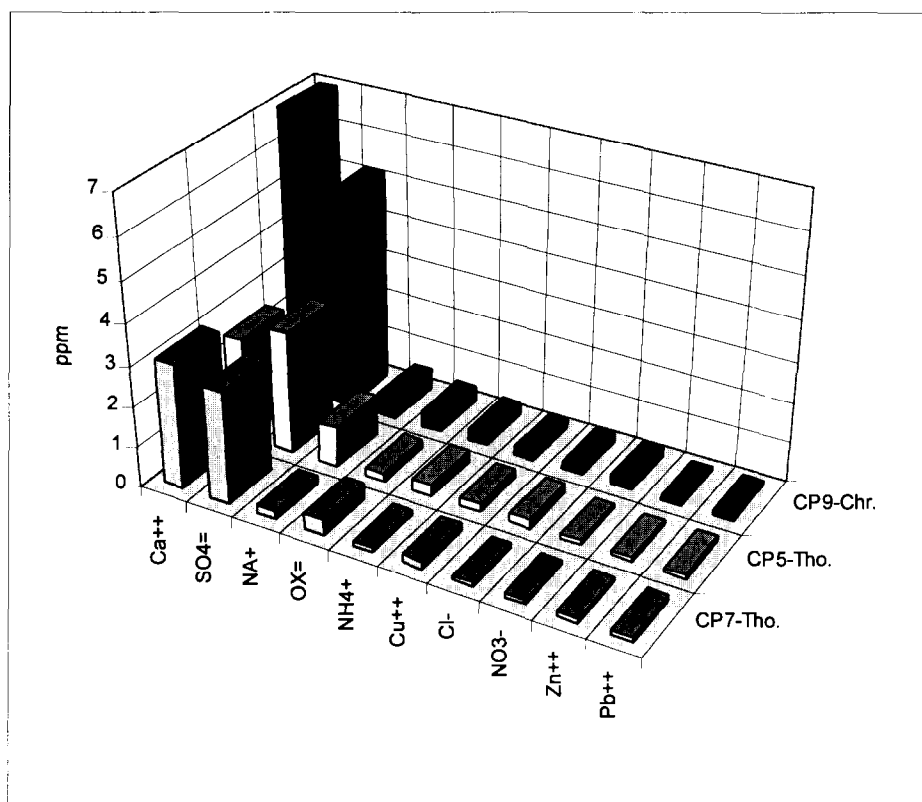


Fig. 10. Ion exchange chromatography (IEC) of three kinds of patina.

deturpant layers but enriches the percentage of free chlorinated, dangerous salts (e.g. Nantokite) in the patina, which can enhance active corrosion processes in the future. Soluble salts, moreover, are the most responsible for transport and distribution between alteration layers, and are consequently responsible for dynamization of the decay processes.

Thus, the importance of determining and monitoring, during all restoration steps, the quality and quantity of soluble ions. These considerations determine the need for careful washing of cleaned bronzes and parallel monitoring of residual soluble salts. Electric conductivity (EC) first and then atomic adsorption spectrometry (AAS) and IEC [9] can give the accuracy required for monitoring the removal of chlorides. The amount of chloride increases after the first step of mechanical cleaning which removes the shielding upper crusts and patinas and frees the deep chloride present near the bulk; after washing with pressurised distilled water the amount of soluble salts decreases (Fig. 9).

Also in this case a specific method of sampling washing water solutions was carried out by the Scientific Laboratory of OPD, gathering a fixed amount of distilled water per unit area.

It is also interesting to note different amount of soluble components between patinas and crusts; the former were richer in gypsum, Tutton's salt and other more soluble compounds. The effects of weathering on St. Thomas statue were, moreover, the presence of less gypsum and other soluble salts than on that of Christ, which was deeper in the niche (Fig. 10).

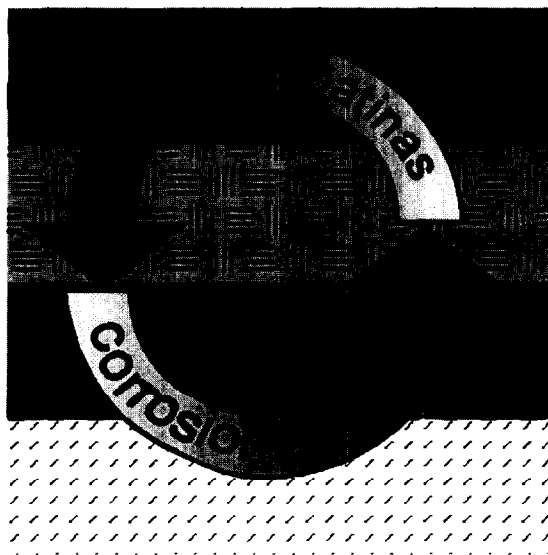


Fig. 11. Genesis of alteration layers.

7. Conclusions

The concurrence of all the illustrated scientific and analytical competence allowed more important considerations:

(1) the metallurgical studies indicated two different, yet chronologically close, manufacturers and casting technologies and confirm the non-homogeneity of ancient alloys, important information for conservators;

(2) the studies of alteration, both on surfaces and in sample cross-sections, enabled elucidation and determination of the layering of decay and alteration products; spectroscopic analysis on cross sections revealed the elemental distribution of chlorine, the most important corrosion agent on outdoor bronzes;

(3) spectrophotometric and diffractometric studies on gradually sampled ground crusts and patinas, even if great respect of masterpiece integrity limited the impact of sampling, enabled determination of several kinds of salt and the formulation of a hypothesis for the mechanism of the dynamic process of bronze corrosion – in simple terms copper and other metals, mainly Sn, Pb, etc., were oxidised and extracted from the bulk metal (as Nantokite) by chlorine and moved up, after combination with oxygen (to form Tenorite and/or Cuprite), to the first patina layer, where they came in contact with soluble ions from upper layers and deposits, like sulphate, carbonate, nitrate, oxalate, etc., generating the upper patina salts, mixed with crust compounds (Fig. 11);

(4) detection and monitoring of soluble salts as chlorides is a determinant tool for correct prosecution of restoration; the careful water wash seems to be a right method to remove a dangerous source of corrosion.

A particular concept attracts me as a conservation chemist – the idea of a slow chemistry, chemistry of low kinetic speed that is responsible for relentless transformation of materials, for the genesis of hardly obtainable compounds or for their extraordinary stable and ordered morphology. I mean a concept that, through the analysis of alteration of historical–artistic artifacts, made of substances that are still in use today, such as metals and alloys, bricks and mortars, clayware and glasses, etc., can bring new information about the durability of the materials, the process of long-term alterations and to their resistance to the various environments and atmospheres, taking advantage of a very wide and varied range of cases.

So, at present in the Scientific Laboratory of OPD experimentation to quantify and identify the alteration mechanisms on bronze specimens is in progress; it is carried out through study of bronze behaviour under thermohygrometric cycles and simulated urban pollution in a special climatic cabinet where it is possible to introduce different concentrations of corrosive gases, such as chlorine and sulphur dioxide, and UV light, and through study of alteration genesis and quantification.

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References

- [1] N. Ammannati, E. Martellucci and G. Mei, "l'Incredulità di S. Tommaso". Analisi delle leghe e indagini sui processi e i prodotti di alterazione. Caratterizzazione metallurgica del bronzo mediante SEM ed EDS. *OPD restauro*, 3, Centro Di Ed., Firenze, 1991.
- [2] M. Leoni, La tecnica della fonderia nella bottega del Verrocchio. 'Il maestro di Leonardo. Il rest ~ auro dell'incredulità di San Tommaso di Andrea del Verrocchio', 91–107, Silvana Ed., Milano, 1992.
- [3] G.P. Bernardini, M. Corazza and F. Olmi l'"Incredulità di S. Tommaso". Analisi delle leghe e indagini sui processi e i prodotti di alterazione. Indagini ottiche e spettrochimiche sulla prima zona di corrosione. 'OPD restauro', 3, Centro Di Ed., Firenze, 1991.
- [4] A.D. Scott, Bronze disease: a review of some chemical problems and the role of relative humidity, *J. Am. Inst. Cons.*, 29 (1990) 193–206.
- [5] F. Olmi, C. Sabelli and R. Trosti Ferroni, l'"Incredulità di S. Tommaso". Analisi delle leghe e indagini sui processi e i prodotti di alterazione. Indagini mineralogiche sulle patine di alterazione. 'OPD restauro', 3, Centro Di Ed., Firenze, 1991.
- [6] M. Matteini, A. Moles and M.R. Nepoti, l'"Incredulità di S. Tommaso". Analisi delle leghe e indagini sui processi e i prodotti di alterazione. Caratterizzazione dei prodotti di superficie mediante FTIR. 'OPD restauro', 3, Centro Di Ed., Firenze, 1991.
- [7] C. Lalli and G. Lanterna Il campionamento ed il prelievo: fasi critiche per la corretta impostazione di una campagna analitica. 'Kermes' 14, 15, 16, Nardini Ed., Firenze, 1992–1993.
- [8] C. Manganelli Del Fà and M. Matteini, The Lion of Braunschweig, II. Investigation on patinas and crusts, 'Maltechnik Restaurierung', 3, Munchen, 1983, 178–186.
- [9] C. Lalli, M. Matteini and I. Tosini, l'"Incredulità di S. Tommaso". Analisi delle leghe e indagini sui processi e i prodotti di alterazione. Controllo dei componenti solubili delle patine mediante IEC e AAs. 'OPD restauro', 3, Centro Di Ed., Firenze, 1991.