

CHEMICAL CHARACTERIZATION OF SURFACE CORROSION PRODUCTS PRESENT ON OUTDOOR BRONZE MONUMENTS

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ABSTRACT

A detailed chemical examination by FTIR, XRD and Py/GC-MS of corrosion products present on three outdoor bronze statues exposed to urban, rural and marine environments has confirmed how the patina formation mechanism is controlled by the type of pollutant species present in atmosphere. Py/GC-MS analysis has demonstrate that no previous organic treatment has been applied on analysed outdoor bronzes and the organic patina composition doesn't seem to be very different depending on the different exposure environments. The chemical organic composition and particularly their relative concentration in samples collected from bronze surface zones submitted to different rain leaching could be considered as responsible for the build-up of corrosion product.

1. INTRODUCTION

The formation of brownish-green and greenish-blue corrosion products layers on bronze objects upon exposure to the atmosphere is the most common evidence for the interaction of atmospheric substances with metal surfaces. This layer is designed the patina, a name derived from the green crust often found on archaeological bronzes. Until now not all the details concerning the patina formation processes were well understood by corrosion scientists although the knowledge of bronze decay in outdoor exposure has been appreciably improved in the last years by applying damage function and the parameter “*t_w*” (time of wetness) to measure the electrochemical corrosion rate ¹. Uniform corrosion of a metal surface is rather exceptional; many

corrosion phenomena, in fact, are both of electrochemical and/or purely chemical nature and depend also from the kind of surface orientation and exposure.

The composition of outdoor corrosion products do not reflect directly the atmospheric composition but clearly is related to those atmospheric constituents whose products possess "certain" solubilities, crystal structures, chemical reactivities and formation rates ². Nevertheless, some important problems must be still further studied and resolved as :

- the definition of a theoretical patina formation model ;
- the study of copper chloride and copper oxalate in relation : their source and role in surface corrosion processes;
- the measurement of patina leaching, caused by rain water and atmospheric pollution ;
- the characterization of the organic substances present as patina constituents : their source and role in patina formation.

Bronze patinas are chemically complex structures and their main chemical constituents are well known : the minerals commonly found as bronze patina constituents appeared to be those which would be thermodynamically stable under atmospheric exposure ³.

While there is a wide literature concerning the composition of inorganic soluble and insoluble copper species found in patinas, not too much work has been carried out to characterize the trace organic constituents that could play an important role in the patina formation⁴ or that can be related to old patination or restoration processes ^{5 6}.

This contribution attempts to highlight the importance of characterizing both the inorganic and organic trace patina constituents with the aim at better understanding the formation mechanisms and whether or not the bronzes were covered with organic coatings. The latter understanding is very important from the restoration and conservation point of view ^{7 8}.

This contribution is based on the patina characterization of three renaissance italian outdoor bronze monuments exposed to urban, rural and marine environmental condition and were investigated using X-Ray Diffractometry (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Pyrolysis-Gas Chromatography-Mass Spectrometry (PY-GC-MS).

2. SAMPLING SITES

Powdered patina samples were collected from the surface of three outdoor bronze monuments exposed to three different environments :

Gregorio XIII is a bronze statue, located in Bologna at the top of the Town hall central portal in a position 20 meters height from the ground , made by Alessandro Menganti and casted in 1579 by Anchise Censori. Together with

the Neptune bronze statue located in the same square and casted by Gianbologna some years later, it is one of the most important Bologna symbols and its image frequently appears inside books dedicated to the city. The surrounding environment is characterized by a low level of air pollution due to the presence of a restricted vehicular traffic area ;

the bronze statue representing Sisto V was casted by Tiburzio Vergelli in 1587 and is located in the central town square of Camerino, a small city situated in the central Italy over an hill 700 meters above the sea level with an environment characterized by the absence of industrial plants. In spite of this situation the square has been utilized for a long time as a parking place for city buses ;

the third statue, casted by Sebastiano Sebastiani in 1614, represents another pope called Paolo V Borghese and is located in Rimini a very famous sea town. The surrounding is typically marine and the square where the statue is located, starting from about 15 years ago, become a restricted vehicular traffic area.

3. EXPERIMENTAL

For this work two analytical techniques commonly used for the characterization of the inorganic constituents has been used : x-ray diffraction and Fourier transform infra-red spectrometry. The latter due to its high versatility and sensibility could be used not only for the characterization of the crystalline and non-crystalline inorganic compounds but also to detect some particular organic substances that after need to be better analyzed with more sophisticated techniques. The infra-red analyses in fact give positive identification results only if the unknown organic substance is present in very large amount.

When possible a microscope cross section observation has been carried out on patina samples to better understand the corrosion layers stratification and the possible presence of any kind of inclusions.

X-Ray Diffraction analyses were performed on powdered corrosion product patinas scratched from the bronze monuments surfaces selectively from the outermost layer toward the inner ones (letter "U" attached to the sample number means upper corrosion layer whereas "D" means the inner one) using small bistoury. The following equipment and operating condition were used: Siemens Khristalloflex IV, Cu Ka radiation (1.548 Å) with Ni filter; 40 Kv, 20 mA. The computer evaluation of the diffractograms was carried out using a software package and in comparison with the JCPDS Powder Diffraction File.

For infra-red analyses the patina samples (about 1 mg) scratched in powder form from the metal surfaces were incorporated into KBr and the relative spectra from 4000 to 400 cm-1 were recorded on a Philips model 9624 FTIR

spectrophotometer operating at a nominal resolution of 4 cm⁻¹. Fifty interferograms of each sample were collected. The assignment to a particular crystalline compound was made by comparing the unknown spectrum with reference FTIR spectra obtained from mineralogical samples previously confirmed by XRD analyses.

Analytical pyrolysis coupled to gas-chromatography and mass spectrometry (PY-GC-MS) is a degradative technique to study large and non-volatile organic molecules such as natural and synthetic polymers, wood, painting ligands, fibers, resins⁹. All these kind of materials are commonly used in artistic works and PY-GC-MS has proved to be a suitable identification technique because it requires micrograms samples with minimal manipulation and good reproducibility. Relatively few papers appear in literature concerning the use of Pyrolysis to characterize art works^{10,11,12,13,14} and, even less, outdoor monuments corrosion patinas^{5,15,16}.

Pyrolysis alone may be considered as a finger printing technique but by coupling it to a gc-mass spectrometer it is possible to characterize the nature of the eluted fragments and to give suggestions about the original material composition.

Pyrolysis was performed with a CDS Pyroprobe 100 set at 800 °C, directly connected to the injection port (T = 250 °C) of a Varian Saturn capillary gas-chromatography/ ion trap mass spectrometer equipped with a Supelco SPB5. Chromatographic conditions were : temperature pyrogram from 50°C to 290°C at 5°C/min holding the initial and final temperature for 5 and 15 minutes respectively. The split injection mode was used (split ratio 1:100). Mass spectra (1 scan s⁻¹) were recorded under electron impact at 70 eV using ion trap detector Release 4.0, from m/z 40 to 450. Weighed samples (about 5 mg) were pyrolysed in helium carrier gas at 800°C with the ramp control off and pyrolysis time of 10 seconds.

4. RESULTS AND DISCUSSION

4.1. XRD and FTIR observations.

The results of corrosion products and phases determined by X-ray diffraction and infra-red spectroscopy on Gregorio XIII (A), Sisto V (B) and Paolo V Borghese (C) are shown in Table 1.

Table 1

Bronze	Sample	Exposure	Color	ant	bro	tut	gyp	ata	qz	moo	wed	other
A	G1U	Protected	Black				###		###			
	G1D	Protected	Green			»	»»	»	»	»		
	G2U	Protected	Black				###		##	##		fel#
	G3U	Protected	Black				###		###	##		fel#
	G4UD	Wetted	Green			»»	»	»	,		»	nit
	G5UD	Wetted	Green/ Blue					###	##		#	

	G5D	Wetted	Green/ Blue					eee				
	G6	Protected	Green				eee		ee	ee		
	G7	Wetted	Green	ee		eee	ee		ee		e	
	G8	Wetted	Black						eee	e		fel
	G9	Washed	Green									
	G10	Washed	Black				e		ee	eee		
B	CAM1	Washed	Black		oo			oo	o			nit ^o
	CAM2	Protected	Black				ooo		o	oo	oo	
	CAM3	Washed	Green		ooo							nit ^o
	CAM4	Protected	Black				ooo		o	oo	oo	
C	PaoloV1	Protected	Black				ooo		o	o		nit ^o
	PaoloV2	Protected	Black/ Green				ooo	oo		oo		nit ^o
	PaoloV3	Washed	Green									sil
	PaoloV4	Wetted	Green/ Blue				oo	ooo		o		nit ^o
	PaoloV5	Wetted	Green				o	ooo		ooo		nit ^o

Table 1. Corrosion products and phases determined by XRD (e), FTIR (o) and by both (v). Compounds present in high proportion are marked with three dots, those present with two dots, those present only in very low proportion with one dot. The corrosion products are indicated as: ant [antlerite $\text{CuSO}_4 \times 2\text{Cu}(\text{OH})_2$], bro [brochantite $\text{CuSO}_4 \times \text{Cu}(\text{OH})_2$], tut [tutton's salt $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \times 6\text{H}_2\text{O}$], gyp [gypsum $\text{CaSO}_4 \times 2\text{H}_2\text{O}$], ata [atacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$], qz [quartz SiO_2], moo [mooloite $\text{Cu}_2\text{O}_4 \times n\text{H}_2\text{O}$], wed [weddellite $\text{CaC}_2\text{O}_4 \times 2\text{H}_2\text{O}$], nit [gerhardite $\text{Cu}_2\text{NO}_3(\text{OH})_3$ or copper nitrate, calcium nitrate etc..], fel [feldspar], sil [silicate material].

The corrosion patina composition summarized in Table 1 clearly shows a correlation between bronzes and the environment. This correlation is particularly evident in Paolo V Borghese statue where the large amount of copper chloride atacamite can be correlated to the marine environment rich in chloride salts. Being atacamite soluble in weak acid it is present only in zones isolated from the aqueous surface layers (samples PaoloV2, PaoloV4 and PaoloV5). What it is really uncommon is the high concentration of atacamite on the statue of Gregorio XIII. In this case old restoration processes involving the use of hydrochloric acid as cleaning agent could be responsible.

No mixed sulfate-hydroxide copper salts (antlerite and brochantite) were detected on Paolo V statue in good agreement with the presence of a marine environment which is mainly characterized by high atmospheric concentration of chloride, low levels of acidity and low levels of reduced and oxidized sulfur gases. On the contrary in Bologna, where acidity environment and oxidized sulfur are expected to be higher than in Camerino, the formation of basic sulfate mineral antlerite (sample G7) is favoured compared to brochantite (samples CAM1 and CAM3) as confirmed by the analyses carried out some years ago on the Neptune's bronze statue standing on the same square¹⁷.

All patina collected from protected or partially wetted zones are characterized by the common presence of a large amount of deposited gypsum mixed with other components, like silica, typical of wind-blown dust and deposited atmospheric particles regarded as the main components of the "black crusts" atop of the green corrosion layers¹⁸.

The heavily washed zones (samples G9 and PaoloV3), characterized by green corrosion products in a fine powdered form not attached to the metal surface, gave results that need to be examined thoroughly in the future using other analytical techniques like Ion Chromatography. XRD in fact shows the absence of crystalline compounds and FTIR only confirms the presence of hydrated soluble salts, probably copper chlorides and sulfates.

The presence of copper (mooloite) and calcium oxalate (weddelite) so fully detected on bronzes exposed to different environments is not well understood but it seems to be correlated to the reaction between copper and the degradative oxidation products of organic substances^{8, 19,20}.

The presence of Tutton's salt on Gregorio XIII statue (samples G1D, G4UD and G7) is quite uncommon. Some suggestions only can be drawn about the possible source of this very soluble corrosion product, already detected in same exposition zones of other bronze statues²¹. The interaction between bronze and ammonium salts whose presence in fog is expected to be very high and the dejection of pigeons could be a possible source of formation.

4.2. Py-GC/MS observations.

In tables 2,3 and 4 for each bronze monument the relative concentration of eight organic substances or pyrolytic fragments of aromatic nature with different functions and the total of the seven more intense n-alkane and n-alkene peaks obtained from py-gc-ms patina samples are shown.

The relative concentrations were obtained using the area of ion monitoring of three different ions typical of each mass spectra as reported in column three of each table and ions 71, 85, 99 and 69, 83, 97 for the evaluation of n-alkanes and n-alkenes respectively. The n-alkane and n-alkene values are relative to the sum of seven more intense hydrocarbon peaks.

Table 2

Organic compound	Scan	SIM	G1	G1D	G2	G3	G4U	G5D	G6	G7	G8	G9	G10
Pyridine	108	52+79+80	42,1	39,6	52,4	57,3	32,6	48,5	35,2	20	18,6	0	29,4
Benzonitrile	471	103+104+50	10,2	6,6	7,5	8,8	16,5	14,4	12,4	24,6	18,5	6,7	7,4
Phenol	519	65+66+94	7,7	3,3	11	3,1	0,6	4,9	4,9	0	6,1	1,5	0
Cyanopyridine	555	104+76+50	8,9	4,9	5,9	8,9	4,7	6,7	5,6	0	4	0	0
Benzoic Acid	1300	122+105+77	0	0	4,4	2,3	4	4,9	8,8	10,8	8,9	0	0
Phthalic Anhydride	1538	104+76+50	10,2	18,1	6,2	5,2	14	2,5	19	16,9	17	1,4	0
Dicyanobenzen	1559	128+129+98	1,2	6,6	0,9	3,1	3,5	5,4	3,1	1,5	11,4	0	0
Phthalimide	1805	147+103+74	11,5	16,4	10,5	10,6	19,6	9,6	9,9	13,8	14,8	0	0
S Alkanes		99+85+71	3,1	0	0,1	0	1	0	0	0	0,3	61,8	0
S Alkenes		97+83+69	5,1	4,4	0,5	0,5	3,3	1,2	0,5	12,3	0,3	28,5	63,2

Table 2. Py-GC/MS results of corrosion patinas collected from Gregorio XIII bronze statue.

4.2.1. Gregorio XIII bronze statue.

The results reported in table 2 show high relative concentration values of pyridine, benzonitrile, phthalic anhydride and phthalimide compared to the hydrocarbonic component concentration. In figure 1 is reported the pyrolytic trace of sample G6 with the indication of the eight peaks indicated in table 2.

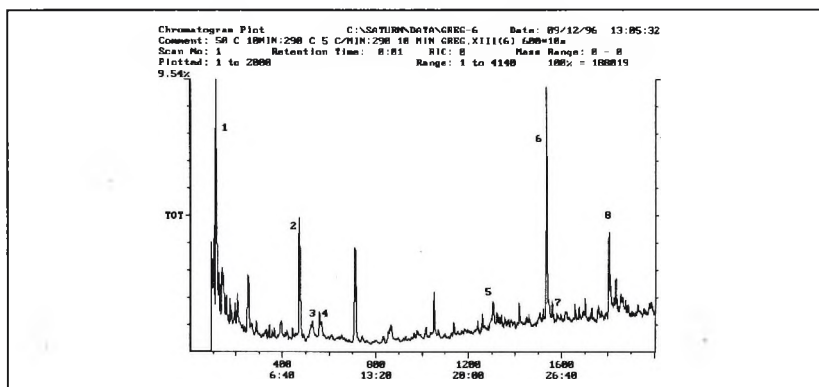


Figure A. TIC pyrogram of sample G6.

Samples G9 and G10 show a pattern completely different from the others and the pyrogram (Figure 2), reporting the total ion current trace together with the monitoring relative to the ion typical of alkanes and alkenes series, gives an indication of samples of hydrocarbonic nature.

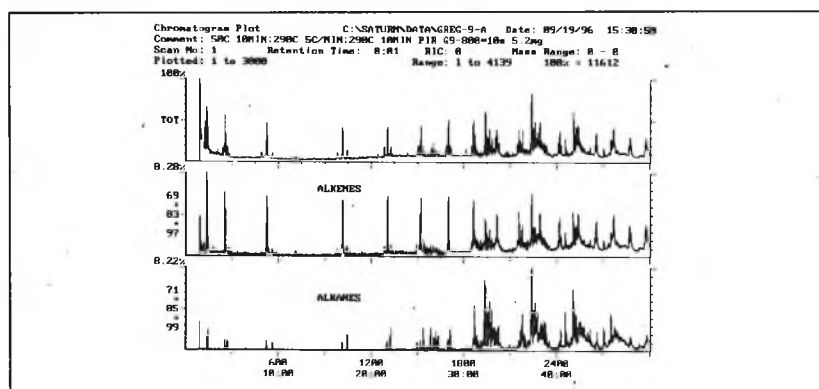


Figure 2. TIC pyrogram of sample G9.

4.2.2. Paolo V Borghese bronze statue.

The organic composition shown in Table 3 is very similar to that of Gregorio XIII bronze statue having the same ratio between polar aromatic compounds versus hydrocarbons as function sample exposition..

Table 3

Organic compound	Scan	SIM	PAOV	PAOV2	PAOV3	PAOV4	PAOV5
Pyridine	108	52+79+80	51,5	45,6	5,1	41	24,5
Benzonitrile	471	103+104+50	12,8	32,6	16,4	33,6	23,3
Phenol	519	65+66+94	20,4	4,5	7,8	6,2	3,8
Cyanopyridine	555	104+76+50	6,1	2,4	6,6	4,2	2,7
Benzoic acid	1300	122+105+77	0	4	0	0,5	3,6
Phthalic anhydride	1538	104+76+50	1,3	1,2	7,6	2	5,6
Dicyanobenzen	1559	128+129+98	0,7	0,3	0	0,2	1,1
Phthalimide	1805	147+103+74	2	1,3	0	0,5	11,9
S Alkanes		99+85+71	0	0,6	2,5	0	0
S Alkenes		97+83+69	3,9	7,4	55,1	11,7	23,1

Table 3. Py-GC/MS results of corrosion patinas collected from Paolo V Borghese bronze statue.

4.2.3. Sisto V bronze statue.

As observed for the other bronzes the analytical results presented in Table 4 confirm the presence of hydrocarbons and nitrogenated aromatic compounds but they show also the absolute absence of any other aromatic compounds such as phthalic anhydride and phthalimide. Although this particular behavior needs to be still investigated the high relative hydrocarbon concentration found in samples collected from washed zone compared to protected ones is still confirmed. In Figure 3 the SIM pyrolytic trace of sample CAM3 is characterized by a series of hydrocarbons with a carbon preference index (CPI) near to one. CPI has been utilized as a diagnostic tool and represent the odd carbon number homologs sum, considered in a specific retention range, versus the even carbon number into the same range.

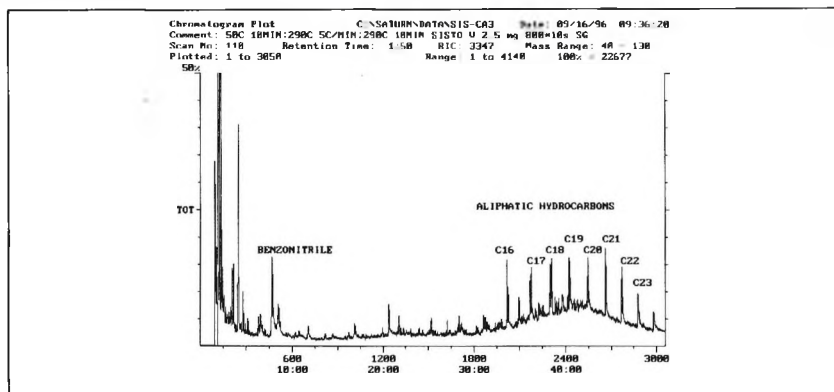


Figure.3. TIC pyrogram of sample CAM3.

Generally a CPI value close to one, combined with a relatively low carbon number of the most intense alkanes, suggests an anthropogenic origin from fossil fuel combustion.

Table 4

Organic compound	Scan	SIM	CAM	CAM	CAM
Pyridine	108	52+79+80	4,1	8,3	46,3
Benzonitrile	471	103+104+50	5,1	47,6	40,7
Phenol	519	65+66+94	0	0	0
Cyanopyridine	555	104+76+50	0	0	0
Benzoic acid	130	122+105+77	0	0	0
Phthalic anhydride	153	104+76+50	0	0	0
Dicyanobenzen	155	128+129+98	0	0	0
Phthalimide	180	147+103+74	0	0	0
S Alkanes		99+85+71	17,3	31,5	5,6
S Alkenes		97+83+69	73,3	12,6	7,4

Table 4. Py-GC/MS results of corrosion patinas collected from Sisto V bronze statue.

The analysis of sample CAM2 taken from a washed bronze zone gave results completely different from the others showing (Figure 4) a pyrolytic pattern typical of a polyfluorinated structure characterized by the elimination of -CF₂ fragments of 50 m.u. The possible presence of a fluorinated polymer applied to the bronze during a surface protecting trial could be a possible source explanation.

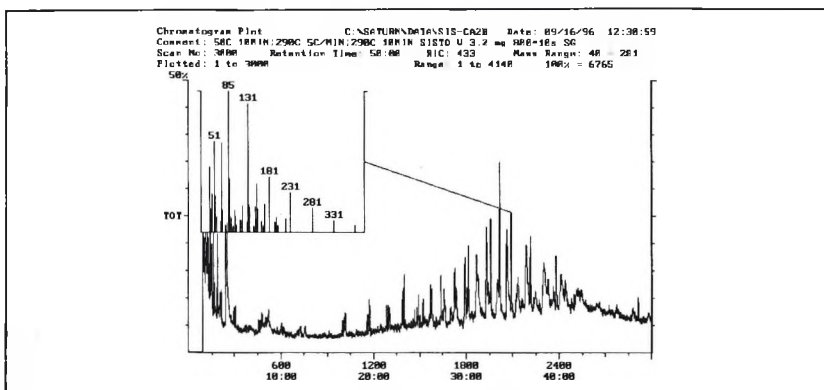


Figure 4. TIC pyrogram of sample CAM2.

5. CONCLUSIONS

Py-GC/MS analyses clearly demonstrate that no previous organic treatments as been applied on analyzed outdoor bronzes.

As described before the inorganic patina composition differences are in good agreement with the different kind of bronze exposure, being characterized by the presence of sulfate hydroxide copper salts in city and rural environments compared to marine where copper chlorides are predominant.

The inorganic patina composition doesn't seem to be correlated with the organic one. No wide differences in organic composition, in fact, can be drawn between samples collected from bronzes considered. The main difference is the absence of aromatic substituted compound on samples collected from Sisto V bronze statue.

Nevertheless some interesting consideration can be drawn viewing the organic composition of patinas in respect to their different kind of exposition (protected, wetted or washed). The presence of all the organic species inside the corrosion products collected from protected or partially wetted bronze zones confirm their binding role in patina formation (Figure 5).

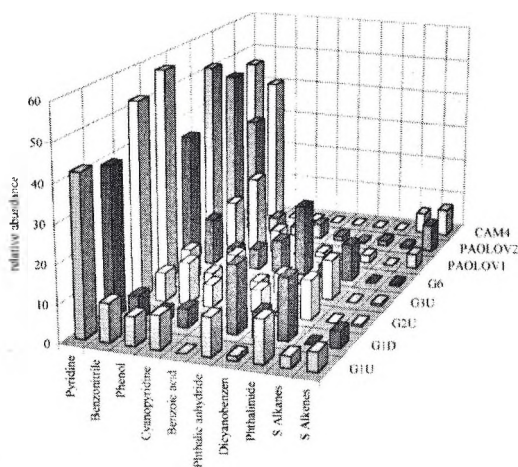


Figure.5. Organic composition of patina samples collected from protected bronze zones.

On the other hand, samples collected from zones submitted to the rain leaching are mainly characterized by an high hydrocarbon fraction with polar aromatic compounds drastically reduced and, in some cases, some nitrogenated aromatic species still present (Figure 6).

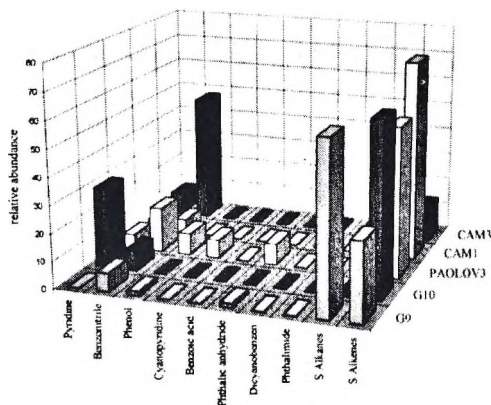


Figure.6. Organic composition of patina samples collected from washed bronze zones.

Preliminary chemical and mineralogical analyses of the patinas confirm some hypotheses on possible formation mechanisms. Patinas contain organic compounds typical of anthropogenic emission sources, although some important differences should be further studied.

Further analyses are being carried out on samples coming from other bronze monuments to shed light on this important point.

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