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Atmospheric corrosion of outdoor bronze artefacts: the case study of 'Katarsis', by Magdalena Abakanowicz

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Abstract.
The conservation of cultural heritage metallic items is deeply connected to the investigation of the corrosion phenomena affecting the metallic surface and to the study of the influence of the surrounding environmental parameters. This paper describes the case study regarding the metallic artwork 'Katarsis' of the Gori Art Collection at Fattoria di Celle (Pistoia, Italy), created by the artist Magdalena Abakanowicz. An in-situ multi-analytical approach was employed in order to assess the conservation state of the statues and to ensure their long-lasting preservation. In particular, X-rays fluorescence (XRF), Raman spectroscopy (RS), and X-Rays diffraction (XRD) were used for the identification of the corrosion products, mainly sulphates, and to identify the employed alloy. In this paper, the preliminary results will be presented and discussed.

1. Introduction

The investigation of the corrosion mechanisms that lead to the formation of corrosion patina on bronze artworks surfaces exposed outdoor can provide useful information for the definition of appropriate conservation plans. Indeed, it can help to identify the corrosion products and also to investigate the influence of environmental parameters on the corrosion behaviour of the artifact material, thus defining the overall conservation state and taking appropriate measures for its long-lasting conservation [1, 2, 3].

This paper presents the characterization of the conservation state of a bronze artwork exposed outdoor, which is part of the Gori Art Collection, situated in Fattoria di Celle, in Pistoia (Italy) [4]. This collection was founded in Prato (Italy) in 1950 and then enriched in the following decades thanks to the contributions of many international artists. Since 1970, the Gori Collection was moved to the private garden of the Fattoria di Celle, a location large enough to host all the artifacts. The overall artistic concept is to create a space where sculptures and multi-material installations are directly connected to the surrounding environment, without any separation. A previous study characterized three bronze statues belonging to the collection, highlighting different corrosion morphologies related to different exposure to the environment [6]. Actually,

Figure 1. 'Katarsis' by the artist Magdalena Abakanowicz.

various micro-climates can establish even on a single artifact due to changes in the rate of wet-dry cycles. Because of this, it is of paramount importance to assess the conservation state of these metallic artifacts using techniques available in-situ, so as to correlate the chemical composition of the corrosion patina to the actual environmental conditions.

The present case study refers to the artwork 'Katarsis' by the artist Magdalena Abakanowicz. The opera, which is composed of thirty-three bronze 'figures', was made in 1985 and installed in the private garden of the Fattoria di Celle [5], with no protection from the environment.

Different analytical techniques, successfully employed for cultural heritage items investigation [6], were employed to characterize the bronze items. In particular, X-Rays Fluorescence Spectroscopy (XRF) was exploited for the identification of the elemental composition of the constituent alloys. Furthermore, the identification of the corrosion products present on the metallic surface was performed by means of Raman Spectroscopy (RS). Lastly, X-Rays diffraction (XRD) was performed on some samples collected from some bronze figures.

In this paper, the preliminary results obtained on some of the elements of the 'Katarsis' are reported.

2. Materials and methods

2.1. The bronze artwork: Katarsis' by Magdalena Abakanowicz

'Katarsis', the artwork subject of this study, was made by the artist Magdalena Abakanovich in 1985 and it is placed in an outdoor space, within the gardens of the Fattoria di Celle, in Santomato (Pistoia, Italy). The artist lined up thirty-three bronze 'figures' in four rows. Seen from the one side, the figures are the repetition of six models, while the view from the other side highlights that each figure has been modelled individually [5]. In Fig. 1 it is possible to observe a picture of the overall appearance of the 'Katarsis' and a detailed of the internal structure of some figures. It is important to notice that the surface of each figure presents a different distribution and appearance of the corrosion products. The measurements were performed on some of the 'figures', as part of a wider monitoring project still in progress, and the preliminary results are presented in this paper.

2.2. X-Ray Fluorescence

X-Rays Fluorescence Spectroscopy was employed to identify the chemical elements of the alloy. The XRF spectra were collected using a Bruker Tracer 5i analyzer. The instrument is provided with a Rhodium (Rh) anode and a 20 mm^2 silicon drift detector. Measurements were collected in the following experimental conditions: 40 kV voltage, 20 μA current. In addition, the Cu-

Ti-Al filter and the 3 mm collimator were chosen. All data were processed through the Artax Spectra (8.0.0.476) software to subtract the background and correct any elemental interference.

2.3. Raman spectroscopy and XRD measurements

The chemical and structural characterization of the corrosion products was carried out through the coupled use of Raman Spectroscopy and X-Rays diffraction.

Raman spectra were collected in situ by means of the portable 'i-Raman Plus'. This instrument is equipped with a 532 nm excitation laser and BWS465-532S spectrometer, that works in the range from 150 cm^{-1} to 4200 cm^{-1} (with a resolution of 7.3 cm^{-1}). The measurements were performed using a laser power value of 6 mW and an integration time of 30 s.

For the XRD analysis, some micro-samples were collected from the artefacts. The 'PAN analytical X'Pert PRO' instrument was employed for the analysis. The measurements were performed using a Ni-filtered $CuK\alpha$ radiation (Kα_1 [Å]:1.54060, Kα_2 [Å]:1.54443), a voltage of 40 kV, a current of 40 mA, a step size of 0.026° and a scan speed of 0.047746°/s. The patterns were collected in the range from 10° and 90°. The acquired patterns were analysed by means of the HighScore Plus software.

3. Results and discussion

XRF measurements allowed to identify the constituent elements of the alloy. In particular, the following elements were identified: Cu, Zn, Sn, Fe, Se, Pb, Ni. As an example, Fig. 2 shows the spectrum acquired on one of the bronze figures, while the main characteristic X-ray line energies (keV) of the identified elements are reported in Table 1.

It is possible to describe the artworks constituent material as a lead-bronze alloy. The presence of selenium can be explained considering the selenium corrosion-resistant coating, usually used on modern bronze sculpture.

It is worth to notice that the peak at 20.216 KeV corresponds to characteristic Kα line of rhodium and it is due to the anode material.

The application of RS on different points on the bronze figures allowed to identify the corrosion products mainly as sulphates, in particular as brochantite. In Fig. 3 a collected spectrum

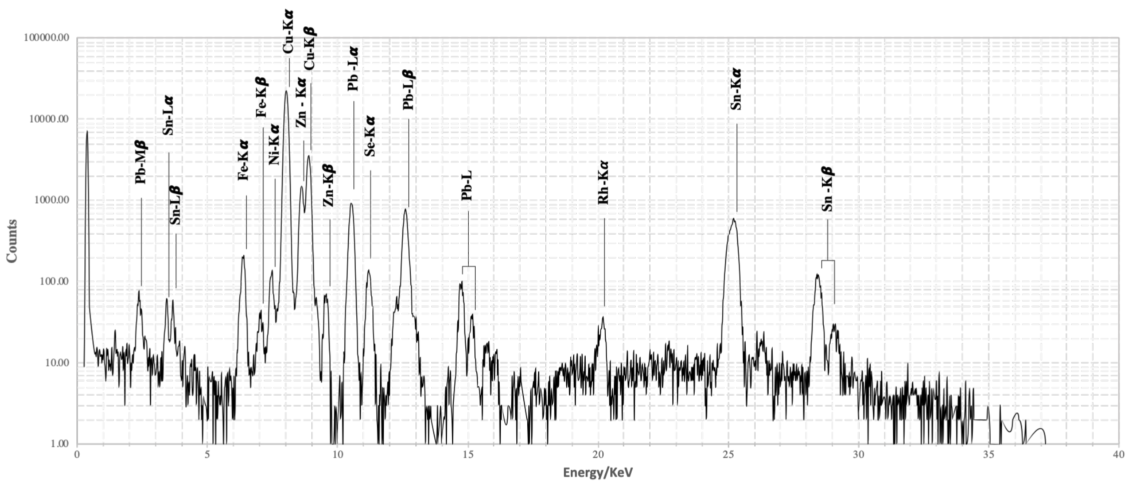

Figure 2. XRF spectrum acquired on one of the 'figures' of the 'Katarsis'.

Table 1. Main characteristic X-ray line energies (keV) of the identified elements of the XRF reported in Fig. 2.

Element	Kα-lines	Kβ-lines	Lα-lines	Lβ-lines
Cu	8.046	8.904		
Zn	8.637	9.570		
Fe	25.271	28.485		
Se	11.224			
Pb			10.551	12.614
Ni	7.480			
Sn	25.271	28.485	3.444	3.663
Rh	20.216			

of brochantite is reported, as an example, together with a reference spectrum of brochantite (RRUFF ID: 060117) [7].

The nature of the corrosion products was confirmed also by XRD. Indeed, the collected pattern, displayed in Fig. 4, shows the characteristic peaks of sulphates and confirmed the presence of a mixture of brochantite (RRUFF ID: 100199, atacamite (RRUFF ID: 050098) and quartz (RRUFF ID: 040031), which is probably due to external contamination.

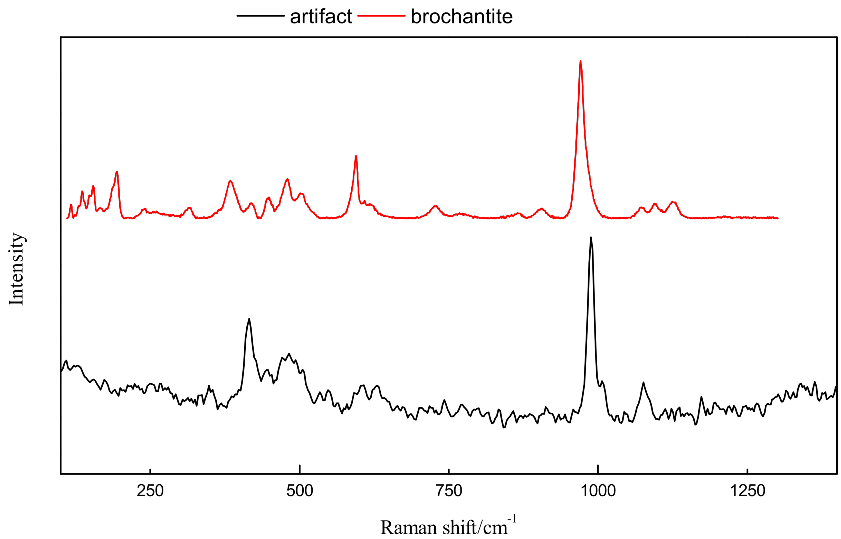

Figure 3. Raman spectrum measured on one bronze figure and reference of brochantite.

4. Conclusions

In this paper, an in-situ investigation of the bronze sculptures constituting the artwork 'Katarsis' by Abakanowicz is reported. In particular, thanks to this study, it was possible to characterize the corrosion products present on the artifacts surfaces and to investigate the elemental composition of the alloys. Moreover, the corrosion products were identified mainly as sulphates and in particular, brochantite.

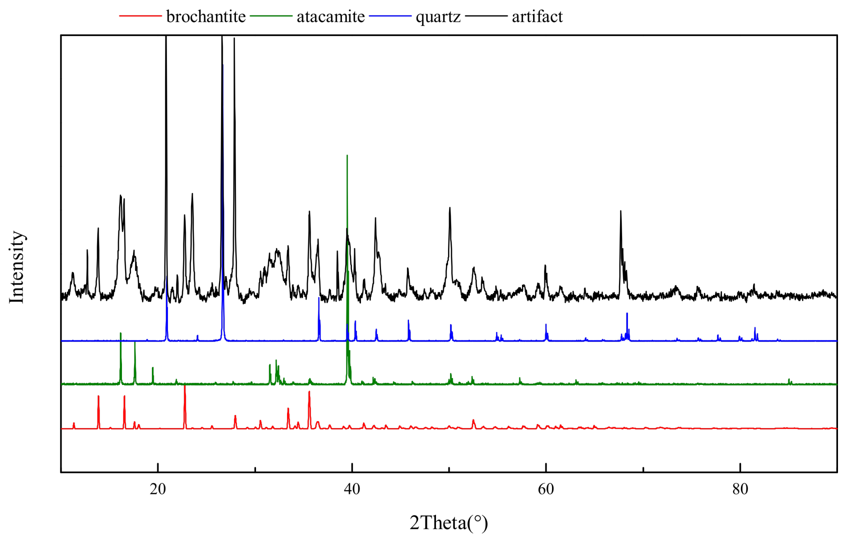

Figure 4. XRD pattern of a corrosion product sample collected on the same area analized by RS, whose spectrum is shown in Fig.3, and reference of brochantite, atacamite and quartz.

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