XRD analysis of patinas on the monument dedicated to Saint Oronzo, Lecce

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Abstract
The monument dedicated to Saint Oronzo is placed in the homonymous square in the city centre of Lecce (Southern Italy). This monument consists of an internal wooden structure that is completely covered with copper sheets, lying on a concrete base about 1.5 meters high, which is placed on a Roman column about 29 meters high.
The restoration of this manufact started in June 2018 and, first of all, non-destructive analyses are planned as proposed in the time-schedule. In this paper, we show the results of X-ray diffraction (XRD) analysis of the *patinas* both of the statue and of the column in order to evaluate their composition.

Keywords: outdoor statue, copper, *patina*, corrosion, XRD

1. INTRODUCTION

The *patina* of copper or bronze statue has different chemical composition depending on numerous parameters such as alloy composition, environmental conditions (for instance, urban, rural, marine and industrial), location of the statue (for instance in outdoor, sheltered areas and museum) and exposure time [1–4]. The *patinas* develop spontaneously over time on copper or bronze objects due to their chemical reactions with the environment that creates corrosion compounds of various colour (for example green, red, bluish, brown and black) and different composition (copper oxide, copper sulfide, copper chloride, copper sulfate and copper carbonate) [5–8]. In particular, the degradation compounds most commonly found in ancient bronze objects are [9–10]: Cu_2O (cuprite), CuO (tenorite), Cu_2S (chalcocite), CuS (covellite), $CuCl$ (nantokite), $CuCl_2·2H_2O$ (eriochalcite), $Cu_2Cl(OH)_3$ (atacamite), $Cu_2Cl(OH)_3$ (botallackite), $Cu_2Cl(OH)_3$ (clinoatacamite), $Cu_3SO_4(OH)_4$ (antlerite), $Cu_4SO_4(OH)_6$ (brochantite), Cu_2OSO_4 (dolerophanite), $Cu_4SO_4(OH)_6·2H_2O$ (langite), $Cu_4SO_4(OH)·6H_2O$ (posnjakite), $Cu_4SO_4(OH)·2H_2O$ (wroewulfite), $Cu_2(CO_3)(OH)_2$ (malachite), $Cu_3(CO_3)_2(OH)_2$ (azurite).
Jambor *et al*. in 1996 reported for the first time the clinoatacamite as a new polymorph mineral of $Cu_2(OH)_3Cl$ [11]. Therefore, previous reports on paratacamite should probably be assigned to clinoatacamite instead.
The identification of copper corrosion products is an essential contribution in the field of conservation of cultural heritage since it is a help for the subsequent work of restorers. For this reason, in this work we show the results of X-ray diffraction analysis of the *patinas* of

the statue dedicated to Saint Oronzo (Lecce, Southern Italy) before restoration started in June 2018.

2. MATERIALS

2.1. Description of statue

The Saint Oronzo statue was built in Venice in 1739 and it is 5.15 meters high. It has an internal wooden structure, completely covered with copper sheets, which are held together by copper nails. The thickness of copper sheets is about 1 mm. The original copper nails are about 2 to 5 cm long.

Actually, the statue is placed on a concrete base (2.65×2.65 m^2) about 1.5 meters high, which is positioned on a Roman column about 29 meters high. During the last restoration performed from 1982 to 1987 numerous copper rivets (containing iron) were added to keep the copper foils together. Unfortunately, the use of these rivets induced disseminated corrosion phenomena over the entire surface of the statue, which are visible to the naked eye.

2.2. Instrument

XRD studies are performed on the statue, on the concrete base and on the Roman column to identify the mineralogy of the degradation compounds. The samples are pounded in an agate mortar to a fine powder, homogenized and subsequently analysed by using a diffractometer Rigaku model Mini Flex with Cu-K_{α} radiation (λ = 0.154 nm). The measurements are carried out with 30 kV of accelerating voltage, 15 mA of current, scan angle in 2θ from 10° to 80°, with step size of 0.01° and scan speed of $0.05° \cdot s^{-1}$. Three scans for each measurement are performed. The obtained XRD patterns are manually compared with standards once from the database www.rruff.info (atacamite R050098, brochantite R060133, calcite R040170, cuprite R050384, graphite R050503, gypsum R040029, murdochite R110122). Table 1 summarizes the description of the analysed samples and the Figure 1 shows the sampling points.

3. RESULTS

Figure 2 shows the XRD pattern of the analysed samples. These spectra give evidence that in both metallic *patinas* there is the presence of cuprite. This oxide represents the protective *patina* that normally covers copper monuments exposed to outdoor conditions. In particular, the dark *patina* (diffused in regions not exposed to leaching) is characterized by the presence of atacamite. This compound is the result of the interaction between copper and chlorine compounds. The green *patina* (diffused in regions exposed to leaching) is characterized by the presence of brochantite. This compound is soluble in an acid environment and therefore responsible for green-coloured dripping on exposed copper objects in outdoor environmental if washed out with slightly acidic water.

XRD pattern of sample 1 (black dripping on concrete pulvino) shows the presence mainly of calcite and gypsum, typical compounds used in cementitious material in the form of powders, and of murdochite. The existence of lead, an element not found in the copper *patinas*, is justified in view of the presence of a lead plate placed at the pedestal of the statue on which the wooden structure rests.

XRD pattern of sample 2 (green dripping on concrete pulvino) shows the presence mainly of calcite. The weak signal at 2θ equal to 16.2° is due to atacamite, confirming that its drip from the copper statue is the cause of the green coloured areas. Sample 3 (black dripping on Roman capital) is also characterized by the presence of calcite as main phase. The black colour is due both to the presence of carbon particles and to a dripping of murdochite (that contains lead) that comes from the statue's pedestal. Sample 4 (green dripping on Roman capital) is mainly characterized by calcite. Furthermore, a weak signal of atacamite is evident. This is reasonable considering it as a leaking of atacamite coming from the metallic statue, which determines the light green colouring on the capital.
Sample 5 (black/gray area not exposed to washouts on Roman capital) shows the presence of gypsum as the main phase and calcite. The graphite signal is also present and this may be due to carbon particles deposited in not washed region, which determine the dark colour.

Sample	Description of sample
G	Green *patina*, copper sheet exposed to leaching
D	Dark *patina*, copper sheet not exposed to leaching
1	Black dripping on concrete pulvino, south side
2	Green dripping on concrete pulvino, south side
3	Black dripping on Roman capital, south side
4	Green dripping on Roman capital, west side
5	Black/gray area on Roman capital (volute), north-west side

Table 1: Description of the analysed samples

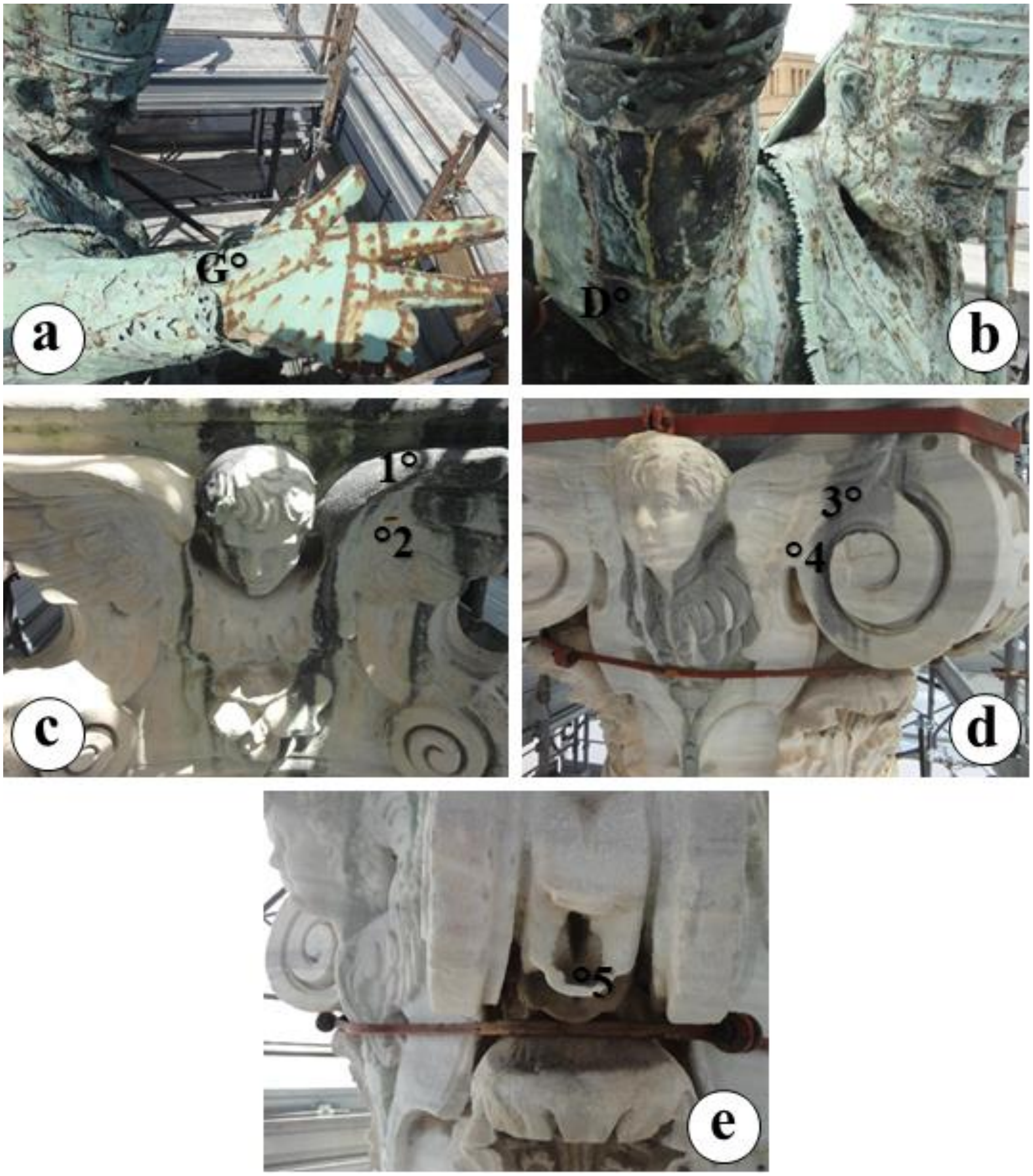

Figure 1: Sampling points. Green patina of copper sheet exposed to leaching (a), dark patina of copper sheet not exposed to leaching (b), black and green dripping on concrete pulvino (c), black and green dripping on Roman capital (d) and black area on Roman capital (e).

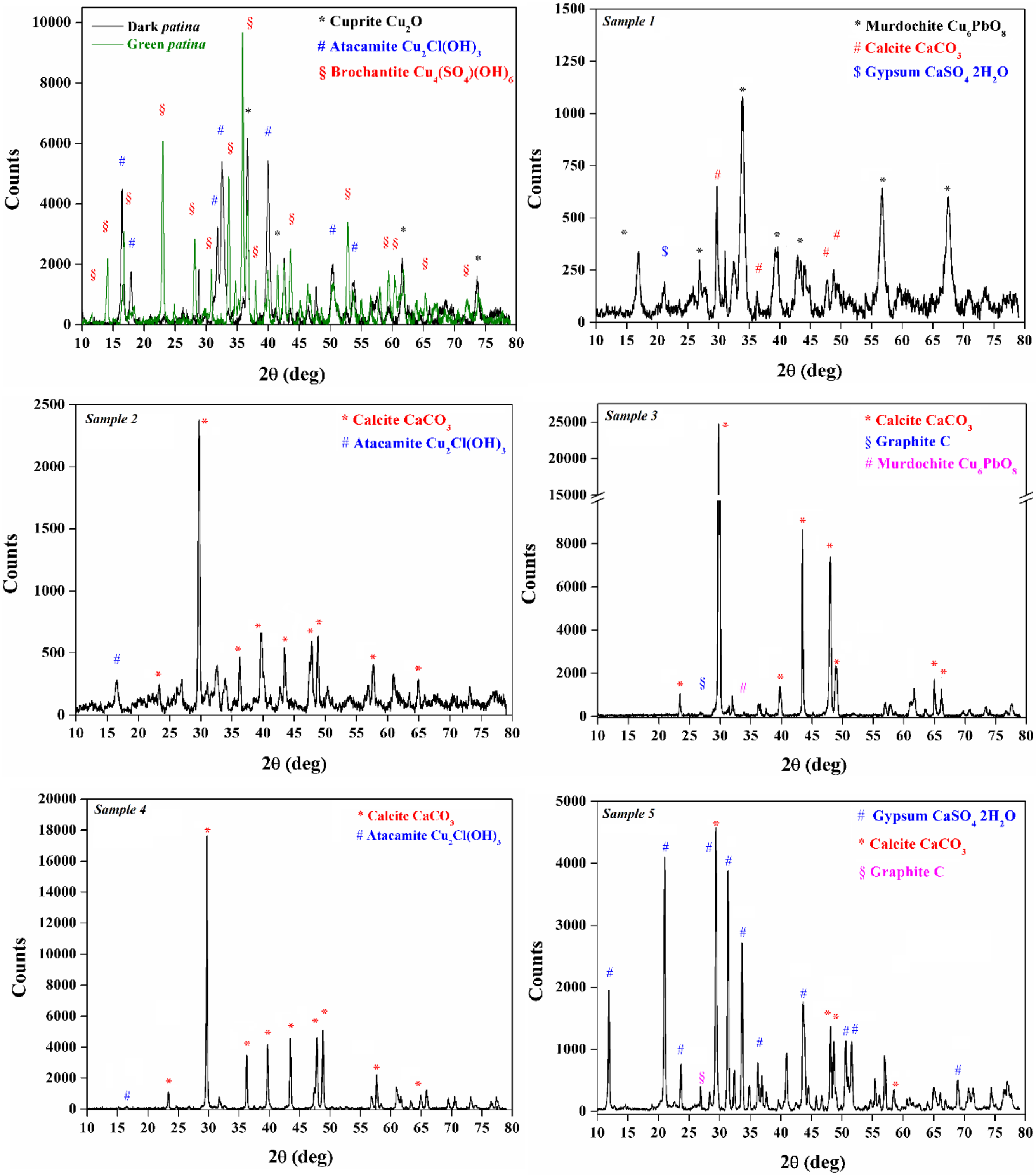

Figure 2: XRD pattern of analysed samples

4. CONCLUSIONS

XRD analyses allowed to study the chemical composition of the surface products of the outdoor monument dedicated to Saint Oronzo in Lecce, Italy.

The results of the metal *patinas* showed the presence of copper corrosion products such as cuprite, atacamite and brochantite as a consequence of the exposure to the outdoor environment. Fortunately, the analysis has also allowed to exclude the presence of clinoatacamite, a well-known compound that determines the corrosion of copper-based alloys. The samples taken from different drips on the concrete pulvino showed both the presence of characteristic compounds for cementitious materials (such as calcite and gypsum) and the signal related to the dripping of atacamite. It is also demonstrated the presence of murdochite in traces due to the lead plate at the base of the statue. The samples of the Roman capital show the existence of calcite, gypsum, murdochite and atacamite, and even of carbon deposit in the regions not exposed to leaching.

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