Surface analytical evaluations of patina formation on outdoor bronzes and laser cleaning potentials

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Introduction:

The history of copper patina on bronze surfaces on outdoor sculptures and in architecture can be traced back to its corrosion resistance and prestigious appearance (Vanino and Seitter, 1903). Environmental influences that lead to the formation of patina layers have changed considerably due to changes in atmospheric emissions over the past decades. Bronchantite, $Cu_4(OH)_6SO_4$, is the most stable patina phase in a neutral and moderately acidic, humid environment containing SO_2. The patina that formed on an internal terrain in the industrial atmosphere therefore consists mainly of bronchantite. As industrial immissions have become cleaner and with lower SO_2 content, the expectation that copper and bronze would 'naturally' turn green, an ideal that developed in the early industrial era due to pollution, can no longer be fulfilled. In Austria, e.g., SO_2 emissions have been reduced by 59.4% since 2005 and by 85.7% since 1990 (Anderl et al., 2022). The main reasons for this decline are a reduced sulphur content in mineral oil products, the installation of desulphurisation units and the shutdown of coal-fired power stations. As a result, dark stained appearances of old bronze sculptures and roofing sheets are increasingly common. Novel maintenance plans are therefore urgently needed with regard to conservation.

Material:

Representative local patina samples from the memorials of Emperor Josef II, Vienna (1795-1807), of King Gustav II Adolf, Gothenburg, Sweden (1854), of Maria Theresia, Vienna (1887), and also from the Quadrigas (1885) on the roof of the Austrian parliament, Vienna (Pichler and Weber, 2000) were taken with scalpels and analysed. The study of characterisation and production of artificial patinas, such as reliable model systems and mock-ups, plays a key role in the field of cultural heritage. Therefore, stable artificial brochantite conversion layers were synthesised by a solution-chemical technology (Pichler, 1998, pp. 63–69) at outdoor sheetings (e.g. Otto Wagner Church in Steinhof, Vienna) but also as dummies for preliminary laser cleaning interventions (Giesriegl et al., 2023, pp. 45–53).

Methodology:

Alloy analyses were performed with atomic absorption spectral analysis and energy dispersive X-ray microanalysis for the elements copper, tin, lead, zinc, nickel, antimony, iron and arsenic. These data were then related to the systematic surface investigations of representative Austrian historical outdoor monuments and copper roofing sheets using surface analytical methods such as colourimetry, atomic absorption spectral analysis, scanning electron microscopy, energy dispersive X-ray microanalysis on polished sections, colourimetry, but also by laser-induced breakdown spectroscopy depth profiling. Patina powder samples were analysed using X-ray diffraction. The patina stratigraphy of metallographically prepared samples was analysed under a light microscope (polar light). The synthesis of artificial brochantite patination layers using a solution chemistry process was applied to the entire tambour panelling of the Otto Wagner Church in Steinhof, Vienna, and also to dummy samples for laser experiments (Pichler, 1998, pp. 63–69). The laser system used for LIBS and cleaning was a frequency quadrupled single Kr-flashlight pumped neodymium doted yttrium-aluminium-garnet (Nd:YAG) laser with a Q-switch system and two harmonic generation modules. It produced 4 ns pulses at 266 nm with a maximum repetition rate of 10 Hz and with a maximum average output power of 44 mW at 10 Hz. The plasma emission was collected and focussed onto an Echelle spectrograph equipped with an intensified charge coupled device (ICCD) camera.

Results and Conclusions:

Alloy composition and metal microstructure analyses of the artefacts allowed detailed evaluations of the bulk material with regard to casting details, e.g. Sn in bronzes, and also of the patinas and their corrosion conversion layers including contaminations. Brochantite was often found as the main mineral component of the patina. Quartz from fly ash also occurred. The patina stratigraphy of the metallographically prepared samples was analysed in respect to the distribution of certain elements (e.g. Cu, Sn, S, and Cl) under a light microscope and using energy-dispersive X-ray analysis. The studies have shown that there is a higher tin content in the outer regions of green areas compared to the outer regions of black zones. It is assumed that in areas that have not been regularly irrigated, deposits and corrosion products cover the originally formed Sn oxide, whereas in areas that have been continuously exposed to rain, they have been cleaned and the less soluble substances such as Sn oxide, brochantite or atakamite remained. These informations are crucial for the design of novel conservation interventions.

Discussion:

Common interventions are stripping off the natural patina by e.g. metallic wool, abrasive pads, abrasive tools, peening with sand, blasting with glass beads or granulates, ultra-high pressure water, and chemicals. Minimal interventions, however, should maintain the patina while removing deposits of soot, dust and corrosion products that disfigure the surface. This should also maintain the ageing value. Such a selective cleaning approach may consider low-pressure water, degreasing, Nylon brushes, scalpels, vibrating and rotating tools, blasting, chemicals, but also photonic procedures, such as laser cleaning. This has already become an established conservation cleaning treatment for a range of artefacts, including stone, ceramics, paintings, and the most commonly encountered metals in cultural heritage, i.e. copper, iron, silver and gold (Schreiner et al., 2008; Kautek, 2010, pp. 331–349). A careful selection of the laser wavelength, pulse duration and operating conditions is then crucial for the laser cleaning outcome (Garbacz et al., 2010a, pp. 693–701; Garbacz et al., 2010b, pp. 457–466; Sansonetti et al., 2015, pp. S28-S33; Grigor'eva et al., 2017, pp. 1–4; Di Francia et al., 2021, p. 148820; Bertasa and Korenberg, 2022, pp. 100–117; Siano, 2004; Siano et al., 2012, pp. 419–446; Shen et al., 2023, p. 87; Giesriegl et al., 2023, pp. 45–53).

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