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Croatian Appoxiomenos alloy composition and lead provenance study

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A B S T R A C T

An ancient bronze statue of an athlete with a strigil (known as Apoxiomenos) – was raised from the north Adriatic Sea in 1999. In order to help to determine its place and date of manufacture various scientific techniques were used. ^{14}C dating performed by the Accelerator Mass Spectrometry (AMS) on the organic material found inside the statue gave calibrated dates between 100 B.C. and 250 A.D. Non-destructive analysis performed by portable X-Ray Fluorescence (XRF) system and external beam Particle Induced X-Ray Emission (PIXE) spectroscopy could not provide representative results for metal alloy composition due to the electrochemical deterioration of the surface of bronze in seawater. This was observed by the analysis of alloy cross-sections performed by the proton microprobe. The analysis showed much higher lead concentrations on the surface of the bronze than inside, confirming that realistic alloy composition can be only performed on samples taken from at least 0.6 mm below the surface. Subsequent micro-PIXE analysis on metal cross-section showed inhomogeneous lead concentrations between 1 and 12%. Lead isotope analysis for provenance investigation has been done on 15 samples using Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). Analysis showed that lead isotope composition is consistent with some of the lead ores originating either from the Eastern Alps or from Sardinia. Altogether, the results lead to the conclusion that the statue is not of a Greek origin, but most probable it is a Roman copy of the Greek original.

1. Introduction

A bronze statue of the athlete with a strigil – the Apoxiomenos – was discovered in 1996 at the depth of 45 m in North Adriatic close to the island of Lošinj, and initially left on the seabed. At the end of 1998 the finding was reported to the Croatian government which organized vast archaeological investigation in the area. The statue was complete, and the majority of its surface was covered with a layer of corrosion products (atacamite, paratacamite, tenorite, cuprite, cerussite, cotunite) and substantial quantities of calcareous encrustations (Michelucci, 2006). As it was seen in 1999, when the statue was recovered from the sea, these calcareous encrustations protected the bronze from the electrochemical deterioration. However, the back of the statue, which was buried in the sand, was to a large extent corroded. The restoration and conservation process started immediately with the slow desalinization procedure that was performed in the collaboration of the Croatian Conservation Institute (HRZ) from Zagreb and Opificio delle Pietre Dure (OPD) from Florence. Desalinization was first carried out in a pool of tap water, and later in mildly alkaline water. After desalinization process the statue was fixed in a hexagonal cage and encrustations were removed solely by mechanical means (scalpels, needles, micro-chisels and ultrasound probes) totally respecting the original patina which was preserved on the front and on head of the statue. The restoration process was completed in 2005 when the statue was exhibited for the first time in Zagreb.

During the restoration process, comprehensive investigations of the statue by many physical and chemical methods were performed by OPD and HRZ as well as other partners (Michelucci, 2006). Two of the results obtained during these investigations are particularly important for the present study: ^{14}C dating and alloy analyses. The dating was performed by AMS on three samples of organic material (wood and peach stone) that were found inside of the body of the statue. Radiocarbon age of these samples was found to be between 1840 and 1970 BP, which corresponds to a calibrated

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date between 100 BC and 250 AD with 68% probability (Michelucci, 2006). Alloy analysis was done on a number of samples by Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES) and Scanning Electron Microscope/Energy Dispersive Spectrometry (SEM/EDS) on corroded and non-corroded samples. ICP/AES analysis made mainly on corroded samples gave high lead concentrations (10–20%), while SEM/EDS analysis of non-corroded samples showed much smaller lead concentrations in the range between 1.3 and 3.9% (Michelucci, 2006). Based on the ^{14}C dating results and the comparison of the casting technology with the Youth of Salamis and on the Hypnos in the Shelby White collection which indicated unambiguously roman techniques (Saladino in Michelucci, 2006), the Roman date for the statue has been assumed.

In order to clarify lead concentration levels in bronze of the statue, we performed additional detailed analysis of bronze composition by three independent X-ray based analytical techniques, including portable XRF spectrometry, external beam (in-air) PIXE and micro-PIXE in combination with the proton microprobe.

Lead isotope analysis was performed by MC-ICP-MS in order to identify the source of the lead minerals used by the comparison with the existing databases of lead isotope ratios for the lead ores from the known ancient lead mines.

2. The athlete cleaning a strigil – historical significance of a statue

The Croatian Apoxyomenos (Fig. 1), is an athlete who has just completed his bout or his exercise and is shown at a moment of relaxation when he is totally intent on cleaning his body. This might perhaps be the depiction of a winner, or just of a general personification of ‘the athlete’.

In ancient Greece athletes would scrape the layer of oil, sand and sweat off their bodies with the strigil (Gr. *stlengis*, Lat. *strigilus*) after exercising or competing. The procedure of scraping the body (Gr. *apoxyesis*) was translated into the celebrated and much-loved depiction of the athlete in Greek art – in his role as Apoxyomenos, the scraper.

The eight replicas so far known are a clear indication that the Athlete in the act of cleaning a strigil was a well known Greek original. In antiquity the art market was evidently interested in producing copies of it. Among these are three bronzes of large dimensions: the one from Ephesus, that is now in the Kunsthistorisches Museum in Vienna (Austria), the head displayed at Kimbell Art Museum in Fort Worth (TX, USA), once kept in Venice, and the mentioned Croatian statue.

There are also three marble sculptures of large dimensions of Roman origin: one statue is now in the Galleria degli Uffizi of Florence (Italy), a head is in the Torlonia collection in Rome (Italy) and another head, probably found in Rome, is now in the Hermitage in St. Petersburg (Russia). There is also a basalt statue of large dimensions (Castel Gandolfo, Italy) and a small one in marble (Boston, USA) (Michelucci, 2006).

3. Experimental

3.1. Samples

Samples taken from the sculpture (shown on Fig. 2, and described in Table 1) were mostly crystallized formations with corrosion products. They were taken from the sculpture during the conservation–restoration work with micro mechanical tools, and later selected with a stereo microscope for MC-ICP-MS analysis. It was not possible to take metal samples from the surface because of the historical and artistic importance of the sculpture. Therefore, the samples were taken from accessible locations on the interior surfaces of the statue. Only six metal samples were taken (samples no. 6, 12, 13, 14, 15 and 16), five from the sculpture and one from the base. Sample number 15, taken from the base, was in part reserved for lead isotope analysis. This sample was taken with intention to check if the lead in the base was made from the same lead ore as the lead in the bronze of the statue, because of a theory that the base was made of several parts of pre-existing monument assembled together (Michelucci, 2006). Samples no. 6, 12, 13, 14 and 16, taken from inside of the sculpture, were embedded in polyester resin and polished mechanically to make cross-sections. The cross-sections were investigated using inverted optical microscope Olympus GX 51 with DP 25 microscope camera. Only samples no. 14 and 16 were pure metal and samples no. 6, 12 and 13 were corrosion products with metal. From surfaces of all cross-sections, chunks of metal were scraped for lead isotope analysis. Mentioned pure metal samples no. 14 and 16 were analysed for alloy composition by micro-PIXE, and results were later compared with alloy analysis made previously on different samples by OPD (Michelucci, 2006).

Fig. 1. Photography of Croatian Apoxyomenos.

3.2. X-ray spectrometry analysis

X-ray spectrometry is recognised as one of the best non-destructive techniques for elemental analysis of metals. It is fast, sensitive, multi-elemental, and in its portable version (or in case of PIXE by using an external beam) it can be non-invasive as well. In this work, external beam PIXE and portable, tube excited XRF