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Chronological assessment of *della Robbia* sculptures by using PIXE, neutrons and luminescence techniques

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ABSTRACT

Portuguese museums and private collectors gather a variety of Italian glazed terracotta sculptures attributed to the *della Robbia* workshop, particularly active between the 15th and 16th centuries. Compositional studies of the paste using INAA, PGAA and XRD and enamel using PIXE, and luminescence protocols, were used as a tool to ascertain the attribution of the sculptures to *della Robbia* workshop. Geochemical and mineralogical patterns were defined enabling to express the production recipe. The luminescence ages were found to be between 1380 and 1640 in some cases with high uncertainties. The compositions of the blue glazes were proved to be similar to other measured on *della Robbia* sculptures from French and Italian collections based on cobalt pigments. Arsenic behaviour, which is associated to cobalt in most cobalt-minerals, is rather peculiar, as it was already found in other *della Robbia* sculptures enabling a chronological framework, pointing to a production after 1520. Based on the results, most of the analysed sculptures implies a *della Robbia* production, and only a few point to a composition and chronology not related with that workshop.

1. Introduction

Sculptures attributed to *della Robbia* workshop, a family who run one of the most renowned Renaissance workshops during the 15th and 16th centuries, make part of Portuguese collections from national museums and privates [1]. This family business is mainly due to the work of Luca della Robbia (1400–1482) and his nephew, and chief artist Andrea (1435–1525) and his children [2]. There are sculptures attributed to *della Robbia* in the National Museum of Ancient Art (MNAA), National Tiles Museum (MNAz), Calouste Gulbenkian Foundation (FCG), in Monastery of Jerónimos (MJ), and a probable attribution on fragments found in Quinta da Bacalhoa, Berardo Foundation (FB) [3]. The attribution to the artist is mostly based on art-historian approaches, which assigns them to their most success period from the end of the 15th to the first quarter of the 16th century. There are several works including compositional discussion (mainly of the glaze) of *della Robbia* sculptures i.e. from the Louvre and the Bargello museum [4–8], and only a few targets to explore ceramic body composition [9–11]. So far, only one work has been done on the Portuguese collections [12], including a detailed chemical and mineralogical characterisation of ceramic body using nuclear techniques, confirming *della Robbia* Italian workshop attribution, on the basis of compositional similarities of the body and other published *della Robbia* sculptures, as well as based on similar technological procedures. In this work, a different methodological approach is used and applied to a larger set of *della Robbia* sculptures, including both the ceramic body and glaze composition, especially aiming to contribute to solve *della Robbia* attributions issues, as well as, chronological validation, by measuring the paste composition, applying luminescence protocols and PIXE analyses of the enamel glaze.

2. Materials and methods

The set of terracotta reliefs studied belong to MNAA, MNAz, FCG, MJ and FB collections. In addition to ceramic body characterization of the medallions from these museums [12], a set of sculptures from the MNAA Museum (S. Leonardo; N. S. Estrelas; N. S. Desfalecida; Sacrarium, Sacrarium base), the MJ museum (S. Jeronimo and St.

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Antonio), and several fragments from FB collection were analysed. In general, they are considered work of Andrea della Robbia, or even Giovanni della Robbia his son, both active during the last quarter of 15th century and the first quarter of the 16th century.

Irradiations for instrumental neutron activation analysis (INAA) were done using the Portuguese Research Reactor (Bobadela) as neutron source; more details in [13]. The cold neutron Prompt Gamma Activation Analysis (PGAA) measurements have been performed at the Centre for Energy Research, Hungarian Academy of Sciences – founding member of the Budapest Neutron Centre; more details in [14]. INAA and PGAA enabled to obtain the concentration of 39 major, minor and trace elements. The mineralogical composition was achieved by X-ray diffraction (XRD) of randomly oriented powder specimens using a Philips diffractometer, Pro Analytical; more details in [15]. Chemical elements behaviour with temperature was considered [16] when discussing chemical data. The PIXE measurements were performed at the 5 MV Van de Graaff accelerator of the Wigner R.C. to study four glaze colours: blue glaze, dark blue glaze, light blue glaze, white blue glaze; more details in [17]. Luminescence dating was performed at the CTN, IST laboratory, comprising the dose measurements in the quartz grains of ceramic body, and the dose rate measurements in the laboratory, in the object and in the environment surrounding the object; more details in [18,19].

3. Results and discussion

The majority of sculptures analysed from the museum's collections have the same kind of mineralogical associations, with minor differences in the minerals proportions, with the exception of one sculpture from the MJ. The general mineralogical association comprises quartz, gehlenite, wollastonite, calcite, K feldspars as basis components, in different amounts, prevailing the first three mentioned minerals. In most of the samples, plagioclase and hematite have been detected in trace amounts, and in some cases probably diopside. As it was already known about other *della Robbia* sculptures [12] the main pyrometamorphic phases found (wollastonite, gehlenite and a "ceramic pyroxene" probably fassaite-diopside type slightly Fe, Mg and Ca rich) are clearly related with Ca-rich ceramic pastes [20]. For most of the sculptures, mineralogy points to a common raw material and technological procedures in accordance with recipes from the epoch, using marly clays heated up to around 900 °C.

The chemical analysis of ceramic bodies also indicates the resource to calcareous clays, most of them with lime contents around 25 wt% CaO. In some cases, the broad distribution of the concentration of some elements (Zn, Sb, Rb, Zr, Ba, and REE) observed within each sculpture is explained by both contamination from glaze during sampling, and the presence of minor amounts of detrital materials in original raw material. Therefore, within the same sculpture, like previously found for the medallions, also heterogeneous chemical composition was found for the analysed sculptures of this work (Fig. 1). Being the MNAz more REE enriched. But noteworthy differences were found for one sculpture from the MNAA museum (N. S. Estrelas), one sculpture from the MJ museum (S. Antonio) and for all the analysed fragments from FB collection.

So, we can point to the resource of marly clays for the generality of the studied sculptures, and considering the negative Ce anomaly, to carbonate rich clays of marine origin, as found for other abroad *della Robbia* sculptures and medallions from Portuguese collections [8,10–12,23]. In this work, the novel data added to the studied sculptures from Portuguese collections, emphasises that some of them were produced with the resource to different raw materials, particularly for the aforementioned MNAA sculpture, MJ sculpture, and FB fragments. Thus, contributing for the discussion of the della Robbia attribution of some known sculptures of Portuguese collections.

In this work, new data including the composition of the blue glazes obtained by PIXE, became a very useful approach for the discussion of both the attribution and the chronology. The obtained results for most of sculptures analysed from MNAA are similar to other measured on

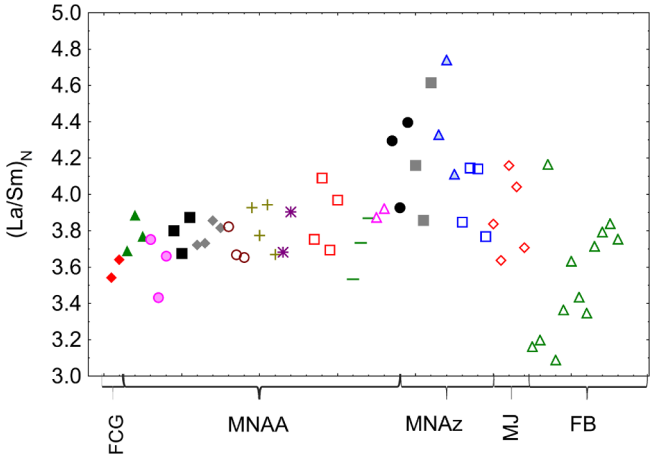

Fig. 1. La/Sm ratio normalized to chondrites against samples of della Robbia sculptures from FCG, MNAA, MNAz, MJ and FB. Each set of similar symbols corresponds to samples from the same sculpture. (Chondrite data from [21,22]).

della Robbia sculptures [5–9], being all the blue based on cobalt pigments. The most probable raw material for the glaze comprises Co found in Ni-Co-As-Bi formations. Renaissance artists or their local suppliers must have received their stock of blue pigments from the Erzgebirge (Saxony) [8], where cobalt is found in Ni-Co-As-Bi formations superimposed (admixed) with silver minerals and pyrites, considered the source of cobalt between the 13th-18th centuries. The glaze composition, besides contribute for the raw material identification, also contributes for the chronological discussion. The arsenic behaviour, which is associated to cobalt in most Co-minerals, is rather peculiar, and can give relevant clues on chronologies [7,8]. The As contents are variable in the studied cases ($0.3\% < As_2O_3 < 3\%$), as already found for sculptures dated after 1520 (Fig. 2). Therefore, we have a chronological boundary given by the As content of the glaze, pointing to Andrea della Robbia and sons work.

Regarding the luminescence ages, the results obtained for the production of the sculptures are between 1380 and 1640, in some cases with high uncertainties. In any case, the analyzed pieces do not appear to be fake or late copies of Renaissance originals. However, for the S. Antonio sculpture and the FB fragments a more recent chronology was obtained, which threaten the traditional ascription to *della Robbia* or other contemporary workshop. Nevertheless, the spread of some luminescence results, enhance the need of the development of laboratory protocols for sample preparation and luminescence measurements of low sample amounts and carbonate rich materials.

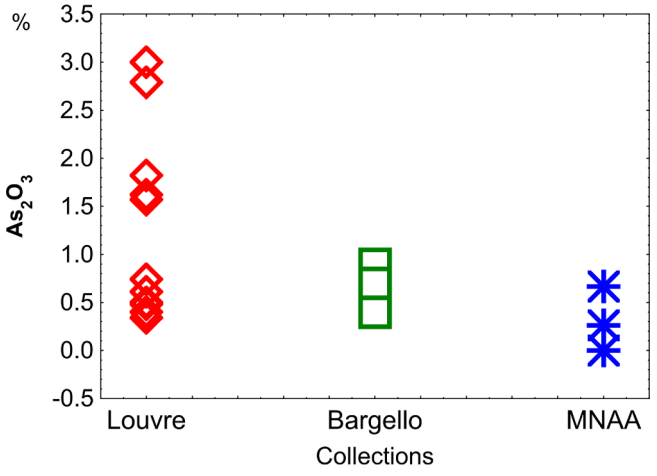

Fig. 2. Arsenic concentration of glaze obtained by PIXE, from MNAA, Louvre [9] and Bargello [5] della Robbia sculptures collections.

4. Conclusions

Ceramic body composition allowed to identify the type of raw materials used for the majority of studied sculptures – marly clays, with a few exceptions. In some cases, different REE patterns with positive Eu anomaly and middle REE enrichment were observed, pointing to the use of calcite rich veins of diagenetic origin occurring in the marls. Compositional results obtained for Portuguese museum collections assigned to *della Robbia* agree with results obtained for other objects found in Italy and France, as well as the same recipe – firing temperatures ≥900 °C and use of similar marly clays. PIXE results of the glaze composition (Co enriched), enabled to identify the type of raw material used, as well as, considering the As content, make chronological inferences, reinforcing the *della Robbia* workshop production of most of the analysed sculptures pointing to a production after 1520. The luminescence results in some cases show high uncertainties, but indicating *della Robbia* epoch, with the exception of FB fragments, which are more recent then Renaissance sculptures. Also a different attribution was obtained for one MNAA and one MJ sculpture.

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