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Nuclear techniques applied to provenance and technological studies of Renaissance majolica roundels from Portuguese museums attributed to della Robbia Italian workshop

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Abstract Artistic and historical examination of high-quality glazed terracotta sculptures displayed in various Portuguese museums point to their production in della Robbia workshop of Florence (Italy). A multitechnique analytical approach is applied for the first time to these sculptures, aiming to confirm their origin. Materials were analyzed using Instrumental Neutron Activation Analysis, Prompt Gamma Activation Analysis and X-ray Diffraction. The compositional results are similar to other della Robbia sculptures, suggesting a common origin for the raw material that was identified as carbonate rich marine origin marly clay. The applied firing temperatures was proved to be around 900 °C. The differences found within each sculpture are explained by the production technique of assembling separate parts to produce these huge sculptures, and the clay pit heterogeneity.

Keywords Prompt gamma activation analysis (PGAA) · Instrumental neutron activation analysis (INAA) · X-ray diffraction (XRD) · della Robbia Portuguese collections · Renaissance Italian sculptures · Provenance and technological studies of terracotas

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Introduction

Ceramic artefacts, an important humankind expression since pre-history, are one of the most important and abundant remains. Several questions arise from these artefacts, namely related with provenance and technological issues. Particularly important are the compositional characterization of ceramic pastes and related raw materials, the separation of local products from imported ones, as well as the identification of workshops and/or production technologies. Therefore, data concerning the composition (chemical and mineralogical) of the object by using analytical approaches are crucial. Obviously, one of the main concerns when dealing with cultural heritage objects is to preserve the integrity of the object, as possible, especially when dealing with museum's collections. Portuguese museums assembly a variety of glazed terracotta sculptures comprising objects for private use (devotional images, altarpieces) and decorative (big medallions mainly for walls decorations) attributed to della Robbia, a family who directed one of the most famous Renaissance workshops during the 15th and 16th centuries. In this work a group of medallions from the National Museum of Ancient Art (MNAA), the National Tiles Museum (MNAz) and the Calouste Gulbenkian Foundation (FCG) collections is studied [1]. The exploratory plastic and iconographic analyses enable us to assign them to a period from the end of the 15th to the first quarter of the 16th century, which coincides with the peak of success of della Robbia family workshop. Mainly due to the work of Luca della Robbia (1400–1482) and his nephew, and chief artist Andrea (1435–1525) and his children [2–5].

The main goals are to address for the first time the question of the consistency of "Portuguese" della Robbia sculptures by looking at the chemical and mineralogical composition of the ceramic body of a set of medallion sculptures, in order to obtain more information on the way in which the objects were manufactured. Therefore, technological procedures, determination of the nature of raw material, their homogeneity degree, and confirmation of the workshop attribution, will be a major goal, also inquiring into their authenticity and rectifying the artistic attribution of the sculptures. In addition, the establishment of a database including compositional studies of ceramic body from della Robbia works is a long term major goal. This is especially significant considering the existence of other sculptures in Portugal doubtfully attributed to the same Renaissance workshop. This became a relevant challenge, when we realize that, for the Portuguese collection no compositional studies were ever performed. At an international level, most of the existing work discuss the glaze composition of della Robbia sculptures [6–17], and only a few were devoted to the ceramic body composition characterization [14, 18, 19]. In this later case, most of them only discuss major elements results.

A relevant issue of this work is the multi-methodological approach, especially to obtain compositional data of ceramic body by using non-invasive and micro-invasive techniques, in order to minimize the damage of the museums pieces, as much as possible. Micro-sampling was the only option in the study of the museums roundels, with the resource to high sensitivity analytical techniques. We have applied Instrumental Neutron Activation Analysis (INAA) and X-ray diffraction (XRD) on 35 objects, and complementary Prompt Gamma Activation Analysis on 5 objects.

The chemical and mineralogical compositions of the objects have been determined from samples taken or using intact fragments of the objects. In most cases, the elemental compositions have been measured by INAA at the Portugal Research Reactor (Campus Tecnológico e Nuclear, Instituto Superior Técnico) and the mineralogical components have been identified using XRD at Centro de Ciências e Tecnologias Nucleares– C2TN. In case of five objects, fragments have been investigated, using PGAA, too.

The applicability PGAA on archaeometry of pottery has been proved in various investigations [20, 21]. PGAA is a non-destructive bulk analytical method, capable to determine concentration of major- and some trace components. This nuclear method is applicable for 'bulk' analysis, and is an ideal tool to determine the average composition of ceramics. PGAA is based on the detection of prompt- γ-photons, emitted in the (n, γ) reaction [22].

PGAA and INAA are perfect complementary methods for elemental analysis, as PGAA is applicable to quantify all the major components and is one of the very few methods that can quantitatively determine H and B among the light elements in geological origin materials. Furthermore, PGAA provides an average composition of an irradiated few cm^3 volume in a fragment or in an untouched object, without any sampling. Since the neutrons can penetrate into deeper layers of the investigated objects, it was desirable to apply PGAA to reveal the composition of the ceramic's body. For standardization of the Budapest PGAA instrument, former standardization measurements have been performed for the whole range of chemical elements in the Periodic Table [23, 24]. Since, the applied k_0-method is comparator method, no repeated measurements of standards and the unknown samples are necessary.

On the other hand, INAA is capable to identify a greater number of trace elements, especially the REEs using a few mg sample taken from the object. The integrated compositional data can help in identification of the raw materials of the ceramics with a better efficiency [25–27]. Besides that, X-ray diffraction is very useful when discussing production technologies issues, like the firing temperatures, as well as, in raw materials ascription, and correlations with chemical composition [28, 29].

Materials

In this paper a set of eleven wall roundels (medallions) attributed to della Robbia Italian workshop are studied, comprising six medallions from the National Museum of Ancient Art (MNAA), four from the Tile National Museum (MNAz) and one from the Calouste Gulbenkian Foundation (FCG) (Table 1). Some of these pieces would have the primary function of being a decorative wall hanging, but also devotional. In Renaissance works of art, fruit and vegetables were often used for purely decorative purposes, but they could also serve a wide variety of emblematic functions and symbolic meanings [30–33].

Generally, the studied sculptures have various problems of conservation. The complex conservation of the sculptures raised several important questions and called for special care and attention on sampling procedures and its location, to be representative of the whole ensemble of parts. Sampling of the order of 300 mg in the inside area of the piece was done, after careful selection of more adequate location for drilling with a diamond drill bit (boreholes), in a way not to put into question the integrity of the objects, avoiding the glaze and extracting only the inner ceramic body.

The overall thickness of the medallions clay wall is difficult to measure due to the presence of relief motifs of various sizes and shapes, as well as to the backing cover in some cases (in wood, not original), but in general we may point to approximately 10–15 mm thickness. For INAA and XRD, a multiple sampling has been performed in each

Table 1 A list of the sculptures analysed

National Museum of Ancient Art				
Photo	*Details & current Location*	*Diameter x Thickness max. (cm)*	*Reference*	*Sampling points*
	National Museum of Ancient Art – Deposit Room: Frame "Della Robbia" in a marble medallion with Virgin with Child and St. John the Baptist, ascribed to Ordoñez (c.1509-1525)	83 x 16	MNAA-FVCJ 1	Inner rim. Borehole in the blue scaly rim of the decorated frame (close to the marble medallion) (pink-orange clay)
			MNAA-FVCJ 2	Outer rim. Borehole between green leaves surrounding the blue scaly frame (pink-orange clay)
			MNAA-FVCJ 3	Outer rim. Borehole behind a pinecone (pink-orange clay)
	National Museum of Ancient Art –Room 55: Medallion Dario – (c.1509-1525)	75 x 10	MNAA-MD 1	Outer rim. Borehole between green leaves (orange clay – coarser then others from MNAA medallions)
			MNAA-MD 2	Central Image. Scrape of white wing of the hat (cream-white clay)
			MNAA-MD 3	Borehole between green leaves (orange clay)
	National Museum of Ancient Art –Room 55: Medallion Virgin with Child and St. John the Baptist – (1475-1500)	76 x 5	MNAA-MVCJ 1	Borehole behind a green leave (pink-orange clay)
			MNAA-MVCJ 2	Scrape of white halo of the virgin (cream-white clay)
			MNAA-MVCJ 3	Borehole behind a white flower (cream clay)
	National Museum of Ancient Art –Room 55: Medallion Coat of Arms of Portugal (c.1509-1525)	87 x 10	MNAA-MCAP 1	Borehole close to a quince (pink-orange clay)
			MNAA-MCAP 2	Borehole behind a pinecone (pink-orange clay)
			MNAA-MCAP 3	Borehole behind a green leave (pink-orange clay)
			MNAA-MCAP 4	Borehole behind a green leave (pink-orange clay)
	National Museum of Ancient Art –Room 55: Frame "Della Robbia" in a marble medallion with Virgin & Child and two angels (c. 1509-1525)	142 x 10	MNAA-FVCA 1	Outer rim. Borehole between green leaves (pink-orange clay)
			MNAA-FVCA 2	Outer rim. Borehole between green leaves (pink-orange clay)
			MNAA-FVCA 3	Inner rim. Scrape of white angel wing in one of the 8 surrounding angels in the blue and white frame (cream-white clay)
	National Museum of Ancient Art –Room 55: Medallion Pelican (1509-1525)	87 x 10	MNAA-MP 1	(pink-orange clay)
			MNAA-MP 2	Borehole close to quince leaves (pink-orange clay)
			MNAA-MP 3	Borehole close to quince /green pomegranate (pink-orange clay)
			MNAA-MP 4	Scrape of white wing of the pelican (cream-white clay)

Table 1 continued

Calouste Gulbenkian Foundation				
	Calouste Gulbenkian Foundation -Renaissance Room: Medallion "Faith"	171 x 10	FCG-MF 1	Outer rim. Borehole between green palm leaves (light pink clay)
			FCG-MF 2	Outer rim. Borehole between green lemon leaves (light pink clay)
National Tile Museum				
	National Tile Museum - D. Leonor Chapel (left wall): Medallion Evangelist – St. John (1509-1525)	65 x 10	MNAz-MSJ 1	Borehole in the top rim of the medallion behind the fruits frame in the grey part (grey-cream clay)
			MNAz-MSJ 2	Borehole behind a white fruit (grey-cream clay)
			MNAz-MSJ 3	Borehole in the white fringe around the blue & white center (cream clay)
	National Tile Museum - D. Leonor Chapel (right wall): Medallion Evangelist – St. Marcus (1509-1525)	65 x 10	MNAz-MSM 1	Borehole behind green leaves (cream clay)
			MNAz-MSM 2	Borehole behind green leaves (cream clay)
			MNAz-MSM 3	Borehole between a green leaf and a lemon (cream clay)
	National Tile Museum - D. Leonor Chapel (left wall): Medallion Evangelist – St. Luke (1509-1525)	65 x 10	MNAz-MSL 1	Borehole on green leaves behind a pinecone (cream clay)
			MNAz-MSL 2	Borehole behind a pinecone (cream clay)
			MNAz-MSL 3	Borehole between a green leaf and a lemon (cream clay)
	National Tile Museum - D. Leonor Chapel (right wall): Medallion Evangelist – St. Mathews (1509-1525)	71 x 10	MNAz-MSMT 1	Borehole behind green leaves (cream clay)
			MNAz-MSMT 2	Borehole behind green leaves (cream clay)
			MNAz-MSMT 3	Borehole behind green leaves (cream clay)
			MNAz-MSMT 4	Borehole in the rim of the medallion behind the fruits/leaves frame (cream clay)

piece to check their homogeneity, particularly if any difference occurs between the compositions of the various analyzed motifs, also in order to better establish reference groups.

The enameled terracotta reliefs studied in this work are accepted as work of Andrea della Robbia and his collaborators, executed between the last quarter of the Fifteenth century and the 1st quarter of the 16th century, even a confirmation is needed. Dimensions in diameter are reported in Table 1, and some of them have monumental scale. Because of their age and removal from original position, some of the works are cracked in many places and has been repaired, evidenced by the presence of fills and in painting throughout, as well as of consolidant within some cracks.

Experimental

Instrumental Neutron Activation Analysis (INAA) is one of the methods routinely applied for decades (see Archaeometry special issue—Acknowledging fifty years of neutron activation analysis in archaeology, number 49, 2, 2007 [34] and others [25–27]) and considering the reduced amount of sample needed is also a micro-invasive method for cultural heritage studies. Irradiations for INAA were done in the core grid of the Portuguese Research Reactor (Sacavém), as neutron source, with a thermal flux of 3.96×10^{12} n cm^{-2} s^{-1}; $\phi_{epi}/\phi_{th} = 96.8$; $\phi_{th}/\phi_{fast} = 29.8$ [35]. Two standards from the Institute of Geophysical and Geochemical Prospecting (IGGE) GSR-4 (sandstone) and GSS-1 (soil) were used. Two aliquots of each standard were used for internal calibration (Quality Assurance). The following elements were possible to quantify by INAA: Na, K, Fe^t, Sc, Cr, Co, Zn, As, Ga, Br, Sb, Rb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th, U More details of the INAA method are given in Gouveia et al. [36], Gouveia and Prudêncio [37], and Dias and Prudêncio [38]. Relative precision and accuracy are, in general, within 5%, and occasionally within 10%.

The Prompt Gamma Activation Analysis measurements have been performed at the PGAA instrument installed on a guided cold-neutron beam of the Budapest Research Reactor [39, 40]. The typical thermal equivalent neutron flux in the sample position of the PGAA station is 7.6×10^7cm^{-2} s^{-1}. The prompt- and delayed gamma photons are detected using Compton-suppressed HPGe detector. The neutrons are highly penetrating particles, and the elements of interest have high-energy gammas (e.g. above 2 MeV), therefore the PGAA measurements provide the average bulk composition of few centimeter-thick objects. Between the sample chamber and the HPGe detector, Lead gamma-ray collimator was applied with a diameter of 30 mm, while the neutron beam collimator have been set to 10, 24, 44 and 100 mm^2 in order to optimize the count rate for the detection electronics. A 64 k multichannel analyzer has collected the spectra, the acquisition time for the measurements have been chosen to be between 2300 s and 56,200 s, to collect statistically significant counts in the spectra. The spectra have been evaluated off-line, using the Hypermet PC software [41]. For the element identification and calculation of concentration, the comparator, or k_0-method [24] is used. The spectrum evaluation procedure is based on the BNC's PGAA library [23] and the 'ProSpero' Excel-based macro [24]. The accuracy of the major elements concentration data is between 1 and 5%, while that of the trace elements can be as high as 10–15%. The main source of the uncertainty is the counting statistics of the prompt-gamma peaks [42].

At the Budapest PGAA facility, the following elements were possible to quantify: Si, Ti, Al, Fe^t, Mn, Mg, Ca, Na, K, H, Cl, B, Nd, Sm and Gd; occasionally S, Sc, V and Cr. As it is typical in geochemistry, the concentrations of the major components are given as of oxides. The amount of oxides is calculated according to stoichiometry.

With the application of both INAA and PGAA a total number of 39 chemical elements—including major, minor and trace elements with special regards to the rare-earths—were quantitatively measured; 7 of the above elements have been identified by both methods which provides an opportunity for comparison.

The mineralogical composition of the bulk samples was achieved by XRD of randomly oriented powder specimens using a Philips diffractometer, Pro Analytical, with Cu Kα radiation at 45 kV and 40 mA, a step size of 1° 2θ/min from 3° to 70° 2θ. To estimate quantities, we measured the diagnostic reflection areas, considering the full width at half maximum (FWHM) of the main minerals [28, 43] and then weighted by empirical factors or calculated parameters [29, 44, 45]. Mineralogical phases and phase transformations with temperature were analyzed according with Brown ad Brindley [46], Trindade et al. [47–49] and Cultrone et al. [50]. Also chemical elements behavior with temperature was considered [49] when discussing the chemical data.

Results and discussion

The mineralogical composition of the roundels

The ceramic body of the different components of each medallion has the same mineralogical association, only with minor differences in the proportions of the identified minerals. Quantitative XRD results (Table 2) indicate that the samples taken from each roundel consist mainly of quartz (SiO_2), gehlenite ($Ca_2Al_2SiO_7$), wollastonite ($CaSiO_3$), calcite ($CaCO_3$), K feldspars ($KAlSi_3O_8$) as framework constituents, in different amounts. In addition, plagioclase ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$) and hematite (Fe_2O_3) have been detected in trace amounts, as well as in some cases probably diopside ($CaMgSi_2O_6$).

The mineralogical composition gives indication of the nature of the raw material, as well as, of technological procedures. Considering the firing products detected in the ceramic bodies, calcite and gehlenite have an opposite proportion, that is, when calcite collapse we assist to the

Table 2 Mineralogical composition (%) of the ceramic body of Della Robbia sculptures

Reference	Quartz	K-Feldspar	Plagioclase	Calcite	Gehlenite	Wollastonite[a]	Hematite
FCG-MF 1	23	–	–	–	44	33	
FCG-MF 2	43	7	–	–	42	8	
MNAA-FVCJ 1	20	–	12	14	28	26	
MNAA-FVCJ 2	18	–	–	12	43	27	
MNAA-FVCJ 3	29	tr	7	12	38	14	tr
MNAA-MD 1	37	12	–	28	22	tr	
MNAA-MD 2	38	13	–	–	22	27	
MNAA-MD 3	29	6	11	11	23	20	
MNAA-MVCJ 1	37	5	5	8	20	25	
MNAA-MVCJ 2	34	11	2	18	20	15	
MNAA-MVCJ 3	34	4	2	–	40	19	1
MNAA-MCAP 1	36	7	6	30	21	–	
MNAA-MCAP 2	40	5	5	22	28	–	
MNAA-MCAP 3	44	4	4	16	29	3	
MNAA-MCAP 4	41	4	6	23	14	8	4
MNAA-FVCA 1	36	–	11	11	26	16	
MNAA-FVCA 2	36	11	–	14	19	16	4
MNAA-FVCA 3	23	10	5	–	27	28	7
MNAA-MP 1	35	7	7	18	17	18	
MNAA-MP 2	27	–	5	13	41	14	
MNAA-MP 3	32	4	4	14	22	24	
MNAz-MSJ 1	27	5	7	15	35	11	
MNAz-MSJ 2	37	6	11	12	14	20	
MNAz-MSJ 3	30	3	4	15	39	8	
MNAz-MSM 1	27	7	5	16	24	22	
MNAz-MSM 2	30	11	5	7	25	22	
MNAz-MSM 3	29	6	–	19	31	15	
MNAz-MSL 1	28	4	4	12	39	13	
MNAz-MSL 2	31	7	–	5	35	22	
MNAz-MSL 3	38	10	8	13	14	17	
MNAz-MSMT 1	47	5	8	35	5	–	
MNAz-MSMT 2	50	4	7	20	19	–	
MNAz-MSMT 3	33	–	12	19	18	18	
MNAz-MSMT 4	7	–	10	22	43	18 (Diopside)	

[a] Difficulty in wollastonite and diopside differentiation. In a few cases it is possible to identify "ceramic" pyroxene (probably fassaite-diopside type slightly iron, magnesium and calcium rich as it is usual in calcium-rich ceramic pastes)

gehlenite formation, pointing to firing temperatures around 900 °C, but also intermediate stages with the presence of both minerals in different proportions occur. Uncompleted decomposition of calcite has been found in almost all ceramic bodies. It is also important to enhance the difficulty in distinguishing diopside dealing with pyroxenes ($XYSi_2O_6$, where X and Y are two divalent cations or a monovalent and a trivalent cation) formed during the firing of Ca-rich silicate ceramics. During the firing of Ca-bearing ceramic bodies clinopyroxene ($(Ca, Mg, Fe, Al)_2(Si, Al)_2O_6$) is usually formed in very small crystals, and is generally referred to as diopside, despite the uncertainty concerning diffraction data. But detailed analyses point to the fact that these "ceramic clinopyroxenes" present wide chemical analogies with fassaite (Ca, Na)(Mg, Fe^{2+}, Al, Fe^{3+}, Ti)[$(Si, Al)_2O_6$], with an abundance of aluminium and ferric iron, and an excess of wollastonite molecules with respect to the diopside-hedenbergite series ($CaMgSi_2O_6$ to $CaFe^{2+}Si_2O_6$), and they are referred as peraluminous diopside, rich in ferric iron, or Al-rich pyroxene [47, 48, 50, 51]. However, this "ceramic pyroxene" formed between 800 and 1000 °C has a slightly different compositional field, when compared with the compositional fields of natural fassaite and diopside [52], but similar and consistent with the occurrence of fassaitic pyroxene in pyrometamorphosed calc-silicate rocks. So, in the case of the studied della Robbia medallions, the main pyrometamorphic phases are wollastonite, gehlenite and a "ceramic pyroxene" probably fassaite-diopside type slightly iron, magnesium and calcium rich as it is usual in calcium-rich ceramic pastes. Due to firing temperatures reached, no clay minerals are detected, as they have all collapsed and transformed, but they also may have been the carrier minerals of some chemical elements, like Mg and Fe.

Mineralogical results point to a common raw material and technological procedures in accordance with recipes from the epoch. Most of what is historically known about workshop practice and production of *maiolica* comes from Piccolpasso's treatise, I Tre Libri dell'Arte del Vasaio from 1548 [53]. The Luca della Robbia workshop was detailed examined by Kingery [6, 7, 54] in that treatise, where is clearly enhanced the calcium importance in making a clay body hard and with less chances of warpage. In addition, it is mentioned that the Ca content of chalky clays like genga was usually about 20% in della Robbia ceramic bodies. Several advantageous of using calcareous clays are highlighted, particularly when voted to big sculptures, like the studied ones. One important advantage is that they fire to a pale buff colour even when they contain several percent of iron oxide [50, 55], and so, the body colour is more readily concealed by a tin-opacified glaze than in the case of red firing non-calcareous clays. They also tend to have higher thermal expansion coefficients than non-calcareous clays, closely to those of lead-alkali glazes, so with less risk of glaze crazing during the cooling following the second firing [56, 57]. They need less firing control, producing pottery of consistent quality, due to the formation of new crystalline phases and to the fact that their microstructures remain essentially unchanged over the 850–1050 °C firing temperature range, also reducing the shrinkage during firing [58]. This higher lime contents of the bodies of the della Robbia sculpture could merely reflect differences in the available clay sources, or a deliberately action, as the decrease in shrinkage during firing that results from this higher lime content would have facilitated the fitting together of the parts of the more complex della Robbia sculpture. On the other hand, the increased rigidity and strength associated with the increased lime content would have been an advantage in the case of larger pieces of sculpture [3, 57, 59] like the studied ones.

The chemical composition of the roundels

The chemical analysis of the ceramic bodies also indicates that the analyzed roundels were produced with calcareous clays, most of them with lime contents around 25 wt% CaO. The total iron oxide contents of clay bodies were normally in the range 3.5–7 wt% $Fe_2O_3^t$, but no red colored was appeared, as the calcareous clay bodies were buff colored since, instead of forming hematite, the iron oxides were incorporated into calcium iron silicates. Only, in a few cases, the presence of iron oxides was detected, and in trace amounts.

Chemical analyses obtained by INAA for the 11 artefacts in a total of 35 samples are listed in Tables 3 and 4, together with the europium and cerium anomalies.

In some studied cases, a broad distribution of the concentration of some elements was found within each medallion, particularly for sample MNAz-MSM 3 higher values of Ga, As and Sb, and lower values of LREE and Th, for sample MNAz-MSJ 2 higher values of Ga, Eu, Tb, and Yb and for sample MNAA-FVCA 3 higher values of Co and Zn. This later sample is different from the others taken from the same medallion, as it was acquired from the white angel wings surrounding the blue and white frame, and the other two samples from the ceramic body of the roundel, behind the fruits. This heterogeneity might be explained by a contamination occurred during sampling, due to chemical elements of the glaze and color of leaves and fruits, like As, Sb, Co and Zn, as samples were taken close to diverse motifs and enamels.

Also differences were observed in the REE contents within the same object, with the presence of both positive and negative europium anomalies (Fig. 1; Tables 3, 4). One expected scenario is the use of a carbonate rich raw material, with negative europium anomalies, but with veins which behavior reflects diagenetic processes, as highlighted by the positive Eu-anomalies found. In this way it is comprehensible the REE patterns found for some of the medallions. The observed variability in REE contents and patterns may also be due to the presence of minor amounts of detrital materials in original raw material. Two main features can be addressed, the different REE fractionating and the europium anomaly, that is negative in most of the samples, but in some of them also positive. This is the case for the medallions exposed in the MNAz—"the Evangelists" collection, and in one sample from the "Dario" medallion (MD) and from the Pelican medallion (MP), the latter two pieces belonging to the MNAA collection. These same sculptures reveal also slightly higher contents of Zr and Ba. Nevertheless, there are common features between all samples, like the negative cerium anomaly (Fig. 1; Tables 3, 4).

The potential raw materials

The chemical composition of the studied medallions, point to the resource of marly clays, and considering the negative

Table 3 Concentration of elements obtained by INAA for medallion sculptures from MNAA museum attributed to the bottega of della Robbia; Europium and Cerium anomalies

Ref.	MNAA-FVCJ 1	MNAA-FVCJ 2	MNAA-FVCJ 3	MNAA-MD 1	MNAA-MD 2	MNAA-MD 3	MNAA-MVCJ 1	MNAA-MVCJ 2	MNAA-MVCJ 3	MNAA-MCAP 1
Na2O	0.87	1.08	0.98	1.17	1.66	1.28	0.88	1.25	1.01	1.13
K2O	1.68	1.95	1.89	1.61	1.89	1.63	1.69	1.95	1.94	1.64
Fe2O3T	4.51	4.50	4.60	3.63	4.02	3.67	3.59	3.82	4.25	3.80
Sc	12.1	12.1	12.3	9.37	10.5	9.38	9.37	9.87	11.1	9.73
Cr	109	105	108	81.8	101	87.0	81.2	100	114	85.5
Co	18.9	17.2	17.6	29.0	47.4	76.5	23.7	19.7	16.8	14.8
Zn	97.5	101	100	158	131	95.9	97.5	111	169	91.5
Ga	14.4	8.64	12.0	8.70	11.1	12.9	11.8	14.9	15.4	12.0
As	2.51	4.33	6.32	11.1	5.91	2.63	3.7	5.27	1.64	4.99
Br	8.03	6.39	1.77	3.25	5.29	4.08	4.26	3.47	3.45	2.57
Rb	92.3	94.4	88.8	73.5	81.5	70.2	70.9	76.9	83.0	71.0
Zr	108	119	134	203	174	143	102	113	133	117
Sb	0.93	1.01	104	312	5.81	465	213	1.57	187	178
Cs	6.16	6.26	6.18	4.44	4.93	4.52	4.74	4.70	5.32	4.44
Ba	357	323	371	323	347	280	293	296	350	295
La	28.6	30.8	30.3	25.2	27.7	24.7	25.1	26.5	28.3	25.7
Ce	58.1	63.0	53.5	44.8	57.8	41.8	42.4	47.4	50.2	43.9
Nd	27.8	29.0	28.7	21.6	28.2	36.4	28.0	26.6	32.9	27.3
Sm	4.86	4.97	5.04	4.21	5.06	4.23	4.14	4.52	4.58	4.33
Eu	1.11	1.1	1.12	3.72	1.09	0.95	0.89	0.94	1.06	0.95
Tb	0.61	0.60	0.69	0.56	0.55	0.50	0.50	0.60	0.74	0.51
Yb	2.35	2.25	2.36	1.89	2.41	1.89	1.78	2.03	2.25	1.88
Lu	0.35	0.31	0.36	0.32	0.32	0.28	0.26	0.30	0.34	0.26
Hf	2.82	2.89	2.98	2.97	3.68	3.11	2.81	3.63	3.54	2.92
Ta	0.91	1.04	1.02	0.63	2.55	0.80	0.79	0.83	0.93	0.82
W	1.58	2.05	1.43	1.43	59.0	2.71	3.23	2.45	3.62	1.34
Th	8.47	8.48	8.48	6.66	7.69	6.76	6.80	7.48	8.05	7.08
U	0.61	1.48	0.94	1.23	2.00	1.06	1.41	2.55	1.72	1.90
Eu/Eu*	0.95	0.96	0.83	0.85	0.96	0.71	0.76	0.83	0.80	0.78
Ce/Ce*	0.72	0.70	0.69	2.74	0.70	0.71	0.68	0.65	0.69	0.70

Ref.	MNAA-MCAP 2	MNAA-MCAP 3	MNAA-MCAP 4	MNAA-FVCA 1	MNAA-FVCA 2	MNAA-FVCA 3	MNAA-MP 1	MNAA-MP 2	MNAA-MP 3	MNAA-MP 4
Na2O	1.09	1.24	1.18	1.25	1.22	1.16	0.76	1.04	0.97	0.99
K2O	1.42	1.83	1.63	1.75	1.65	1.72	1.77	2.66	2.16	1.60
Fe2O3T	3.56	3.68	3.75	4.11	3.75	4.23	3.68	4.98	4.12	3.82
Sc	9.26	9.49	9.84	10.3	9.01	10.8	9.34	12.7	10.6	9.75
Cr	88.6	88.5	87.1	101	79.6	121	89.1	143	99.4	120
Co	13.8	16.0	14.6	53.9	416	40.4	34.4	20.5	16.1	26.7
Zn	90.6	113	84.1	154	131	1050	105	142	124	145
Ga	11.4	15.5	16.3	14.4	15.1	15.0	12.3	13.5	15.6	12.7
As	12.1	13.1	4.41	14.6	56.9	11.1	5.23	5.08	14.3	7.90
Br	3.58	4.06	2.85	5.00	3.71	6.48	4.31	6.12	2.34	8.93
Rb	68.3	74.8	72.7	91.6	70.2	76.5	69.2	98.9	81.4	76.9
Zr	136	98.5	116	133	90.7	125	142	136	120	73.0
Sb	15.2	613	62.5	80.7	124	3.10	162	105	665	2.94
Cs	4.25	4.58	4.43	4.82	4.65	5.21	4.61	6.36	5.50	5.53

Table 3 continued

Ref.	MNAA-MCAP 2	MNAA-MCAP 3	MNAA-MCAP 4	MNAA-FVCA 1	MNAA-FVCA 2	MNAA-FVCA 3	MNAA-MP 1	MNAA-MP 2	MNAA-MP 3	MNAA-MP 4
Ba	289	287	294	342	323	413	697	586	456	341
La	24.1	25.7	25.8	26.4	25.1	28.2	24.8	31.6	28.3	24.7
Ce	44.9	43.5	45.3	52.4	37.0	49.6	41.7	56.9	47.1	48.2
Nd	24.5	26.6	22.4	24.4	18.2	26.2	19.7	29.6	41.0	29.8
Sm	4.05	4.18	4.24	4.33	4.29	4.84	3.96	5.25	4.50	4.22
Eu	0.99	0.96	0.91	1.04	0.88	1.01	3.62	1.57	1.02	0.94
Tb	0.61	0.56	0.61	0.51	0.51	0.62	0.49	0.64	0.70	0.45
Yb	1.78	1.81	1.97	1.86	1.76	2.14	1.76	2.38	2.01	1.95
Lu	0.27	0.26	0.30	0.29	0.23	0.32	0.28	0.30	0.33	0.31
Hf	3.01	2.80	2.99	3.10	2.71	3.25	2.57	3.6	3.21	2.95
Ta	0.79	0.91	0.83	0.83	0.71	0.82	0.74	1.00	0.89	0.77
W	1.58	2.24	1.67	15.8	9.36	4.63	3.12	2.72	2.56	18.9
Th	7.27	7.10	7.20	7.43	6.65	7.72	6.62	9.18	7.51	7.28
U	1.17	1.94	1.25	1.32	1.74	1.85	1.23	2.07	1.82	1.62
Eu/Eu*	0.86	0.78	0.84	0.93	0.72	0.83	0.81	0.85	0.71	0.87
Ce/Ce*	0.74	0.71	0.66	0.77	0.65	0.65	2.88	0.94	0.68	0.72

Major elements (Na_2O, K_2O, Fe_2O_3T) in % and trace elements in mg Kg^{-1}

Cerium anomalies are calculated as Ce/Ce* = 3CeN/(2LaN + NdN) and Eu anomalies are calculated as Eu/Eu* = 3EuN/(2SmN + TbN). (N = normalised data to the average of chondrites of Evensen et al. [60])

Ce anomaly (Tables 3, 4), to carbonate rich clays of marine origin. The results obtained from the chemical composition are in agreement with the results of the mineralogical composition.

The clay bodies studied are marl, as it was expected to be characteristic for Italian terracotta objects of the studied period, and from the della Robbia workshop. The craftsman knew very well, that high limestone content of the clay results in a ceramic piece with excellent porosity, strength and weather resistant, that can be fired over a wide range of temperatures and resistant to cracking after lead glaze coating [61]. Visually, the colors of the clay bodies studied are generally the light yellowish-buff indicative of marly clays with only a few objects ranging toward red light pink clay (Table 1). The Florentine river bed clay sources are described by Piccolpasso in his sixteenth century treatise and he notes that the chalky clay used for majolica is distinct from the dense, red clay for cooking wares. There are also previous works [62] that show consistency of the clay bodies used in glazed works by the della Robbia and their contemporaries, in terms of composition, morphology and porosity, with a calcium oxide ranging from 15 to 24 wt%. It is also reported that together with the resource to marly clays, redder clay with more iron and no calcium have been probably used in production painted terracottas, and sometimes it was also used by other contemporary Florentine studios [18]. There are evidences of a remarkable stability in the recipe from Luca the founder, to Girolamo 100 years later, in the analyses of 80 artefacts attributed to the della Robbia bottega [63]. They work with pure, clear and docile pastes made of typical homogeneous marl, remaining light in color after firing. The paste contains some quartz grains as temper and some small clay lenses, which are irregularly widespread within. Mean elemental chemical compositions confirm that the workshop always got its supply from the same place, probably from the quarry acquired by Luca della Robbia in the Val d'Arno and perhaps from Impruneta for the red clays [18]. Impruneta is a town famous for the unique composition of its clay locally called "terra turchina" (blue earth). When it is fired, due to its high limestone content, assumes its distinctive *terra rosa* color.

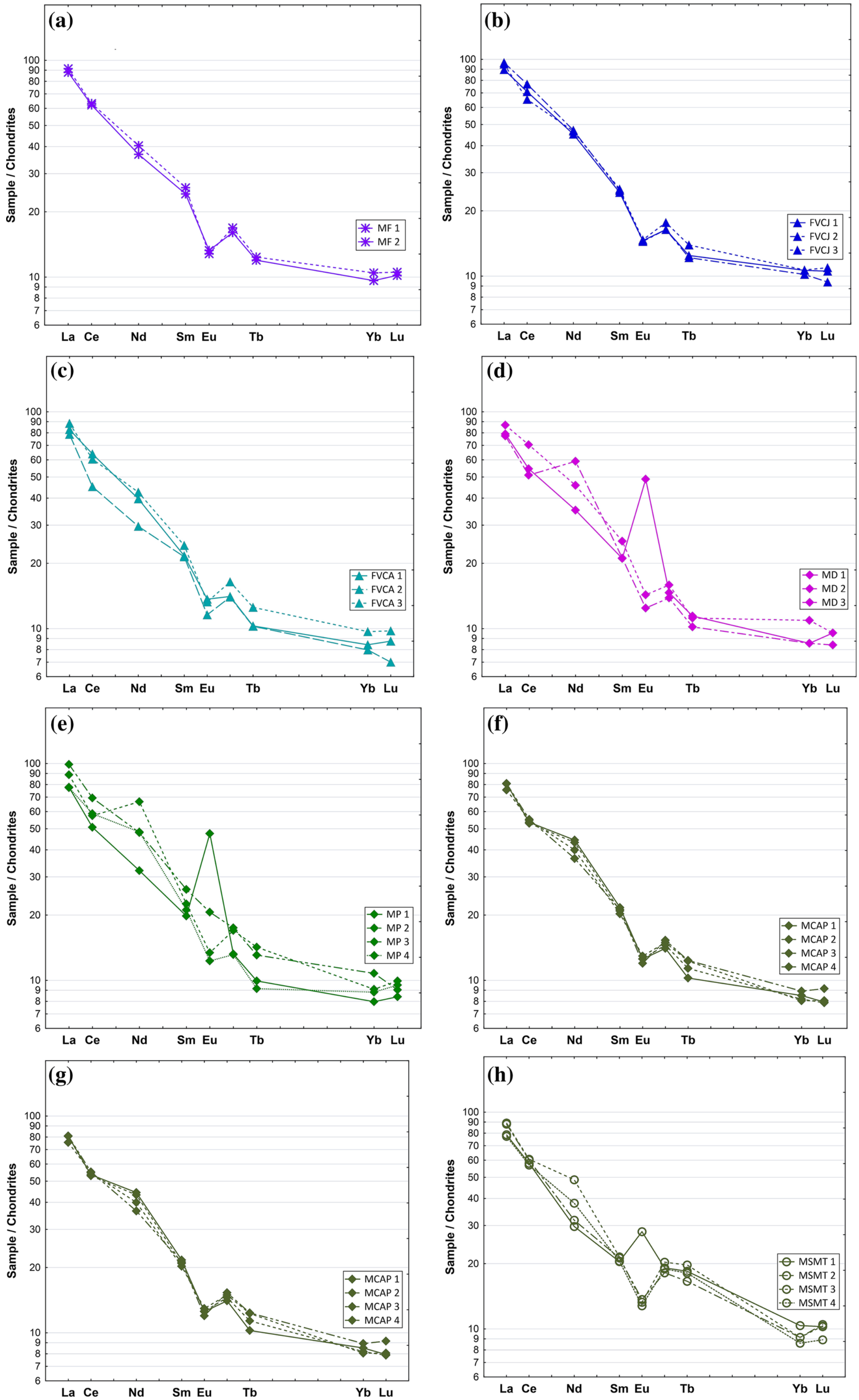
The clay raw material of the studied medallions also points to this location. Especially, when considering the REE behavior, we found that the studied samples show similar rare-earth pattern as the Val d'Arno clays. Previous work concerning the geo-sources study for ceramic production in southern Tuscany, particularly the clays from the Neogene–Quaternary Albegna Basin [64], enhances the distinction of Ca-poor clays (from the Miocene, Pleistocene and Holocene) from Ca-rich clays (Pliocene materials with high CaO contents due to the abundant content of microfossils). The Ca-poor clays are suitable for the production of red stoneware's and dense and frost resistant masonry materials. The Ca-rich clays are used for the production not only of red earthenware but also of hard and porous masonry materials. The Arno Basin mainly consists of Oligocene–Miocene arenaceous-calcareous-marly flysch,

Table 4 Concentration of elements obtained by INAA for medallion sculptures from FCG and MNAz museums attributed to the bottega of della Robbia; Europium and Cerium anomalies

Ref.	FCG-MF1	FCG-MF2	MNAz-MSJ 1	MNAz-MSJ 2	MNAz-MSJ 3	MNAZ-MSM 1	MNAZ-MSM 2	MNAZ-MSM 3	MNAz-MSL 1	MNAz-MSL 2	MNAz-MSL 3	MNAz-MSMT 1	MNAz-MSMT 2	MNAz-MSMT 3	MNAz-MSMT 4
Na_2O	1.04	1.04	1.05	0.85	0.96	0.91	0.94	1.11	0.97	1.14	0.93	0.93	0.98	0.94	0.80
K_2O	1.86	1.87	1.74	1.62	1.65	1.81	1.80	3.09	1.57	2.05	1.69	1.60	1.83	1.79	1.52
Fe_2O_3T	4.44	4.39	4.08	4.10	4.01	4.01	3.73	2.54	3.73	4.26	3.85	4.27	4.17	4.17	3.78
Sc	11.2	10.8	10.7	10.9	10.7	10.6	9.75	6.44	9.68	10.5	9.97	10.5	10.7	10.9	10.0
Cr	117	101	95.8	98.1	86.6	119	97.2	50.0	94.7	107	93.4	99.9	92.4	110	103
Co	18.3	18.1	38.0	19.6	21.5	17.6	17.7	51.2	26.5	19.6	38.1	128	17.2	23.2	39.5
Zn	107	114	86.8	8.85	87.6	95.6	99.1	93.7	121	145	87.8	106	91.9	90.5	90.7
Ga	14.1	14.7	18.0	81.4	14.5	24.6	24.6	70.1	13.8	12.5	11.0	12.0	19.8	15.5	8.65
As	5.31	7.87	1.54	2.74	1.92	4.97	15.0	724	48	9.04	17.3	1.73	1.52	7.02	5.41
Br	1.28	1.15	1.76	2.18	3.25	3.17	4.79	4.10	4.12	1.95	2.89	4.40	3.22	3.10	2.34
Rb	92.0	92.0	83.1	83.0	84.7	83.8	75.5	44.1	73.3	81.9	78.2	82.1	93.5	82.7	76.2
Zr	133	134	142	330	173	172	196	119	127	143	149	152	124	92.6	138
Sb	104	52.9	48.2	38.0	0.94	127	299	3140	751	221	391	144	54.5	113	108
Cs	5.74	5.55	5.17	5.27	5.43	5.20	4.95	3.91	4.96	5.06	4.89	5.44	5.43	5.38	5.01
Ba	305	339	337	335	308	1273	424	135	775	810	265	716	533	603	662
La	29.2	28.1	28.3	28.0	29.1	28.6	26.4	18.7	24.3	28.5	27.8	25.1	28.1	28.4	24.7
Ce	51.8	51.0	50.9	50.9	51.6	49.2	44.1	24.9	43.8	49.0	44.4	47.6	49.3	49.7	46.8
Nd	24.8	22.7	26.0	21.1	27.3	31.3	17.3	14.1	39.7	22.3	28.0	18.3	19.5	30.0	23.4
Sm	5.17	4.84	4.13	4.47	4.15	4.31	4.29	2.54	3.52	3.77	4.24	4.09	4.25	4.30	4.11
Eu	0.98	1.01	1.27	11.9	1.49	2.57	3.66	3.73	2.14	1.00	1.33	2.14	1.04	1.01	0.97
Tb	0.61	0.59	0.90	7.33	0.89	1.43	3.05	2.29	2.54	0.23	1.71	1.64	0.82	0.97	0.89
Yb	2.31	2.13	2.10	8.40	2.15	2.36	3.02	2.23	2.12	2.00	2.23	2.29	2.02	2.02	1.90
Lu	0.35	0.34	0.33	0.36	0.33	0.33	0.27	0.22	0.25	0.33	0.32	0.34	0.35	0.34	0.29
Hf	3.33	3.26	3.62	3.70	3.35	3.44	3.31	2.18	3.15	3.49	3.17	3.40	3.17	3.20	3.04
Ta	0.95	0.98	0.93	1.12	0.88	0.89	0.90	0.61	1.01	0.97	0.88	0.97	0.98	1.03	0.89
W	2.13	4.09	1.68	1.38	1.99	2.12	2.63	7.97	2.15	2.23	1.99	3.08	1.92	2.23	1.61
Th	8.18	8.00	8.07	8.03	8.06	7.67	7.27	4.23	7.09	7.67	7.02	7.54	8.16	7.86	7.32
U	2.05	2.45	1.33	1.76	0.41	0.60	0.59	1.91	1.34	0.59	1.80	0.67	1.30	1.39	0.53
Ce/Ce*	0.85	0.88	0.85	0.89	0.83	0.78	0.83	0.65	0.74	0.83	0.74	0.93	0.87	0.80	0.89
Eu/Eu*	0.60	0.66	0.84	2.43	0.99	1.41	1.38	2.05	0.97	0.92	0.68	1.14	0.69	0.63	0.65

Major elements (Na_2O, K_2O, Fe_2O_3T) in % and trace elements in mg Kg^{-1}

Cerium anomalies are calculated as Ce/Ce* = 3CeN/(2LaN + NdN) and Eu anomalies are calculated as Eu/Eu* = 3EuN/(2SmN + TbN). (N = normalised data to the average of chondrites of Evensen et al. [60])


(a)
Sample / Chondrites
100
90
80
70
60
50
40
30
20
10
9
8
7
6
La Ce Nd Sm Eu Tb Yb Lu
MF 1
MF 2
(b)
FVCJ 1
FVCJ 2
FVCJ 3
(c)
FVCA 1
FVCA 2
FVCA 3
(d)
MD 1
MD 2
MD 3
(e)
MP 1
MP 2
MP 3
MP 4
(f)
MCAP 1
MCAP 2
MCAP 3
MCAP 4
(g)
MCAP 1
MCAP 2
MCAP 3
MCAP 4
(h)
MSMT 1
MSMT 2
MSMT 3
MSMT 4

◀**Fig. 1** REE patterns measured by INAA obtained for the various samples taken at medallions: **a** FCG-MF; **b** MNAA-FVCJ; **c** MNAA-FVCA; **d** MNAA-MD; **e** MNAA-MP; **f** MNAA-MCAP; **g** MNAA-MVCJ; **h** MNAz-MSMT. The average of chondrites of Evensen et al. [60] has been used

structurally complex clay and Neogene marine and fluvio-lacustrine deposits [65–67]. The Ce anomalies in marine carbonate rocks have been considered suitable indicator to unravel paleoceanographic conditions [68–72]. The depletion of Ce relative to neighboring REE is one of the characteristic features of seawater and marine carbonates deposited in the deep sea regions, and is due to the adsorption of Ce onto Fe–Mn particle surfaces by oxidation of Ce(III) to Ce(IV). As mentioned previously all samples have negative cerium anomalies, in accordance with the type of clays found in vale of Arno.

The Portuguese della Robbia medallions in comparison to other della Robbia sculptures

To better validate the assumption of the attribution of the analyzed sculptures to the della Robbia workshop, besides this understanding of the geological and geochemical context of the known used clay source by the family along generations, it is crucial to compare obtained results with other published results. Trying to establish a correlation between the chemical compositions obtained for the studied della Robbia medallions and the existing data in the literature is always a challenge. Firstly, because comparing data from different researchers/and institutions/and methods has risks, since the differences in equipment, measuring conditions, standard samples, etc., strongly influence the measurement results [25, 73]. Secondly, because most of the available data in the literature comprises only major and minor elements and INAA enables to obtain with precision and accuracy especially trace elements. To overcome these issues, and to better establish a comparison between chemical results obtained from diverse methods, and in different laboratories, the use of element ratios is recommended, as well as normalized values, and in this particularly case, we will also compare existing data with major and minor elements obtained by PGAA.

Four sets of published chemical data of ceramic body from della Robbia sculptures will be used in this comparison study (Table 5): (i) data obtained by Bouquillon [18] on 60 samples analysed from the thousands of archaeological sherds found (moulds, ready to use pieces, test material, even a kiln) in the Tuileries in Paris; (ii) data obtained for other contemporary Florentine ceramic bodies of glazed sculptures calcium-rich; (iii) data for non-glazed sculptures with non-carbonated paste [19]; and (iv) data of Robbiana sculptures of the so-called Campana collection, comprising a group of glazed terracotta angels [14]. Regarding the Campana collection, the ICP analyses of the ceramic bodies, and in particular the rare earth contents, suggest a common origin for all the clays. Like to the analysed artefacts by Bouquillon mentioned above, the angels from the Campana collection have fine marly pastes, uniform in texture for all the sculptures, although different

Table 5 Chemical elementary composition of sculptures attributed to the bottega of della Robbia (weight percentages)* and a roundel from the Portuguese collection

Ceramic body	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3
MNAA-FVCJ	**0.90**	**3.90**	**8.90**	**49.5**	**1.99**	**24.2**	**0.65**	**0.14**	**4.97**
Camp 61	1.10	2.49	12.61	52.93	1.92	19.08	0.54	0.11	4.59
Camp 62	0.98	2.53	12.37	49.90	1.89	20.02	0.54	0.10	4.82
Camp 63	1.05	2.50	12.35	50.51	1.89	19.66	0.54	0.11	4.76
Camp 64	1.06	2.63	13.01	53.21	1.98	20.29	0.56	0.10	4.72
Camp 66a	1.03	2.62	13.22	52.71	1.99	21.64	0.59	0.11	4.83
Camp 66b	0.84	2.65	13.00	50.63	2.01	24.17	0.58	0.11	4.76
Camp 67b	0.88	2.61	12.74	49.72	2.03	22.4	0.56	0.11	4.53
Camp 69a	0.89	2.64	13.07	50.62	1.98	23.48	0.59	0.11	4.95
Camp 70	0.85	2.67	13.11	50.55	1.93	23.57	0.57	0.11	5.20
Camp 70V	0.92	2.70	13.08	50.18	1.93	24.12	0.58	0.12	4.80
Mean of 60 DR glazed sculptures	1.07	2.71	13.23	52.23	2.06	22.93	0.58	0.11	4.84
Other florentine workshops glazed sculptures	1.13	3.50	16.01	55.63	3.36	13.03	0.71	0.08	6.34
Other florentine workshops non-glazed sculptures	1.46	3.34	19.29	61.35	3.09	2.77	0.90	0.12	7.51

* "Camp" data obtained in Zucchiati et al. [14]; mean data of 60 della Robbia glazed sculptures obtained in Bouquillon [17]; other Florentine workshops data obtained in Bouquillon et al. [17]

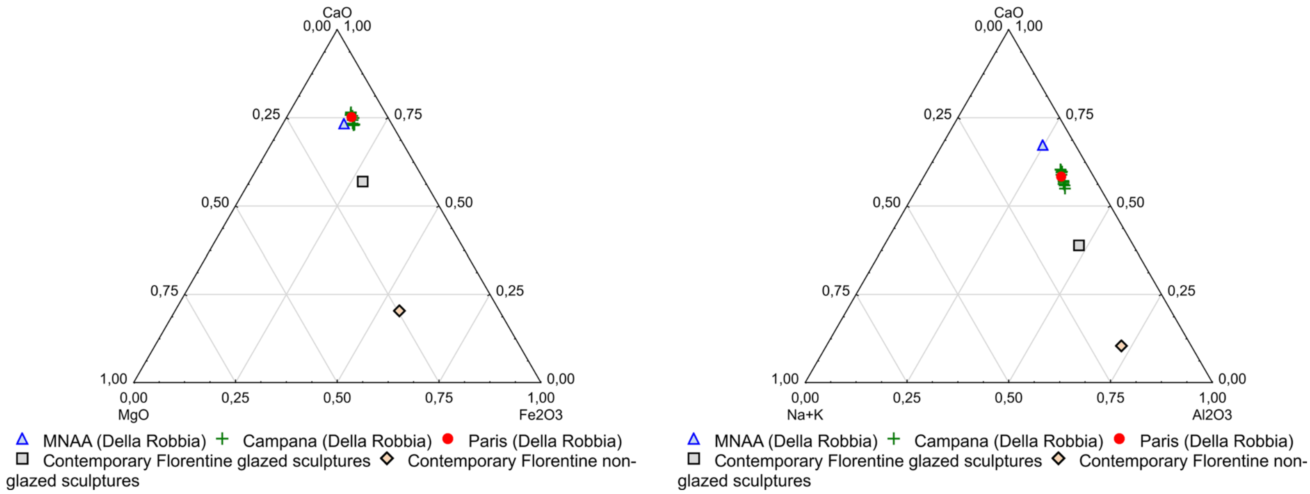


Fig. 2 Plot of ceramic body samples from MNAA and other della Robbia and Florentine sculptures (*glazed* and *non-glazed*) composition in the ternary diagram against Na + K and Al_2O_3 and CaO; and against CaO and MgO and Fe_2O_3

shades of colours were observed (yellowish, pink, grey and reddish), most probably due to a slight change in the firing temperature and atmosphere [14]. The main composition of the artefacts examined is very similar to that obtained from the work Pala di Montalcino [74], from a group of tondi [62] attributed to Andrea della Robbia and from a frieze belonging to the Cora collection at the Faenza museum [7], which is also attributed to Luca della Robbia.

In those published cases, chemical analyses were done by ICP-AES and ICP-MS (Optical Emission Spectrometry with Inductively Coupled Plasma-MS: Mass Spectrometry, respectively) and the results of 10 elements have been available (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti and P). Thus, we have a different set of chemical elements obtained by INAA for our samples. So far, we have obtained comparable PGAA data for only one piece of a MNAA medallion collection, comprising the analysis for 9 of the 10 published chemical elements by the above mentioned authors.

Comparing the studied medallion MNAA-FVCJ in this work with published data of sculptures from della Robbia workshop and other contemporary artists [14, 18, 19, 62, 75, 76], a compositional similarity was observed with della Robbia sculptures (Table 5), not only in a mineralogical point of view (similar to all the other studied medallions in the present work), but also in a chemical point of view. No correspondence was found with other contemporary Florentine workshops of glazed and non-glazed sculptures (Fig. 2).

Conclusions

The glazed terracotta sculptures attributed to the della Robbia workshop of Florence belonging to various Portuguese museums were studied by using INAA, PGAA and XRD. Both the chemical and mineralogical results point to a common raw material—carbonate rich clay of marine origin. The body composition of these della Robbia medallions is similar to published data for della Robbia sculptures.

Concerning technological aspects of the production, a certain compositional heterogeneity was found, which can be explained by the production technique itself (assembling and joining a number of separate parts), and the inherent raw material heterogeneity. The presence of calcium silicate phases (gehlenite, diopside) and of "ceramic pyroxene" fassaite-diopside type slightly iron, magnesium and calcium rich, indicates that the firing temperature reached at least 850 °C, and would not have exceeded 950 °C, like mentioned in other works for similar sculptures; calcite was also detected most probably due to its grain size, as large calcite particles might have survived firing.

Thus the results point to technological procedures associated with della Robia wokshop. This fact together with artistic and historical examination of these high-quality sculptures leads to the attribution of all of them to the della Robbia workshop.

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