

Original article

Non-destructive characterization of Della Robbia sculptures at the Bargello museum in Florence by the combined use of PIXE and XRF portable systems

G. Pappalardo ^{a,b}, E. Costa ^b, C. Marchetta ^b, L. Pappalardo ^{b,c,*}, F.P. Romano ^{b,c},
A. Zucchiatti ^{d,e}, P. Prati ^{d,e}, P.A. Mandò ^{f,g}, A. Migliori ^{f,g}, L. Palombo ^{f,g}, M.G. Vaccari ^h

^a Dipartimento di Fisica, Università di Catania, Viale Andrea Doria 6, 95123 Catania, Italy

^b Laboratori Nazionali del Sud, INFN, Via S. Sofia 44, 95123 Catania, Italy

^c C.N.R., Sezione di Catania dell'Istituto per i Beni Archeologici e Monumentali, Via. A. di Sanguiliano 262, 95100 Catania, Italy

^d INFN, Sezione di Genova, Via Dodecaneso 33, 16146 Genova, Italy

^e Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy

^f Dipartimento di Fisica, Università di Firenze, Largo E. Fermi 2, 50125 Florence, Italy

^g INFN, Sezione di Firenze, Largo E. Fermi 2, 50125 Florence, Italy

^h Museo Nazionale del Bargello, Via del Proconsolo 4, 50122 Florence, Italy

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Abstract

“In situ” non-destructive characterization of the blue pigments present in the ceramic glazes of Della Robbia sculptures have been carried out at the Bargello museum in Florence. PIXE and XRF portable systems have been used to determine the matrix composition and the trace-elements, respectively. The results indicate that the arsenic is present as trace-element only after 1520.

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Research aims

The presence of arsenic in the blue pigments could be used as an indicator of the provenance of raw materials. Recently, the arsenic presence has been found in some blue pigments of the Della Robbia sculptures.

The richest and best known collection of these sculptures is conserved in the Museo Nazionale del Bargello in Florence. By the use of new non-destructive and portable instruments it has been possible to establish that arsenic is present in the Della Robbia sculptures only starting from the 1520.

1. Introduction

Glazed terracotta sculptures have undoubtedly been one of the artistic innovations of the Italian Renaissance brought by Luca Della Robbia in Florence in the first half of the XV

century and continued afterwards by his family and also by the Buglioni's. The distinctive character of glazed terracottas is the smooth, bright, often polychrome cover that has largely contributed to the success of such artefacts (the *Robbiane*) at the Della Robbia time and constitutes today one of the keys for a better understanding of the artists skills and techniques.

Ceramic glazes are complex mixtures of silica, fluxes and metallic oxides, baked at high temperature, whose composition can be conveniently determined for major, minor and trace chemical elements with non-destructive “elemental” analytical techniques [1].

The glaze elemental composition is expected to depend on raw materials and workshop recipes; the precise determination of minor and trace-elements can be particularly important to differentiate [2] or to aggregate [3] groups of objects that are stylistically related, to possibly establish the provenance of the artefact and the origin of pigments as well as to monitor the time evolution of materials and techniques. Since a few years, the polychrome glazes of the *Robbiane* have been extensively investigated on potsherds, whole sculptures

* Corresponding author.

E-mail address: lighea@lns.infn.it (L. Pappalardo).

Table 1
Minimum Detection Limits in PIXE-alpha analysis

	Na	Mg	Al	Si	S	K	Ca	Fe
MDL (%)	0.2	0.09	0.15	0.14	0.08	0.13	0.33	0.93

and polished sections [1]. Particle-induced X-ray emission (PIXE), an ion beam analysis technique particularly suited in the Cultural Heritage field [4,5], has been successfully applied in the above studies performed at the INFN Florence accelerator [6,7] and at the Centre de Recherche et Restauration des Musées de France [1]. In the blue colour the study has shown the most evident changes of raw materials, marked primarily by highly different amounts of arsenic in the pigment, definitely related to time and therefore potentially suitable for indirect dating [8]. In this context analyses of artefacts that have sure author attribution and are dated, on the basis of documents, with high degree of certitude, are of the highest importance to establish a more precise relation of the glazes composition with time.

The richest and best known collection of Della Robbia sculptures is conserved in the Museo Nazionale del Bargello in Florence. It has been extensively studied by art history specialists [9] and offers a unique opportunity of combining archaeometric and stylistic time-related information subject, quite evidently, to the capability of applying non-destructive in situ techniques for the analysis of glazes.

In the present work, we illustrate a new approach, making use of PIXE and XRF portable techniques to determine in the *Robbiana* of the Bargello both the major constituents of the blue glaze matrix (Si, Al, Pb, Sn) and some characteristic elements brought in by the blue pigment (Co, Ni, Fe, As).

2. Experimental methods

2.1. Portable PIXE analysis

PIXE is a well established analytical technique that, due to the behaviour of the ionisation cross-section, strongly de-

creasing with the increasing of Z atomic number, is particularly suitable for light elements analysis [10,11]. A portable system, unique in the world, has been developed at the INFN Laboratori Nazionali del Sud of Catania (Italy), in collaboration with the DIMRI Laboratory of Saclay (France), and the Italian CNR-Progetto Finalizzato BBCC [12,13].

The system, called PIXE-alpha, is made of:

- (i) A 1 mCi ^{210}Po alpha-source assembled in an annular geometry;
- (ii) The beam spot has a 7 mm diameter;
- (iii) A Si-drift detector, 10 mm² active surface, Peltier-cooled, with a resolution of 145 eV at 5.9 keV produced by KETEK and assembled by EIS;
- (iv) A standard acquisition system.

Helium gas is continuously flown between the alpha source and the sample surface so that the PIXE-alpha system can detect elements as light as Na. The good energy resolution enables to distinguish between the K line of S at 2.308 keV from the M line of Pb at 2.345 keV. The measurement time is typically 15–30 min, with the Minimum Detection Limits (MDL) shown in Table 1. As it can be seen the system is able to analyse major-elements of low Z as those constituting the silicate matrix, but cannot analyse trace-elements because of the low intensity of the alpha-source that must be kept below mandatory limits to obey safety regulations. A typical energy spectrum, taken on a petrological standard SCO-1, particularly rich in light elements [14], is shown in Fig. 1. The peaks corresponding to Na, Mg, Al, Si, S + Pb, K, Ca and Fe elements are well recognized.

2.2. Portable XRF analysis

XRF (X-Ray Fluorescence), contrary to PIXE, is suitable for analysis of heavier elements due to the increase of the

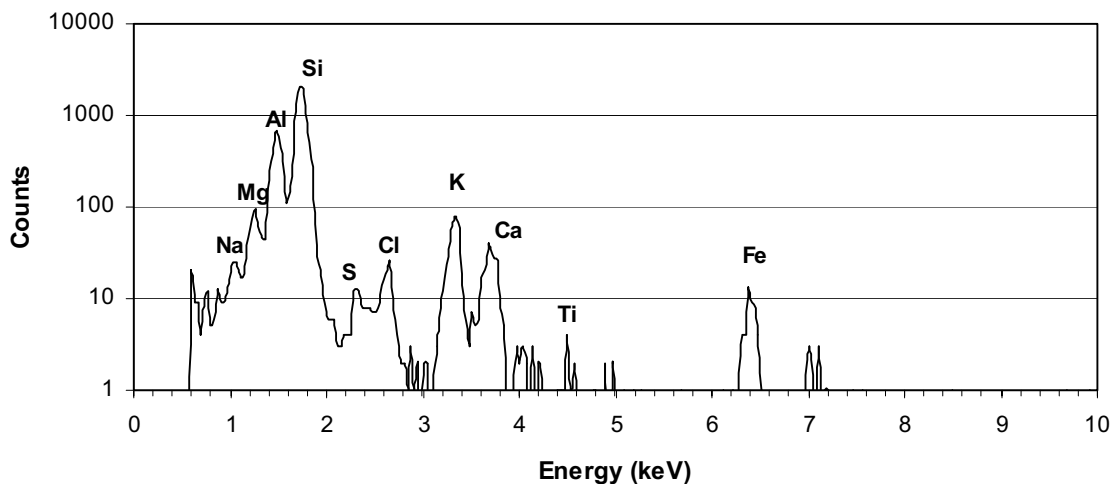


Fig. 1. PIXE spectrum on the Sco-1 standard.

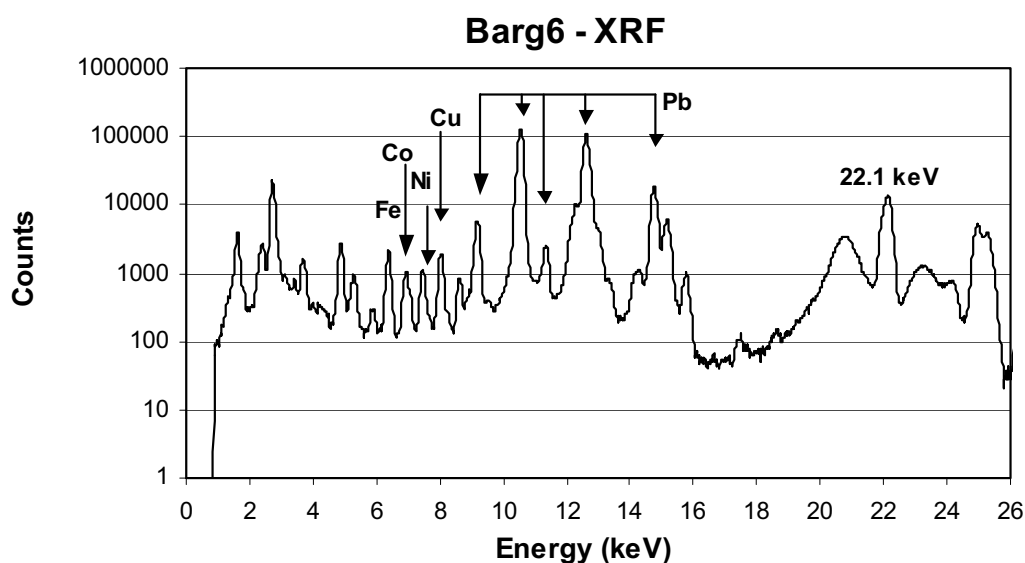


Fig. 2. XRF spectrum of a blue glaze. Medium and high Z elements typical of a glaze are clearly present. Arsenic is not detected in this 1475 Andrea Della Robbia sculpture.

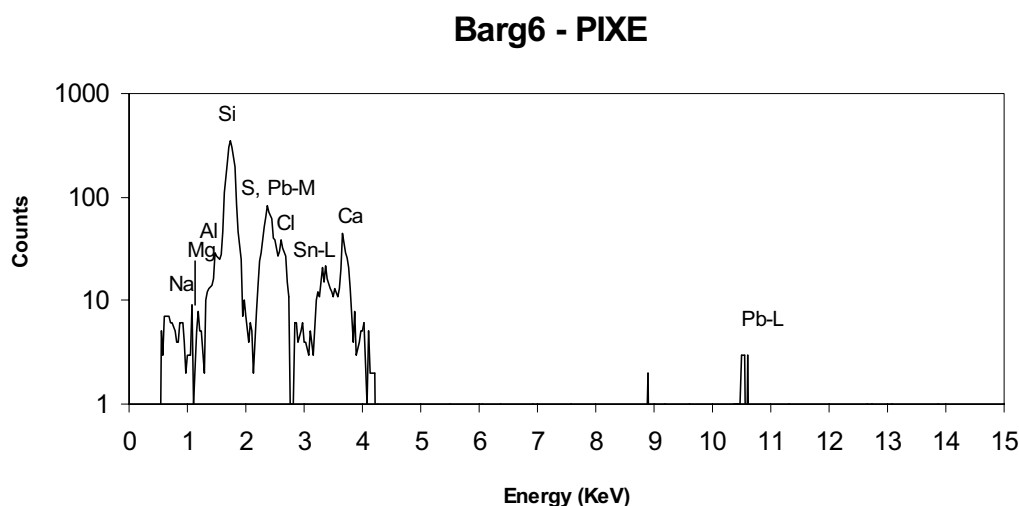


Fig. 3. PIXE spectrum of a blue glaze. Si, Pb-M, Sn and Ca are clearly present.

ionisation cross-section with the increase of the Z atomic number [10,11]. X-rays in our portable system are emitted by three ^{109}Cd radioactive sources assembled in a annular geometry [15,16]. The X-ray energy is 22.1 keV and it is particularly suitable to excite fluorescence in medium and heavy elements like As, Pb (L lines), Rb, Sr, Zr, Y. The detector is a Ge (IGLET-ORTEC), 80 mm² surface. MDL is some tens of ppm. Figs. 2 and 3 show typical PIXE and XRF spectra on blue glazes.

2.3. Calibration and test of the systems

The PIXE and XRF systems were calibrated by using reference standards: the SCO-1 petrological standard for PIXE calibration (see Table 2) and pure elements for XRF.

Quantitative analysis were performed using the Gupix code [17,18] in the matrix option for PIXE and the AXIL QXAS code [19] in the “known low Z-matrix” option for

Table 2

Comparison between measured and certified values (SCO-1 petrological standard) in the PIXE-alpha analysis

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Fe(III) tot
PIXE data	0.8 ± 0.2	2.8 ± 0.4	16.2 ± 2.2	64.7 ± 6	0.3 ± 0.2	3.5 ± 0.4	2.8 ± 0.5	0.7 ± 0.1	5.5 ± 1.6
Ref.	0.9	2.72	13.67	62.78	0.21	2.77	2.62	0.63	5.14

XRF. We have used the PIXE data as matrix input to XRF calculation.

To test the systems a series of glass standard has been measured and the obtained data are shown in Table 3. As can be seen the agreement of measured and certified concentra-

Table 3

Comparison between measured and certified values (various glass standards) in PIXE-alpha and XRF analysis

	PIXE	STD621
SiO ₂	70 ± 2	71.13 ± 0.03
Na ₂ O	11 ± 2	12.74 ± 0.05
CaO	11 ± 1	10.71 ± 0.05
Al ₂ O ₃	3.7 ± 0.7	2.76 ± 0.04
K ₂ O	2.1 ± 0.3	2.01 ± 0.03
MgO	–	0.27 ± 0.03
SO ₃	–	0.13 ± 0.03
XRF		
BaO	<1500	1200
Fe ₂ O ₃	400 ± 120	400
As ₂ O ₃	400 ± 120	300
TiO ₂	–	140
ZrO	<100	70
PIXE		
SiO ₂	49.7 ± 4	42.38 ± 0.18
Na ₂ O	4.5 ± 1.4	4.69 ± 0.07
CaO	4.97 ± 0.7	4.53 ± 0.1
Al ₂ O ₃	8.6 ± 0.9	7.52 ± 0.24
K ₂ O	4.9 ± 0.6	4.14 ± 0.1
MgO	5.1 ± 0.8	4.69
BaO	6.6 ± 0.8	4.67 ± 0.16
PbO	4.3 ± 1.3	4.4 ± 0.17
CdO	3.8 ± 1.0	4.38 ± 0.08
ZnO	–	4.48 ± 0.12
SrO	5.6 ± 1.4	4.55 ± 0.09
PIXE		
SiO ₂	68.22 ± 1	72
Na ₂ O	14.2 ± 1.4	14
CaO	11.2 ± 0.67	12
Al ₂ O ₃	2.9 ± 0.43	2
XRF		
K	<1000	461
Mn	<1000	485
Fe	548 ± 164	458
Co	372 ± 111	390
Ni	596 ± 178	458
Cu	355 ± 106	444
Zn	350 ± 105	433
Rb	377 ± 113	425
Sr	440 ± 132	515
Nb	423 ± 129	–
Mo	438 ± 131	–
Pb	<1000	426
Th	<1000	457
U	781 ± 234	461
PIXE		
SiO ₂	80.0 ± 1.2	72
Na ₂ O	12.7 ± 1.3	14
CaO	12.6 ± 0.8	12
Al ₂ O ₃	3.4 ± 0.5	2

tions is generally good both for elements detected by the PIXE-alpha system (low-Z) and by the XRF system (medium, high Z). It must be observed that the glass standards are intrinsically homogeneous. This is not the case for ceramic glazes [2] at a microscopic level; we can however assume that in the present analysis that involves large glaze areas (1 cm²), the composition is well averaged over the glaze-microstructures.

3. Results of measurements at the Bargello museum in Florence

The blue pigment characterization was the main objective of the present work. The relative flexibility of the equipment, and the remarkable cooperation and assistance of the museum staff, to whom we are deeply indebted, has allowed us to perform a measuring campaign, lasted 1 week and centered on 12 sculptures, without interfering with the public access to the museum. Fig. 4 shows a detail of the system during PIXE-alpha analysis of the blue background of the *Madonna del Roseto*, a masterpiece of Luca Della Robbia.



Fig. 4. The PIXE-alpha set-up during the analysis of the blue background of the *Madonna del Roseto* (Inv. n. 31), a 1460–70 Luca Della Robbia sculpture conserved in the Museo Nazionale del Bargello in Florence. The publication of the picture has been authorized by the Italian Ministero dei Beni e le Attività Culturali. Duplications or reproductions of the picture are forbidden.



Fig. 5. A view of the equipment during the XRF analysis of the blue background of the *Madonna che adora il Bambino* (Inv. n. 21), a Luca Della Robbia sculpture conserved in the Museo Nazionale del Bargello in Florence. The publication of the picture has been authorized by the Italian Ministero dei Beni e le Attività Culturali. Duplications or reproductions of the picture are forbidden.

Fig. 5 shows the entire apparatus during XRF measurement on a *Madonna che adora il Bambino* still from Luca Della Robbia. A few important details can be observed. With the help of a manual micro-gauge the head containing the source is brought in contact with the blue glaze in a zone of the

artefact selected over a flat area of the sculpture in order to assure operation of both the PIXE-alpha and the XRF systems in the best geometrical conditions. The position of the analysis could be marked sufficiently well to allow the alignment of detectors, in the sequence of measurements, with a precision of the order of 1 mm over a 1 cm² irradiation area. PIXE and XRF spectra were collected by standard ADC conversion and displayed on a portable PC for immediate control. Quantitative analysis was performed as with the standards. Tables 4 and 5 shows the final results for each analysed point together with the name of the sculpture, its author and the date of manufacture, which is in most cases drawn by art historian on the bases of speculations and deductions from written document. In only one case, the *Natività* of Giovanni Della Robbia (Barg10), the sculpture base bears to the right the inscription ANO DNI MDXXI. The composition of the blue glazes are similar to other measured on Robbiana sculptures. All the blue is based on cobalt pigments as expected but the behaviour of arsenic, which is associated to cobalt in most cobalt-minerals, is rather peculiar. Arsenic is above detection limits in all sculptures dated after 1520, certainly at or after 1521 since it appears in the *Natività* of Giovanni Della Robbia (Barg10). It is on the contrary absent (below MDL) in the entire Luca production and in the early production of Andrea Della Robbia as well as in part of the Benedetto and Santi Buglioni work. The transition takes place, according to our data, between 1514 (*Noli me tangere* of Benedetto and Santi Buglioni) and 1520 (*Pietà* of Giovanni Della Robbia). The sudden change in arsenic content can provide a before/after dating criterium, which can be of great help in the attribution of Robbiana sculptures of the late period, running from about 1520 up to the death of Santi Buglioni in 1586.

4. Conclusions

The complementary use of portable PIXE and XRF systems has enabled to characterize in situ the ceramic glazes of

Table 4

Pixe analysis. Blue glazes composition. Errors are due to statistics and to the fitting procedure. For error >40% data must be considered qualitative

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	Iron oxides	CoO	SnO ₂	PbO
Barg1			3.5 ± 1.05	52.6 ± 1.0	1.1 ± 0.9		4.9 ± 0.7	4.6 ± 0.9			8.6 ± 2.6	16 ± 1.6
Barg2	2.7 ± 1.9	1.2 ± 0.7	2.4 ± 0.8	40.0 ± 0.8			1.5 ± 0.6	1.3 ± 0.6		2.0 ± 1.6	5.4 ± 2.4	37 ± 2.2
Barg3				33.3 ± 1.7			4.7 ± 0.9	4.0 ± 1.4		5.1 ± 3.6	10 ± 4.0	33 ± 2.6
Barg4		2.1 ± 1.0	2.6 ± 1.3	29.0 ± 1.4	4.8 ± 0.9			2.0 ± 0.8		3.2 ± 2.2	12 ± 1.9	32 ± 2.3
Barg5	3.3 ± 1.6	2.3 ± 0.6	3.4 ± 0.5	41.2 ± 0.8	1.5 ± 0.45		2.8 ± 0.4	1.6 ± 0.5	1.3 ± 0.6		8.9 ± 1.6	29 ± 1.1
Barg6			2.7 ± 0.5	45.8 ± 0.9			3.6 ± 0.7	8.8 ± 1.0			8 ± 2.4	27 ± 1.6
Barg7				34.0 ± 1.4			5.2 ± 1.0	2.9 ± 1.4			16 ± 4.5	34 ± 2.4
Barg8		1.8 ± 1.0	3.0 ± 0.9	31.0 ± 1.2	2.2 ± 1.1		2.8 ± 1.0	3.7 ± 1.1	3.0 ± 1.8		14 ± 3.5	31 ± 1.8
Barg9	4.4 ± 1.3	1.8 ± 0.6	3.7 ± 0.5	35.0 ± 1.0	1.4 ± 0.5		2.2 ± 0.3	3.6 ± 0.5	1.0 ± 0.6		5.6 ± 1.7	36 ± 1.4
Barg10	3.7 ± 1.5	1.1 ± 0.7	1.3 ± 0.65	35.0 ± 1.0			2.0 ± 0.4	4.6 ± 0.7	1.6 ± 0.9		5.2 ± 2.1	36 ± 2.0
Barg11	2.7 ± 2.2		2.0 ± 1.0	30.0 ± 1.8	1.3 ± 0.9		6.0 ± 1.2	5.0 ± 1.0			9.5 ± 4.3	35 ± 2.4
Barg12			2.9 ± 0.7	40.0 ± 0.8		2.4 ± 1.4	2.9 ± 0.3	4.0 ± 0.8	2.6 ± 1.6	4.6 ± 2.3	7 ± 2.8	26 ± 2.0

Note: (1) Must probable iron oxides are Fe₂O₃ and FeO. Due to the experimental errors our calculations do not distinguish between the two oxides. (2) Barg 5 and Barg 11 measurements are two parts of the same sculpture.

Table 5

XRF analysis. Blue glazes composition. Errors are due to statistics and to the fitting procedure. For error > 40% data must be considered qualitative.

XRF	Iron oxides	CoO	NiO	CuO	ZnO	As ₂ O ₃	Name of sculpture	Author	Date
Barg1	1.2 ± 0.4	0.7 ± 0.2	0.6 ± 0.2	1.2 ± 0.4	<0.1	–	Madonna Della mela	Luca Della Robbia	1440–1445
Barg2	0.8 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	0.9 ± 0.3	–	–	Adorazione con cornice di Angeli (center)	Luca e Andrea Della Robbia + Giovanni	1460–1465
Barg3	1.2 ± 0.4	1.4 ± 0.4	1.2 ± 0.4	0.5 ± 0.2	<0.1	–	Madonna col bambino dell'umiltà	Andrea Della Robbia	1465
Barg4	1.8 ± 0.5	0.7 ± 0.2	0.4 ± 0.2	0.3 ± 0.1	<0.1	–	Madonna del Roseto	Luca Della Robbia	1460–1470
Barg5	1.8 ± 0.5	0.7 ± 0.2	0.3 ± 0.2	0.2 ± 0.1	<0.1	–	Madonna che adora il bambino	Luca Della Robbia	1470
Barg6	1.1 ± 0.4	0.3 ± 0.1	<0.1	0.4 ± 0.1	<0.1	–	Ritratto di Fanciullo (Piero di Lorenzo de Medici)	Andrea Della Robbia	1475
Barg7	1.7 ± 0.5	0.9 ± 0.3	0.6 ± 0.2	0.2 ± 0.1	<0.1	–	Annunciazione	Andrea Della Robbia	1505–1510
Barg8	1.3 ± 0.4	0.8 ± 0.2	0.5 ± 0.1	0.4 ± 0.1	<0.1	–	Pietà	Giovanni Della Robbia	1514–1515
Barg9	1.0 ± 0.3	0.8 ± 0.2	0.5 ± 0.2	<0.1	<0.1	0.9 ± 0.3	Noli me tangere	Benedetto e Santi Buglioni	1520
Barg10	0.7 ± 0.2	1.0 ± 0.3	0.5 ± 0.2	<0.1	<0.1	0.7 ± 0.2	Adorazione con cornice di Angeli (frame)	Luca e Andrea Della Robbia + Giovanni	ca. 1520
Barg11	0.7 ± 0.2	0.6 ± 0.2	0.5 ± 0.2	<0.1	<0.1	0.7 ± 0.2	Natività	Giovanni Della Robbia	1521 dated
Barg12	1.7 ± 0.5	1.5 ± 0.5	0.6 ± 0.2	0.2 ± 0.1	<0.1	0.4 ± 0.1	Noli me tangere	Santi Buglioni (Giovanni Viviani)	1530–1540

Note: Barg5 and Barg11 measurements are two parts of the same sculpture.

some selected Della Robbia sculptures exhibited at the Bargello museum in Florence. The obtained data are in range with previous observations on attributed Robbiana but, due to the precision with which such masterpieces are dated, they indicate that arsenic exceeds detection limits only after 1520 and could be used for dating of non-attributed objects on a before/after basis. The sudden appearance of arsenic in association with cobalt is certainly linked to a change of raw materials [20] but more work should be done to relate it to mining sites or preparation procedures.

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