Original research paper

Archaeometallurgical characterisation of Donatello's Florentine copper alloy masterpieces using portable laser-induced plasma spectroscopy and traditional techniques

Salvatore Siano, Juri Agresti

Institute of Applied Physics, N. Carrara, National Research Council (IFAC-CNR), Florence, Italy

We investigated the execution processes and the composition of a set of well-known Florentine copper alloy masterpieces attributed to Donatello: *David*, *San Ludovico*, *Pulpito della Resurrezione*, *Capitello*, and *Amore Attis*. Portable laser-induced plasma spectroscopy was used in order to detect the main elements in the alloys and achieve exhaustive compositional maps of the first three works, which were executed through multiple casting and assembling. The compositions of the others were analysed using traditional techniques. The comparison of the results was extended to some celebrated masterpieces by Ghiberti and Brunelleschi, and with the information provided by documentary sources in order to achieve a preliminary picture of the alloys used by Florentine artists during the Early Renaissance.

Keywords: Donatello, Michelozzo, Ghiberti, Art foundry, Copper alloy, LIPS, LIBS, Early Renaissance

Introduction

The analysis of the composition of copper alloy artefacts and the interpretation of their manufacturing processes has attracted the interest of many scholars since the end of the eighteenth century. The birth of archaeometallurgy in this period was stimulated by new discoveries and methodological advances in archaeology and the simultaneous introduction of analytical chemistry.

Important contributions to knowledge of historic metal production had already been made during the nineteenth century (Caley, 1967; and references therein). Conversely, little attention was dedicated to the technology of Renaissance and Mannerist masterpieces up to the end of World War II. This domain of the art foundry was also neglected in encyclopaedic and thematic books with technical contents (for example, Magne, 1917; Le Normand, 1823; Pettorelli, 1926). Thus, until after World War II the only information on the materials and processes of fifteenth- and sixteenth-century art foundries was in contemporary sources. These include Lorenzo Ghiberti's *Commentarii* (ca. 1445–1455) and the *Zibaldone* by his grandson Buonaccorso (ca. 1496–1511), the notes on the casting of the Sforza monument by Leonardo, the well-known sixteenth-century treatises by the educated elite, artists, casters, and metallurgists, such as Gaurico (1504), Biringuccio (1540) , Vasari (1550), Cellini (1568), the description of the execution of the equestrian group with Louis XIV (Boffrand, 1743), and a textbook by the sculptor and teacher of Florence's Art Academy Francesco Carradori (1802), which often have been discussed.

Interest in the art foundries of fifteenth and sixteenth centuries grew significantly when the modern conservation practices replaced those of the antiquarian tradition and started to be applied to unique copper alloy masterpieces. The restorers were the first to focus on the crafting processes of large sculptures (Bearzi, 1951; Formigli, 1984), while the early reliable information on their alloy compositions were achieved by the scientists involved in the study of the conservation problems of the doors of Florence's Baptistery after the disastrous flood of 1966 (Leoni, 1968; Cesareo & Marabelli, 1976; Parrini, 1982).

Correspondence to: Salvatore Siano, Istituto di Fisica Applicata 'N. Carrara', Consiglio Nazionale delle Ricerche, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy. Email: s.siano@ifac.cnr.it

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Afterwards, a number of studies were dedicated to the materials and methods of the art foundry, most of which have been published in multidisciplinary books.

Florentine sculptures by Donatello (Donato di Niccolò, Florence ca. 1386 – Florence, 13-12-1466) have had known conservation intervention treatments and related technical studies since the 1940s (Bearzi, 1951). Technological data were collected during the treatment of the following masterpieces: the funerary monument of Baldassarre Cossa (the antipope), *Giuditta e Oloferne* (Bearzi, 1951; Leoni, 1988; Europa Metalli, 1988), *Amore Attis* (Siano, 2005; Mugnaini *et al.*, 2014), *David* (Siano *et al.*, 2008, Mugnaini *et al.*, 2014), *Capitello, San Ludovico*, and the *Pulpito della Resurrezione*. We had the opportunity to investigate the production processes and the alloy compositions of the last five of these sculptures. Here, data on their copper alloys and casting procedures are reported for the first time, and discussed in order to draw a general metallurgical picture of Donatello's Florentine production. The study also includes results and considerations on sculptures crafted in the major Florentine art foundry of the first half of the Quattrocento, the time of Lorenzo Ghiberti, and others. This, in order to understand whether or not specific copper alloy recipes were in use during the Early Renaissance.

The possibility of approaching such a difficult problem has been made possible in recent years by the introduction and extensive application of portable laser-induced plasma (or breakdown) spectroscopy (LIPS or LIBS). This is a microdestructive elemental analytical technique based on the spectral characterisation of the plasma plume produced by focusing an intense pulsed laser beam on the material to be analysed. The technique does not involve invasiveness issues, since the analysis is carried out on the very small quantity of laser ablated material. Thus, the technique offers unique characterisation potential for metal artworks (De Giacomo *et al.*, 2008; Fornarini *et al.*, 2009; Anglos & Detalle, 2014).

We have developed and calibrated portable LIPS devices for quantitative analyses of major elements of copper alloys (Agresti *et al.*, 2009; Siano *et al.*, 2009), which were then used for investigating important Renaissance and Mannerist masterpieces. Here, the results recently achieved on Donatello's *San Ludovico* and *Pulpito della Resurrezione*, along with insights on the LIPS compositions previously measured on Donatello's *David* are reported. Furthermore, the *Capitello* and the *Amore Attis* were investigated using traditional techniques. Finally, the discussion also involves new data on the two panels representing the *Sacrificio di Isacco* which Ghiberti and Brunelleschi presented at the well-known contest of 1401 (the competition panels), and some comparison with other copper alloy masterpieces by Ghiberti.

Materials and methods

The portable LIPS device built in-house and used in the present study is equipped with a Q-switched Nd:YAG laser (1064 nm, 8 ns, 50 mJ/pulse) whose beam is focused with a 60 mm focal length lens (spot diameter of 110 μm and intensity of 70 GW/cm^2). The plasma emission is collected through off-axis parabolic mirrors and coupled to the entrance slits of a set of compact spectrometers by means of optical fibres (Agresti *et al.*, 2009). The device has been calibrated for quantitative analysis of binary (Cu-Sn), ternary (Cu-Sn-Pb and Cu-Zn-Pb), and quaternary (Cu-Sn-Zn-Pb) alloys, also taking into account the dependence of the calibration curves on the depth of the microcrater (Agresti & Siano, 2014). The diameter of the latter depends on the pulse energy and number of pulses. At the maximum energy, its value ranges between about 120 and 250 μm for a number of pulses of about 100–1500, respectively.

This instrument was used for analysing the *San Ludovico* and the *Pulpito della Resurrezione* during their recent treatments, which were carried out in 2011–2012 and 2011–2013, respectively. A number of quantitative elemental depth profiles were collected using about 1500 laser pulses in each measurement site, corresponding to a microcrater depth about 600 μm, as derived using alloy samples of similar compositions to those of the two sculptures (Siano *et al.*, 2011).

The typical depth profile of a given element includes an initial modulation zone, dependent on surface alteration phenomena, followed by a gradual stabilisation towards the bulk content. Thus, the latter can be calculated by averaging the pulse to pulse elemental contents along the deeper part of the depth profile. Here, the averages were calculated on 500 laser pulses. The detection limits of Sn, Zn, and Pb were about 0.1 wt% while the uncertainty in a single bulk measurement, calculated by the standard deviation, ranged between 5 and 20%, according to the amplitude of the residual modulations of the specific profile. In some cases, the contents of predominant traces were also measured through specific rough calibrations.

The LIPS characterisation of the *David* was carried out using a similar setup to that described above but operating at a rather lower peak intensity (13 GW/cm^2 achieved by focusing pulses of 10 mJ). Furthermore, the number of laser pulses released in each site was limited to about 400, thus minimising the diameter of the crater and its depth. Bulk compositions were derived by averaging on about 100 laser pulses. The maximum relative uncertainty and the minimum detection limit were 15–30% and 0.5 wt%, respectively.

Several measurements were carried out on the masterpieces noted above, according to the preliminary interpretation of the technological features, accessibility problems, local material situations, and the quality of the data. As mentioned above, the results and discussion also include comparisons with the alloy compositions of other masterpieces by Donatello, Ghiberti, and Brunelleschi, which were achieved using inductively coupled plasma spectroscopy (ICP–OES) and atomic absorption spectroscopy (AAS). The latter were used according to standard procedures based on the dissolution of 20–100 mg of alloy (metal burr taken using a small mill), preparation of suitable samples in aqueous solution, and comparison of the line intensities with the corresponding calibration curves of the various analytes.

Results

The three sculptures analysed using LIPS were cast in pieces, then assembled and integrated using mechanical anchoring and recasting operations (casting-on, hot patches, and hot joining). This holds also for the *Amore Attis*, while the *Capitello* was crafted as a single casting.

San Ludovico

This masterpiece is exhibited in the refectory of the Museum of Santa Croce, Florence. It is known as Donatello's first copper alloy sculpture, dated ca. 1423–1426 (Boffa, 2005), which was commissioned by the Parte Guelfa for their niche on the façade of Orsanmichele, Florence. The figure was cast in several pieces that were separately gilded using the mercury amalgam technique, and then assembled mostly mechanically by means of large copper alloy rivets (Fig. 1). The sculpture is a kind of 3D metal

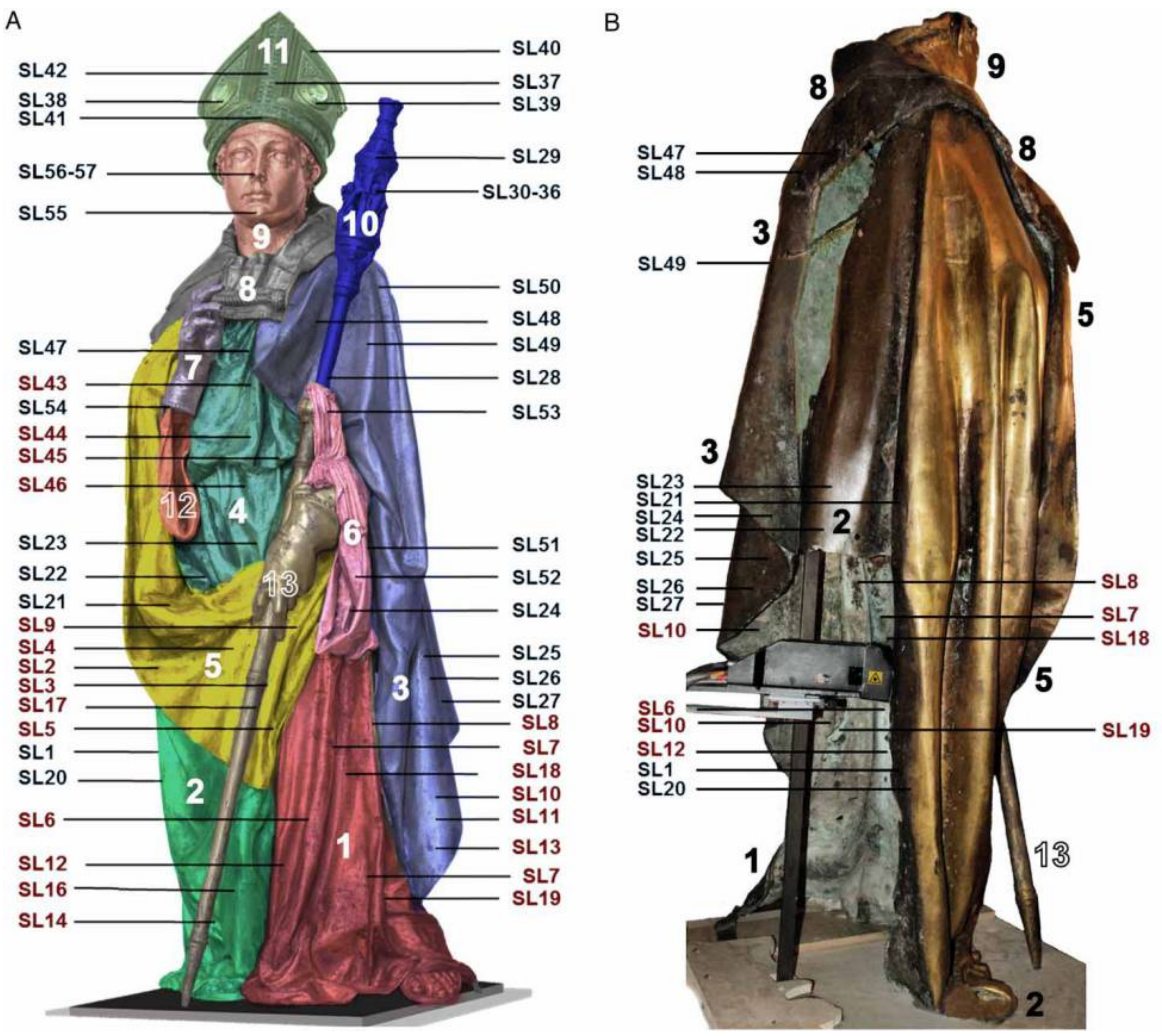

Figure 1 The *San Ludovico:* front views (A) with independent pieces shown in false colours and large white numbers; rear view (B) shown in natural colours with the independent pieces indicated with large black numbers. LIPS measurement sites are also mapped with black the red labels, which refer to measurements performed on the outer and inner surface, respectively.

puzzle crafted by suitably setting and superimposing the contours of modelled and gilded copper alloy slabs. The unfinished *verso* (a typical feature for sculptures exhibited in a niche), allowed us to inspect the inner surfaces of the metal slabs and to perform a set of LIPS measurements from the inside (Fig. 1B).

Several repairs to casting flaws are distributed all over the figure, including cold plugs (applied with hammer and chisel) and hot patches (inserted by pouring molten metal). Some linear recasting in order to fill the gaps between adjacent slabs are also visible from the back aperture, although they mostly seem intended as integrations rather than as hot joins. In Fig. 1 the 13 independent pieces easily recognisable to the naked eye are highlighted in the front view with different false colours and numbers, while the *verso* with five main pieces visible and the LIPS head, is shown in its natural colours. Figure 2 displays typical Zn, Sn, and Pb profiles, which become sufficiently stable after about 300 laser pulses. As expected, Zn and Sn exhibit depletion (dezincification) and enrichment phenomena (Siano *et al.*, 2009), respectively, while Pb modulations can be extended to the bulk because of the segregation of the Pb phase.

As described above, the bulk composition was achieved by averaging over about 500 laser pulses (from 500 to 1000 for the profiles of Fig. 2). The profiles measured on the inner surfaces of the slabs were also exploitable, although they exhibited broader initial modulations and the bulk composition was reached after a higher number of pulses. The LIPS results are plotted in Fig. 3. Most of the pieces, as well as the filler materials, were cast using a quaternary alloy (Cu, Zn, Sn, Pb), a leaded low-zinc brass with a maximum zinc content of about 13% (here and in the following % is expressed as wt%). Pieces 1, 2a, 3, and 8 presented the highest degree of alloying with the following average composition: Cu 85.3% (calculated as

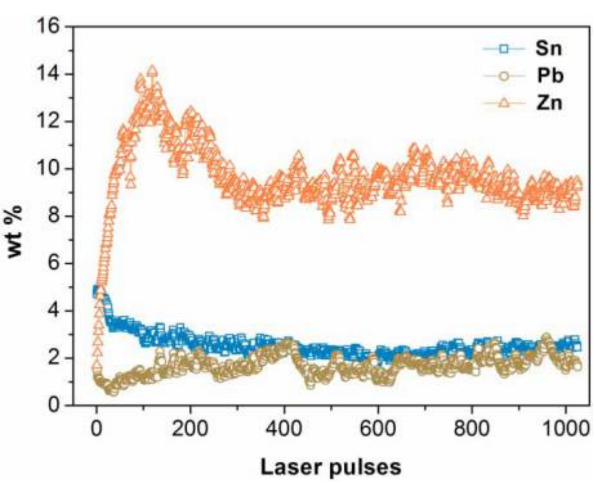

Figure 2 Representative LIPS elemental depth profiles measured on the outer surface of the *San Ludovico*.

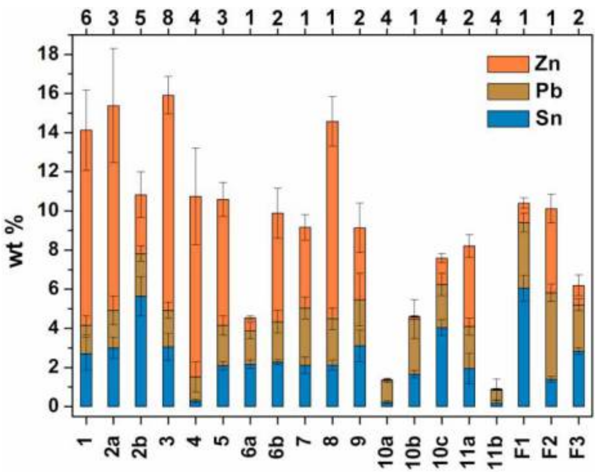

Figure 3 Alloy compositions of the different pieces (see the numbering of Fig. 1) of the *San Ludovico* as measured using LIPS. The top axis reports the number of measurements carried out on each piece.

difference to 100%), Zn 10%, Sn 2.9%, Pb 1.8%, and Fe <0.1%. The presence of a substantially different alloy on the rear zone of piece 2 (Sn 4.6–7%, Pb 1.8–2.8%, Zn 1.5–4.5%, Fe <0.1%) indicated that the latter was made from two independent parts, also confirmed by a subsequent accurate visual examination of its outer surface. A similar conclusion was suggested by the two different alloys of the drapery descending from the crosier to the left forearm (piece 6 in Fig. 1A): Sn 2.1–2.4%, Pb 1.6–2.5%, Zn 5–6.5%, Fe <0.1% against Sn 2%, Pb 1.7%, Zn 0.7%. The analysis of large piece 5 indicated a slightly less alloyed material with respect to pieces 1–4 and 8 but conceptually similar (Sn 1.9–2.3%, Pb 1.5–2.5% Zn 5.7–7.3%, Fe <1%) and even less for the right glove (Sn 2.1%, Pb 3%, Zn 4%). Three poorly alloyed metals were detected for the crosier (piece 10): Sn 0.2%, Pb 1% (handle and first figurine); Sn 1.5%, Pb 3%, Zn 0.2% (two more figurines); and Sn 4%, Pb 2.2%, Zn 1.4% (upper part). The mitre (piece 11) consisted of mostly pure copper with traces of Sn and Pb while a quaternary alloy was detected for a stone housing (Sn 2%, Pb 2%, Zn 4%). Finally, the three filler materials measured (F_{1-3} in Fig. 3) were again quaternary alloys of different compositions.

Capitello

The commission by the Opera della Cintola for the execution of the external pulpit of the cathedral in Prato, Italy, was signed on 14 July 1428 by Michelozzo di Bartolomeo (Florence 1396–1472), who at that time was working in partnership with Donatello. According to documents, the copper alloy *Capitello* beneath the marble pulpit was the first sculptural element the artists executed during the second half of 1433. Art historians unanimously attribute the drawing of the present sculpture to Donatello, but his possible direct contribution to the creation of the model is still under discussion (Lightbown, 1980; Caglioti, 2004; Cerretelli, 2011). However, we discovered the wax model for casting was directly modelled (i.e. without passing through a copy process), which leads to its attribution to Donatello.

Very briefly, this conclusion is based on the observation of a set of peculiar morphological features. The very variable thickness of the metal wall (about 1–4 cm) and the sharp contours of the indentations of the *verso* are incompatible with typical wax casting in a mould (slush cast or manual application). Furthermore, the *verso* presents several evidences of wax application on a rough positive model of the *Capitello* made of gypsum, clayey material, or wood. See for examples the hexagonal indentations of at least two of the three rosettes lying at the background of the scene (highlighted in Fig. 4B with dashed squares), while circular shapes correspond to the two central rosettes terminating the lower part of the two frontal volutes. Similarly, the indentations of the projecting upper terminations of the latter are circular but also include marks left by positive relief. The latter feature is particularly evident for the termination of the lateral volute (Fig. 5) where quite accurate modelling is visible, which recalls to mind the *verso* of another famous work by Donatello.

Figure 4 (A) Three-dimensional model (from Scopigno & Dellepiane, 2011) and the reverse (B) of the *Capitello*.

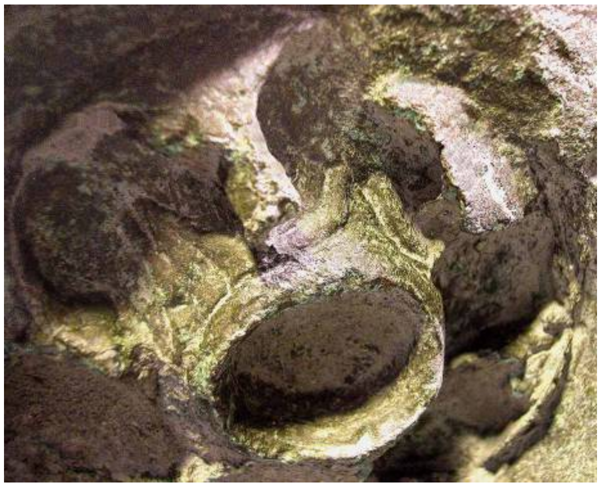

Figure 5 Modelled indentation corresponding to the rosette terminating the lateral volute of the *Capitello*.

The casting of the *Capitello* was perfectly executed without defects, apart from a few very small *lacunae* noticeable along the lower cornice. For this work, the casters used a bronze alloy with tin and lead contents (Table 1) of about 16% and 4%, respectively, which provided high fluidity to the molten metal and a relatively low solidification temperature. Such a composition corresponds to the typical one used for casting bells rather than copper alloy sculptures.

The David *and* Amore Attis

No commissioning documents were found for Donatello's most celebrated masterpiece, which has an uncertain date. According to recent studies (Caglioti, 2008), *David* could have been crafted 1435–1440, the same creation period of the two *Putti* that Donatello realised for the Cantoria in the cathedral in Florence (1437–1438, from documents) and of the *Amore Attis* (no commissioning documents available) (Caglioti, 2005).

We carried out thorough investigations on the production of both works, reported elsewhere (Siano, 2005; Siano *et al.*, 2008; Mugnaini *et al.*, 2014). Here, let us briefly underline that from the technological standpoint both these unique works are strongly influenced by historic art foundry methods but for different reasons. A direct method was used for *David*, as unequivocally witnessed by an internal armature along with the significant and irregular thicknesses of the metal walls (Fig. 6A), the manual surface finishing of the wax model, and other details. Conversely, the regular and thin thickness of the *Amore Attis* (Fig. 6B) along with other details led us to conclude that it was crafted through the indirect forming of a wax model of the body, followed by integration of accessories, and then finishing operations. Both the works have some areas decorated with oil gilding.

Table 1 Elemental composition of the *Capitello*, as measured using AAS

Sample	Cu	Sn	Pb	Zn	Sb	As	Ag	Fe	Ni	Mn	Bi	Cd	Co
CL1	77.15	16.4	3.76	0.195	1.48	0.548	nm	0.237	0.220	0.001	0.000	0.002	0.008
CL2	77.32	16.3	3.73	0.184	1.46	0.551	nm	0.228	0.218	0.001	0.000	0.002	0.008
CL3	77.62	16.1	3.63	0.188	1.48	0.549	nm	0.213	0.213	0.001	0.000	0.002	0.008
CL4	77.16	16.0	4.07	0.192	1.59	0.566	nm	0.198	0.219	0.000	0.000	0.002	0.008

nm: not measured.

The two main pieces constituting the *David* are the base (representing a garland) and the figures (David with the sword and Goliath), which were cast together on the former. However, the figures also present sculptural elements, which were added to the former casting along with several repairs carried out in order to fix some serious casting flaws. A small gap between David's hair and shoulders, as well as between the hair and the temple, support the reasonable hypothesis that the former were mostly cast-on. Other minor integrations include a band and the tassel hanging down from the hat, one band of the lower part, and others. This extensive exploitation of the casting-on procedure was likely intended to maximise realistic rendering with in the round of elements and small gaps. As an example, Fig. 7 displays a view of the upper part where the realism of the accessories on the hat and the long 'wild' locks descending on the shoulders is impressive.

Thirty-seven valid alloy composition measurements were carried out on the outer surface of the *David* and four beneath its base (red labels), as indicated in Fig. 8, while the corresponding results are plotted in Fig. 9. The latter show that all the sculptural elements and repairs were cast using ternary alloys. Although the main alloys of the body, sword, hat, left leg, and Goliath corresponded to that of the main casting of the figure, they were plotted separately in order to show the range of variability observed among the different zones. Their average provides the main alloy of the *David*: Sn (3.4 ± 0.6)%, Pb (4 ± 1)%. The garland was more alloyed and leaded than the figure, a trend which also holds for the hair and the repairs.

Thus, the substantial technological difference noted above between the *David* and the *Amore Attis* is extended to their alloy compositions. The latter was cast using a poor quaternary alloy. As shown in Table 2, AAS analyses of two samples from the feet returned very congruent results indicating a singular quaternary alloy with low contents of tin, zinc, and lead. The composition of the right arm, as measured using AAS, and that of the head, achieved with wavelength-dispersive electron microprobe scanning of small areas (about 1 mm^2) of cross-sections, were qualitatively similar, although some variations in the elemental contents were detected.

Figure 6 Radiographic details of the *David* (A) and the *Amore Attis* (B). The white zone of the latter corresponds to lead filler of a modern repair. See the text.

Figure 7 Detail showing cast-on sculptural parts at the upper part of the *David*.

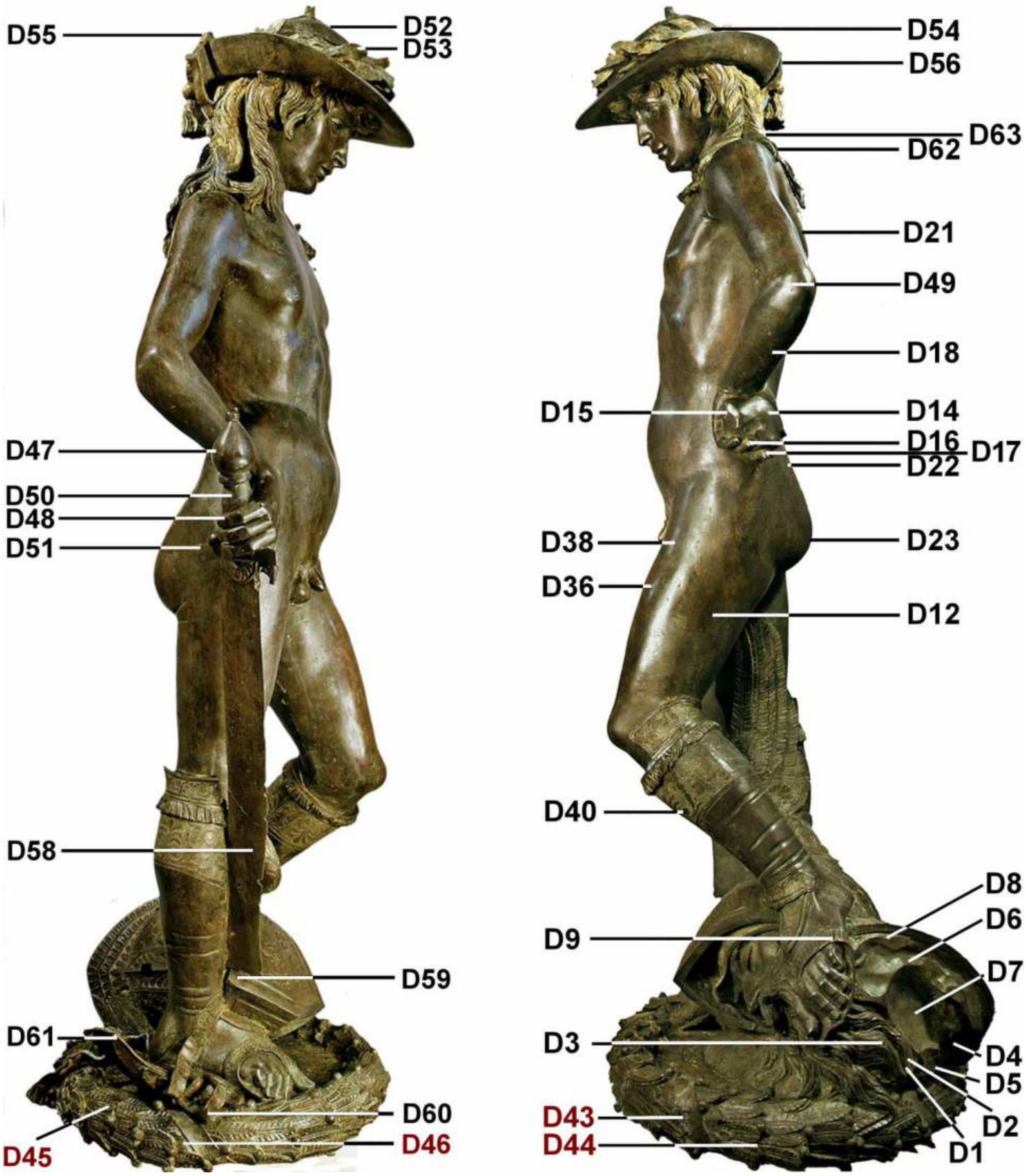

Figure 8 The *David*: map of the LIPS measurements. (Images: Antonio Quattrone, Firenze)

Pulpito della Resurrezione

During the last ten years of his life, Donatello crafted the decorative panels of the parapets of two rectangular pulpits for the Basilica of San Lorenzo, dedicated to Christ's Passion and Resurrection (*Pulpito della Resurrezione*), respectively. Material characterisations of the latter were carried out during the recent treatment, completed in 2014.

The reliefs have significant size (parapet: w × h × d = 3.10 × 1.25 × 1.60 m). They were assembled from several pieces using iron sheets fixed on the inner side with rivets and by pouring molten metal along the inner edges of the reliefs. In some areas, local recasting also partially embedded the iron bars. Figure 10 displays a rough scheme of the different pieces composing the largest relief (resurrection side, 3.10 × 1.25 m), as recognised by naked eye observation. The relatively large linear gaps among the main scene, the superimposed fascia, frieze, and cornice are very evident while their further subdivisions were inferred by carefully observing the mechanical assembly with iron bars, hot and cold patches, plugs, casting defects, and the colour of the metal surfaces. In particular, the subdivision into two main

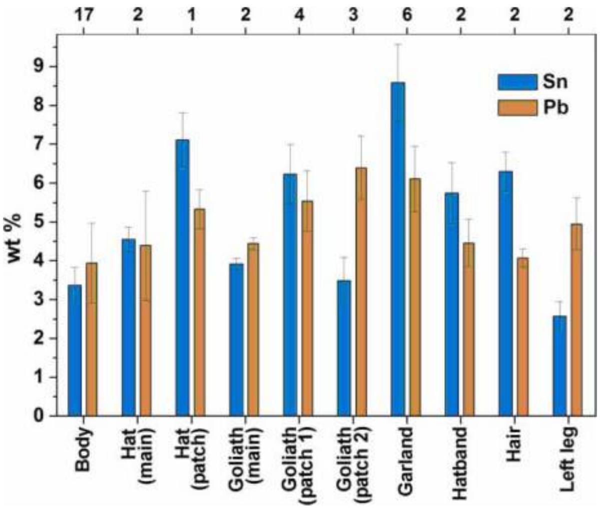

Figure 9 The *David*: results of the LIPS measurements.

pieces of the fascia is highlighted by an evident recasting zone in the middle. Recasting around the central zone is also present on the inner side of the frieze and the cornice, which are also secured with two horizontal iron bars. However, it is unclear whether these indicate intentional castings in pieces, or repairs. In contrast, the four panels of the frieze were certainly separately cast and fixed to the framework by means of local pouring of molten metal and subsequent cold working.

The reliefs of the short sides representing the *Marie al Sepolcro* and the *Pentecoste*, respectively, were each assembled from two superimposed pieces: the scene and the upper architectural motifs (fascia, frieze, and cornice all together). The same holds for the relatively small relief representing the *Martirio di San Lorenzo* on the other long side, most of which is occupied by the entrance to the pulpit. The inner surfaces of all the sculptural elements show many clues indicating that the indirect casting method was used. The waviness of the inner surfaces are compatible with the formation of wax copies of the original model by means of slush casting and successive manual thickening in some zones.

LIPS measurements were carried out on both sides of the reliefs. The complex map of the measurement sites of the main relief is displayed in Fig. 10 with the approximate subdivision described above, while the results of all the four reliefs are reported in Fig. 11. The LIPS analyses of the main pieces, patches, and fillers indicate they were cast using

Table 2 Alloy compositions of the *Amore Attis*

Site	Cu	Sn	Pb	Zn	Ag	Sb	Fe	Ni	As	Co	Mn	Cd	Bi	Au
A_1(r. foot)	87.74	2.92	3.39	3.93	0.10	1.01	0.40	0.19	nm	0.02	0.00	nm	nm	0.00
A_2 (l. foot)	87.87	2.79	2.98	3.88	0.09	0.93	0.37	0.21	nm	0.00	0.00	nm	nm	0.00
A_3 (r. arm)	90.66	4.10	3.32	0.65	0.08	0.49	0.14	0.18	nm	0.05	0.00	nm	nm	0.00
M_1 (hair t.)	90.02	3.49	1.32	2.36	0.21	0.93	0.20	0.23	0.43	0.01	0.01	0.01	0.07	0.05
M_2 (hair m.)	91.87	2.63	0.70	2.39	0.18	0.76	0.24	0.25	0.37	0.02	0.01	0.01	0.07	0.05
M_3 (hair b.)	87.62	3.56	3.13	2.32	0.28	1.19	0.25	0.23	0.47	0.02	0.01	0.01	0.10	0.05

A samples were measured with AAS, M samples with SEM-WDX. nm: not measured. r: right. l: left. t: top. m: middle. b: bottom.

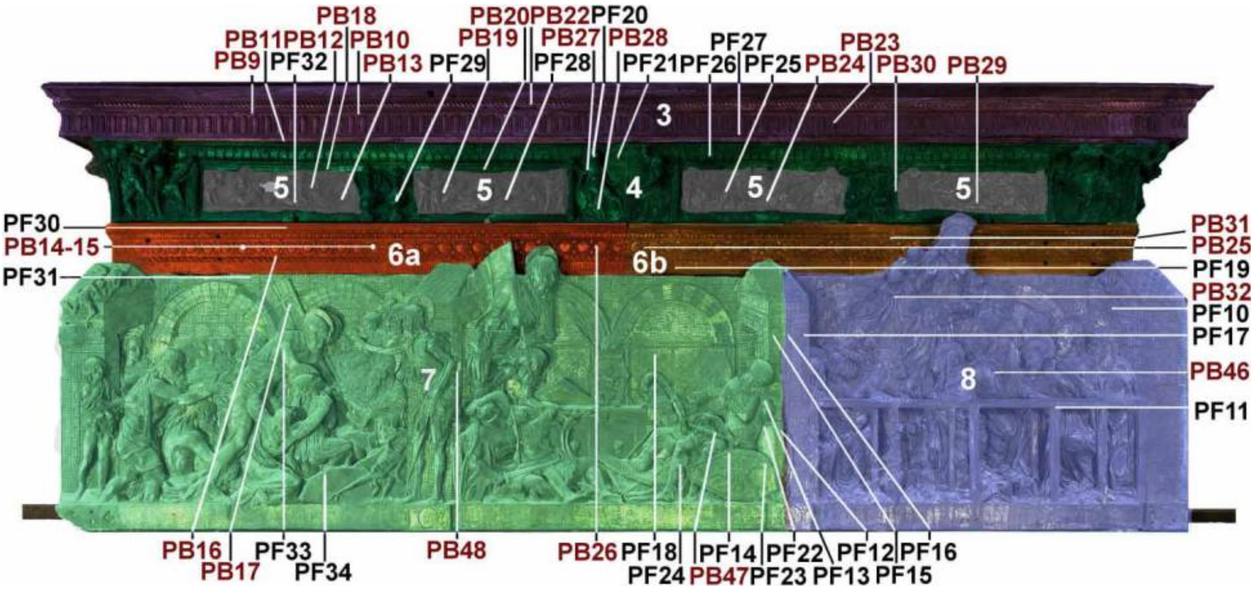

Figure 10 The *Pulpito della Resurrezione:* pieces composing the main relief in false colours with the indication of the LIPS measurement sites.

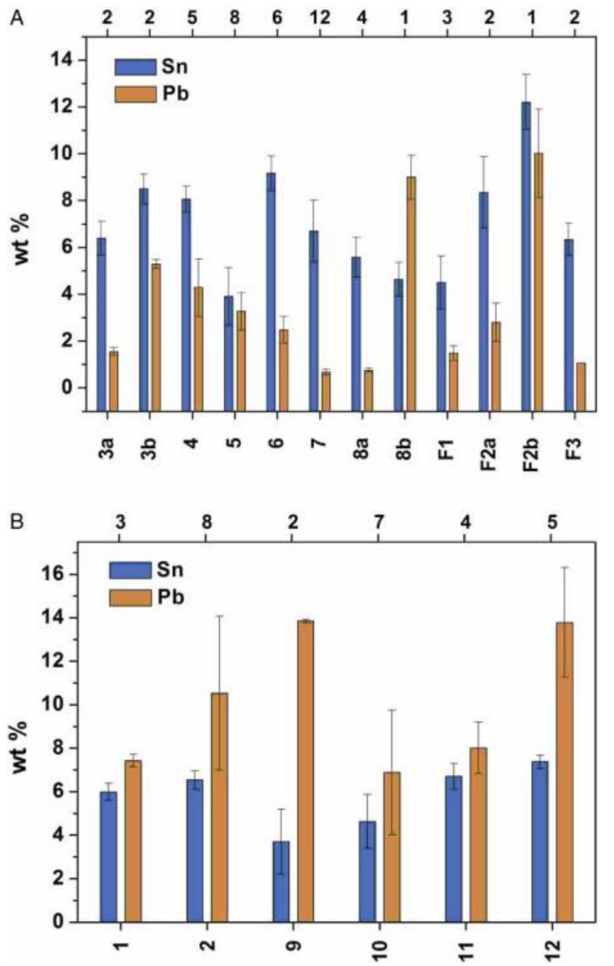

Figure 11 LIPS analyses of the *Pulpito della Resurrezione:* (A) pieces (3–8) and fillers (F_{1-3}) Resurrection side; (B) pieces of the *Marie al Sepolcro* (1–2), *Pentecoste* (9–10), and the *Martirio di San Lorenzo* (11–12) sides.

leaded bronzes. An almost constant tin content of about 6% was found for the four pieces composing the sides of the *Marie al Sepolcro* (1–2) and the *Martirio di San Lorenzo* (11–12), while the two pieces (9–10) of the other short side (the *Pentecoste*) were slightly less alloyed (Sn 4–5%). An average tin content of about 6.7% was found for the Resurrection side but with a larger variation between 4 and 9%. The lead content was rather variable in all the pieces and within each piece. Minimum values below 1% were found in most of the zones, whereas a peak of about 6% was measured on the piece 4 (PF20). Piece 3 presented considerable variations of tin and lead contents in the left (PB9, PB10, PB11, which also included Zn 0.4%) and right (PF27, PB23) sides, respectively, thus suggesting it was cast in two pieces (3a, 3b). Conversely, piece 6, which was apparently cast in two independent parts had a relatively homogeneous composition, whose iron and nickel contents were relatively high (Fe 2-5%, Ni 0.5-2%).

Discussion

The masterpieces of Donatello's Florentine artistic production discussed here exhibited strong technological differences: the thick metal walls of the *David* and of some zones of the *Capitello*, which were crafted with a direct casting method, contrast with the thin walls of *Amore Attis*, mostly executed using an indirect casting method; the high-quality casting of the latter and of the *Capitello* contrast with the many defects and repairs to the *David* and the *Pulpito della Resurrezione*; and finally, the singular construction of the *San Ludovico*.

As is well known, Donatello had various specialised collaborators for casting his masterpieces. Some of these individuals were likely shared among the workshops. Thus, the present study could be more generally relevant to the alloys used in Florentine art foundries during the Early Renaissance rather than only to Donatello's alloys. On the other hand, this does not mean that we completely agree with the tradition and several contemporaneous scholars who foster the idea that the artist did not take part at all to the foundry works of his masterpieces. Certainly, he would have personally prepared the wax models and for the *David* also the core structure (construction of the iron skeleton, modelling, and firing of the core). Furthermore, Donatello certainly had a primary role in finishing his sculptures, which are characterised by a very peculiar chiselling, well recognisable in all his artworks.

Both tradition and modern criticism substantially agree with the definition of Donatello given by Gaurico in 1504: 'the most ancient among the moderns' (Cutolo, 1999). This obviously refers to his figurative choices but some of them necessarily required knowledge of the technical aspects of Classical and Hellenistic bronzes. The artist extensively exploited casting in pieces and consecutive assembling for rendering the realism and dynamicity of the *San Ludovico*, *David*, and *Amore Attis*, whose technological features are very peculiar within art foundry production in the Early Renaissance. The assembly methods were mainly mechanical for the (*San Ludovico*, *Amore Attis*, and the *Pulpito della Resurrezione*), although in all cases rough hot joining or casting-on operations were also carried out. Thus in particular, casting-on operations were mostly exploited for executing the *David*.

In this study, four different type of alloys were found: the low-zinc brass in the *San Ludovico*, high-tin bronze in the *Capitello*, a low-quaternary alloy in the *Amore Attis*, and eventually the leaded bronzes of the *David* and the *Pulpito della Resurrezione*. Such a compositional variety was likely determined by economic and contingent reasons other than functional aspects. At the same time, it is important to note that these alloys do not seem completely random. Their chronological sequence supports a congruent evolution during the Quattrocento, according to present knowledge of copper alloy production in the Late Middle Ages and on Ghiberti's works. Let us discuss this aspect in some more detail.

Brass

Despite the many pieces and the complex construction of the *San Ludovico*, LIPS analysis enabled identification of its most representative alloys. These can be grouped into two similar quaternary compositions with two different degree of alloying and lead content (Fig. 3): that of pieces 1, 2a, 3, and 8, with a total amount of white metals of about 15%, and that of pieces 2b, 4, 5, 6b, 7, and 9 with a corresponding value of about 10%. Furthermore, the strict compositional similarity of the former group and that of the pieces 5, 6b, 7, and 9 is compatible with their execution within the same casting session.

As is well known, during the Middle Ages bronze was mostly replace by brass. The extensive application of the cementation process made the latter much more available than the former (Rehren & Martinón-Torres, 2008; and references therein), which remained in use essentially for casting bells. Tin sources in Europe were few, and scarcely exploited at that time.

The alloys of *San Ludovico* and those of some other contemporary sculptures confirm the replacing of bronze with brass, also involved in the art foundry of the early decades of the fifteenth century. In particular, the composition of Donatello's first metal figure (1423–1425) is similar to that of Ghiberti's *San Matteo* (1419–1422). The AAS analyses of the latter were rather scattered in value (Agnoletti *et al.*, 2003) because of massive segregation phenomena due to the thick metal walls (3–7 cm) and large sizes of the figure (height 270 cm), which was cast in two phases, likely using more than a melting furnace. The main elements of the lower part (first casting) had the following average composition (three samples): Zn (12.9 ± 4.6)%, Sn (4.2 ± 0.4)%, Pb (1 ± 0.1)%. The average composition of the upper part (six samples), which was cast-on the former was: Zn (8.1 ± 1.91)%, Sn (1.9 ± 0.2)%, Pb (0.7 ± 0.1)% (Fe 0.1–0.2%, Sb 0.3–0.5%). The average composition of pieces 1, 2a, 3, and 8 of *San Ludovico* were somewhat in the middle between these two alloys: Zn (10.5 ± 1.7)%, Sn (2.9 ± 0.7)%, Pb (1.8 ± 0.5)%.

The treatise on copper alloy sculptures including compositional recipes, which is closest in date to the Early Reanissance, is that by Gaurico (1504). In his book, the writer provides a precise recipe for casting statues: *Per le statue, dodici libbre di stagno per ogni cento di rame, di cui un terzo di recupero* (for statues 12 lbs of tin for 100 lbs of copper, where one-third of copper is from recycling) (Cutolo, 1999, p. 229). This corresponds to a tin content of 11% or 11–15% (calculation made by taking into account that the Latin word *aes* was used for both copper and bronze). This is close to Biringuccio's definition of bronze (rigorously distinguished from copper by the expert metallurgist and caster), which has a tin content of 8–10% (Biringuccio, 1540, b. V, c. 3rd); also Cellini in his treatise on sculpture names bronze. Conversely, Vasari (painter, architect, and art historian) provides a different composition for the statuary alloy: Statuary metal is made of the combination of two thirds of copper and one-third of brass according to the Italian rule (Maclehose & Brown, 1907, p. 163). Very interestingly, such an idea about the 'Italian rule' survived for a long time and it was reported two centuries and a half later by Carradori in 1802 (Auvinen, 2002). There were hence two diverging ideas on the statuary copper alloys (brass or bronze), whereas for example all the sources discussed agree on the composition of bells: Cu-Sn with a tin content of 17–26%, which is similar to the medieval recipe provided by Theophilus (Hendrie, 1847, p. 307), as well as to modern compositions.

'Two-thirds of copper and one-third of brass' could be a good way for interpreting the compositions of the *San Ludovico*, the *San Matteo*, and other masterpieces (see below) crafted between 1400 and 1430. However, the composition of the master brass is unknown, and the zinc content in brass can significantly decrease when the metal is left melted for a long time. The latter could be one of the possible reasons for the variations in zinc content. In particular, this could explain the lower zinc concentration of the upper part of the *San Matteo* with respect to the lower one, although a further addition of copper cannot be ruled out. The reduction of tin content (from 4.23 to 1.92%) could for example support the latter possibility. Thus, at least in this case, the caster made the alloy by mixing master brass, copper, and tin. The overall averages (excluding fillers and small decorative pieces) of lead were (0.9 ± 0.2)% and (1.9 ± 0.6)%, for these two works. Such low values suggest that lead was likely an impurity of brass, brought into the alloy during the cementation process by impure zinc ores, rather than by a further additional raw component. This is also supported by Gaurico's recommendation to avoid the addition of lead in statuary bronze (Cutolo, 1999, p. 229).

Let us now try to approach the most difficult problem: is there any clue, which can help us to understand whether the recipe two-thirds Cu + one-third (Cu-Zn) was used to make the present alloys? Various authors have experimentally investigated the cementation process in order to determine what is the maximum zinc content that can be achieved. Despite using controlled conditions of true cementation, zinc concentration can exceed 30% (Craddock & Eckstein, 2003; Welter, 2003; and references therein), the present data support a possible zinc

Table 3 Composition (wt%) of the contest panels by Brunelleschi (B) and Ghiberti (G)

Site	Cu	Sn	Pb	Zn	Fe	Ni	Ag	Mn	Au	Co	Sb
B_1 (Relief)	81.19	0.17	1.81	12.11	0.22	0.10	0.064	0.00	0.06	0.00	1.82
B_2 (Bkg Slab)	75.44	0.17	1.96	18.74	0.36	0.10	0.038	0.00	0.04	0.01	1.96
B_3 (Relief)	83.01	0.00	2.13	10.65	0.25	0.09	0.060	0.00	0.06	0.01	2.13
G_2 (Core pin)	82.25	0.47	0.63	14.26	0.16	0.20	0.054	0.00	0.05	0.00	0.63
G_3 (Cast-on)	86.11	0.40	0.76	10.22	0.31	0.11	0.031	0.00	0.03	0.00	0.77
G_6 (Cast-on)	80.81	0.00	0.54	16.14	0.14	0.39	0.03	0.00	0.02	0.02	0.00
G_7 (Main)	81.04	0.42	2.02	12.86	0.25	0.07	0.020	0.00	0.02	0.00	2.02

content around 20%. This is suggested by the highest concentration found in the *San Matteo* (Zn 18.52%), which is not the only artefact with such a maximum zinc content. The preliminary analyses available for the first Baptistery door in Florence by Andrea Pisano are in agreement with such a feature (Squarcialupi & Burrini, 2005). Further important information about the master brass is provided by the competition panels.

Ghiberti tells us: *fu a ciascuno dato Quattro tavole d'ottone … la immolazione di Ysaach e ciascuno de' combattitori facesse una medesima istoria* (each competitor received four brass ingots for crafting a panel representing the *Sacrifice of Isaac*). The competition panels by Ghiberti and Brunelleschi are today exhibited at the National Museum of the Bargello, Florence, and we had the opportunity to analyse them in 2005 using AAS.

The two panels were crafted according to two different procedures but their compositions are very similar (Table 3). Brunelleschi cast a flat background slab on which he attached the various relief components cast independently, whereas Ghiberti cast most of the panel in a single operation, then did some casting-on. As shown in Table 3, the tin content ranged around the trace level, hence this element was not intentionally added. Although the lead content was higher (0.5–2%) it was still low to be considered as an intentional component. In particular, it could come from lead sulphide contaminating calamine and copper ores. Finally, despite its relatively high values, Sb also has to be considered an unintended component associated with copper. Conversely, the high variability of the zinc content is compatible with the addition of copper to the master brass alloy. Practically, the same maximum Zn content as that of the above described four artworks was found for the background of Brunelleschi's panel (Zn 18.74%), while the corresponding maximum of Ghiberti's panel was only slightly lower (16.14%, measured in cast-on sculptural part). This could support the working hypothesis of a master brass with a zinc content around 20%.

The master metal was probably diluted with variable fractions of copper for economic reasons but also for achieving a more suitable alloy, in order to make easier the extensive cold working to be carried out after casting. Furthermore, the moderate degree of alloying of the *San Ludovico*, competition panels, and the North Door and their low lead content, certainly favoured the application of gilding (copper is the best for mercury amalgam gilding and too much lead is unfavourable).

If the master alloy had a zinc content around 20%, the data also show that Vasari's recipe represents an extreme dilution of the former rather than the most used composition, which had completely inverted fractions (two-thirds brass + one-third copper). Finally, the present compositions also suggest that a small and variable percentage of tin was often added.

The leaded bell bronze of the Capitello

The present technological examination supports the attribution of the wax model of the *Capitello* to Donatello. Anyway, the documents show that the casting operations were carried out by Michelozzo and his collaborator Maso di Bartolomeo. The cost of the wax for preparing the model was paid to Donatello and Michelozzo between August and September 1433, while historical notes reporting the payment of the bricks given to Michelozzo for building the furnace, demonstrates that the artwork was already completed on 9 December 1433. To date, no documents have been found reporting information on the purchase of the raw metal, which was much more expensive than wax and bricks.

As shown in Table 1, a slightly leaded high-tin bronze was used, which is congruent with the typical one used for casting bells. We also carried out some SEM-EDX analyses on small fragments in order to verify such an unusual composition, which confirmed the AAS data. The measured lead content was slightly higher (Pb 4%) than the typical values of lead impurities. This could suggest that the raw metals used to achieve the present alloy were bell bronze and a small amount of lead, in order to make practicable the final cold working. The Arte della Cintola could have provided to the artists available bell bronze or alternatively unused or broken bells.

Low Zn-Sn-Pb copper alloys

The composition of the *Amore Attis* offers the opportunity to say a few words on a completely new alloy, which was apparently introduced by Ghiberti during the 1430s for crafting the gilded reliefs of the Porta del Paradiso. He used brass for most of the first large copper alloy sculptures, but for his most celebrated reliefs he invented a new alloy by strongly diluting the master brass discussed above and adding some tin. The ten main panels of the Porta del Paradiso have a composition ranging from Sn 0.7%, Pb 0.8%, Zn 1.1% (with 2.6% of white metals) for the panel depicting *David e Golia*, to Sn 2.1%, Pb 1.4%, Zn 3.4% (white metals 6.9%) of that dedicated to *Adamo ed Eva*. The amalgam gilding of the large panels (about $80 \times 80\ cm^2$) and the extensive cold working carried out after casting, represent good motivation for the selection of such low degrees of alloying. The frameworks of the two wings, which were not gilded, were made of brass, and the maximum zinc content was 14.63%.

As anticipated above, the *Amore Attis* was crafted using a similar alloy to that of Ghiberti's reliefs but with a higher content of white metals. The analysis of samples A_{1-3} (Table 2) gave the following average values for the main alloy: Sn (3.3 ± 0.7)%, Pb (3.2 ± 0.2)%, Zn (2.8 ± 1.9)%. Probably, a small amount of lead was also added to brass, tin, and copper i.e. this could be an intentional quaternary alloy.

Towards Hellenistic leaded alloys

The zinc content of *David* and most of the components of the *Pulpito della Resurrezione* were below the detection limit for the portable LIPS device used in this study. These artworks were cast using leaded bronzes. In principle, the bronzesmith could have employed a master bronze or else directly mixed copper, tin, and lead. As shown in Figs. 9 and 11, both tin and lead content were independently very variable, which could support the latter possibility. However, this does not rule out an option involving the use of master bronze as a raw component. In this respect, it is interesting to mention a set of accounts found in the Cambini book (Corti & Hartt, 1962) dated from 14 October to 19 December 1456. These report that Donatello purchased five lots of raw metals, which were recorded as '100 pounds of broken copper' (perhaps copper from recycling), '237 pounds of brass and bronze', '300 pounds of copper', '150 pounds of bronze', '178 pounds of bronze'. However, especially in non-technical records, the terminology cannot be directly intended in the modern sense since the words 'copper' and 'bronze' could be sometimes ambiguous in a similar way to the Latin term *aes*. Thus, we can observe that brass is reported only once in the records discussed, which supports the preferential use of bronze. The scholars who published the data on metal supplies ordered by Donatello, also hypothesised that these could have been used for casting the *Giuditta e Oloferne*. The analyses of the four most reliable samples taken during the last restoration (1986–1988) gave an almost pure binary Cu-Sn bronze with significant iron content: Cu (86.4 ± 1.7)%, Sn (6.8 ± 1.1)%, Pb (0.6 ± 0.3)%, Zn (0.1 ± 0.1)%, Fe (1.5 ± 1)%, while in two samples Ni 0.6% was also found. A small amount of zinc (1.2–2.2%) was found only in three of the eight small fragments analysed.

The most alloyed part of *David* was the garland (D43–45, Fig. 8) with an average tin content of about 8.5% while that of the body was less than half. Certainly, this low degree of alloying was one of the causes of the casting problems of this masterpiece. Lead was likely added in order to improve the fluidity of the molten metal, although the total amount of white metals was still insufficient in the main alloy (about 7.5% for the body and arm, Fig. 9). For the *Pulpito della Resurrezione* the alloys of the various pieces were generally more fluid thank to higher tin and lead contents, even though for some pieces (3a, 7, and 8) lead could not be added at all.

Conclusions

In this work, we have investigated the composition of a set of copper alloy masterpieces attributed to Donatello using portable LIPS and traditional techniques. The former enabled exhaustive compositional pictures of very complex sculptures, which were executed by means of several independent casting operations. This has allowed an exploration of the important theme of the alloy compositions used in art foundries during the Early Renaissance.

As is well known, tradition regards Donatello as unable to carry out the preparation of the core structures or to perform casting operations. The present large compositional variations could support, in some extent, the idea that the master worked in collaboration with various casters, who were likely shared among different art foundries. This extends the archaeometallurgical value of the present study, which can perhaps be relevant to all Florentine art foundries of the period rather than solely to Donatello. At the same time, we would like to underline that the technological interpretations also provided evidence that the artist operated on the wax models and for the *David* he also worked on the core structure. Furthermore, there are objective clues demonstrating Donatello had to have a crucial role in casting-on operation, repairs and eventually chiselling and patination.

The alloy compositions achieved argue an evolution from medieval alloys (low-zinc brass and bell bronze) towards a composition conceptually similar to that of Classical and Hellenistic bronzes, which often had a tin content around 10% and a low percentage of lead. In between, there is a quaternary alloy used for the panels of the *Porta del Paradiso* and the *Amore Attis*. Such an evolution was likely driven by both economic reasons and technical constraints. In particular, the tendency to return to historic recipes was probably favoured by the increasing exploitation of European mines, which made tin more available. From a technical point of view, likely the fluidity and the relatively lower solidification point of bronze with respect to the corresponding brass played an important role.

The working hypotheses formulated in this study will be a foundation for future research. LIPS analysis can provide a major contribution in order to enrich the present picture by extending its spatial and temporal domains and may eventually enable general conclusions on the copper alloys of Renaissance art foundry to be drawn.

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