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The 12th century bronze doors of Bonanno di Pisa in Monreale and Pisa: Materials and manufacture

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A B S T R A C T

Bonanno di Pisa is, next to Barisano di Trani and Oderisius of Benevento, amongst the most renowned mediaeval Italian bronze casters. Bonanno is responsible for the biggest mediaeval metal door, the almost 8 m high main door of the Cathedral of Monreale, Sicily, built in 1185/1186, and the San Ranieri door of the Cathedral of Pisa, Tuscany, finished in 1180. He was also responsible for the Porta Reale (also Cathedral of Pisa; 1179/1180), which was destroyed in the 1595 fire. Contemporary doors made of bronze or brass are rare: from the 12th century, only about 17 doors are still preserved, nevertheless being part of the biggest complex of mediaeval monumental bronzes. In this paper, the chemical composition as well as manufacturing and assembling of the two preserved doors are discussed. Both the Pisa and Monreale doors were made of leaded tin bronze. In the case of Monreale, chemical analysis confirmed the art historical suspicion that the central leaf was not from Bonanno's workshop, as indicated by a different style and chemical composition. We also identified the types of wood used for the wooden elements of the doors, mainly silver fir (Monreale) and elm (Pisa).

1. Introduction and state of the art

At least three bronze doors were created by Bonanno of Pisa and his workshop. Two of these doors have survived to the present day: one in Pisa and the other in Monreale (Mende, 1994; Boeckler, 1953; Buccolieri et al., 2021, 2023; Dräyer, 1961; Martinelli, 1966; Melczer, 1988; Melczer and Salomi, 1990). To the best of our knowledge and art historical research, no other objects from Bonanno's workshop have survived (or been identified as coming from his workshop). The surviving door in Pisa was formerly located in the Porta San Ranieri, the east portal of the south transept of the Cathedral of Santa Maria Assunta and is now kept in the Museo dell'Opera del Duomo. Additionally, another door from the same workshop in Pisa once adorned the main portal until the great fire in the cathedral in 1595 destroyed it (Mende, 1994). It can be reconstructed from written sources that it was also created by

Bonanno of Pisa (Milone et al., 2004). In the cathedral of Monreale, which was built from 1174 onwards following a commission from the Sicilian King William II (1166–1189), the almost 8-m-high main portal is adorned by another door from the Bonanno workshop.

The dimensions of the door of Pisa have been calculated to be 4.7 x 3.1 m. The door comprises a total of 30 panels. Each panel is decorated with a pictorial field that extends across the entire width of the panel at the top and bottom. The panels of the top row display the enthroned Christ on one side and the enthroned Virgin Mary on the other side. The top row, unlike the other rows, consists of three panels (A1, AB1, B1; C1, CD1, D1) on each door leaf. The panels in row 2–6, each consisting of four panels, are populated with scenes from the New Testament. The narrative commences at the lower left with the Annunciation to Mary (Fig. 1) and continues on the right-hand panel before the row above is read. Additionally, the scenes are accompanied by inscriptions in a

combination of Latin and Tuscan [2, 10]. The four panels on the lowest row depict twelve prophets; they are made of two combined, larger panels on each side.

The Monreale door, measuring 7.8 × 3.7 m, is the largest of all known mediaeval bronze doors. The door depicts scenes from the Old and New Testaments in 44 panels. Four monumental creatures, two lions and two griffins, are depicted in a plinth zone. The pictorial cycle commences at the lower left with the creation of Adam and Eve. The lower section of the wings then depicts the stories from the Old Testament in 12 scenes. Above this is a series of prophets, and above these, finally, the stories from the New Testament in 24 panels. In terms of stylistic and iconographic similarities, the door in Monreale bears a striking resemblance to that in Pisa. The door acts as the main entrance of the cathedral and faces inward towards the narthex. The narthex is set apart from the square outside by a sizable iron fence. It was only opened on important occasions, as it required much effort due to its weight, and its wooden hinges caused significant friction with the walls of the wooden seats in which they were inserted. Presently this door has no lock, and so it remains secured using a wooden crossbar.

Both the door in Monreale and the lost one in Pisa have/had inscriptions. On the side of the right wing of the Monreale door, a panel bears the inscription: *Anno domini MCLXXXVI indictione III Bonanus civis pisanus me fecit.* – In the year 1186, in the third year of the indiction, Bonanno, citizen of Pisa, constructed the aforementioned door (Mende, 1994). In contrast, the now lost main portal of Pisa displayed a more extensive inscription on the door: *Janua perficitur vario constructa decore/Ex quo virgineum Christus descendit in alvum/Anno MCLXXX ego Bonannus pisanus mea arte/Hanc portam uno anno perfeci tempore domini/Benedicti operarii istius ecclesie.* In this text, Bonanno identifies himself as the artist, although it is unclear whether he was the caster or the designer of the model. Mende argues in favour of the former (Mende, 1994). Bonanno also boasts that he made the door in just one year, stating, "I, Bonanno of Pisa, completed this door in one year through my art" (Mende, 1994; Boeckler, 1953). Both doors are dated by the inscriptions, Monreale to 1185 (1186 is according to the Pisan calendar) and Pisa to 1179. The surviving door in Pisa lacks an inscription, yet its stylistic, iconographic and formal similarity with the door from Monreale is such that it can be attributed to the Bonanno workshop as well (Boeckler, 1953). It is therefore reasonable to assume that it was made around the same time as the door of the main portal of the cathedral in Pisa.

The Bonanno workshop employed a similar approach as that of Barisanus of Trani, utilising serialised reproduction techniques that enabled the production of multiple doors in a relatively short period of time. Ursula Mende demonstrated that certain motifs recurred in the

scenes and were partly inspired by ancient sarcophagi and sculptures in the Pisan Camposanto (Mende, 1994). The Bonanno workshop employed the lost wax technique to fabricate the doors, and subsequent engraving and punching were also conducted following casting (Boeckler, 1953). As with the Byzantine doors (Buccolieri et al., 2021, 2023), the doors are composed of individual panels held in place by a frame system and nails. In contrast, the panels in Pisa are sculpturally worked, which allows for the manipulation of overlaps, such as the positioning of trees. Furthermore, a conception of pictorial space is evident, which allows for the depiction of multiple spatial levels within a single scene.

The doors lack any silver or niello inlays; the inscriptions have already been applied in wax and were cast together with the panels. The traces of wax treatment are still clearly visible on the bronze surface, both where the surface was smoothed and the line for positioning the letters. Every single plate was cast in once from one wax model, including letters, figures, buildings, etc. The Monreale door was most likely cast in Pisa and subsequently transported to its destination. This is evidenced by the rectangular shape of the door, which contrasts with the pointed arch of the portal opening. It is evident that Bonanno has not been in Monreale and thus was unable to consider the shape of the portal there (Mende, 1994).

The doors have undergone numerous restorations over the centuries. For example, it is recorded that the wooden components of the Pisa doors were replaced in 1541, prior to the cathedral being burned down. It is likely that further reworking occurred, as the order of the panels today no longer corresponds to that recorded by Ciampini in an engraving and a description in 1690 (Boeckler, 1953) (Fig. 2).

1.1. The door from Monreale

1.1.1. Wooden base

The door consists of two identical wooden bearing wings, each made up of four full-height vertical boards held together by 12 horizontally nailed crossbeams (Fig. 3). At first sight, the vertical boards appear to be made of coniferous wood, while the cross beams appear to be made of ring-porous hardwood. The vertical planks, which are on average 15 cm thick, are not rectangular in section, but are designed to interlock with each other to increase stiffness and interconnectivity.

The door hinges, also in hardwood, are set in a lintel to form the centre of the door opening mechanism. They are made separately and attached to the doors by three U-shaped iron brackets. In addition, the doors rotate on an iron ferrule aligned with the hinges located below. This ring operates in a seat in a metal block that appears to be made of lead. The hinges are still fully functional, but after centuries of

	A	B	C	D
1	Christ Pantocrator		Virgin Enthroned	
2	Harrowing of Hell	Women at the sepulchre	Ascension of Christ	Dormitio
3	Maundy	Last Supper	Taking of Christ	Crucifixion
4	Temptation	Transfiguration	Raising of Lazarus	Entry into Jerusalem
5	Presentation at the Temple	Flight into Egypt	Massacre of the Innocents	Baptism
6	Annunciation	Visitation	Nativity and Annunciation to the	Three Magi with Herodes
7	Prophets		Prophets	

	A	B	C	D
1	Virgin enthroned		Christ Pantocrator	
2	Women at the sepulchre	Noli me tangere	Road to Emmaus	Ascension
3	Last Supper	Taking of Christ	Crucifixion	Harrowing of Hell
4	Temptation	Raising of Lazarus	Entry into Jerusalem	Transfiguration
5	Massacre of the Innocents	Flight into Egypt	Presentation at the Temple	Baptism
6	Annunciation	Visitation	Nativity, annunciation to the shepherds	The Three Magi
7	Hosea und Jesaias	Micha und Joel	Daniel and Amos	Ezekiel and Zacharias
8	Sacrifice of Issac	Three patriarchs	Moses and Aaron	Malachi and Bileam
9	Cain killing Abel	Noah's Ark	Scenes of the Life of Noah	Abraham and the Three Men
10	Expulsion	Adam and Eve at work	Raising of Cain and Abel	Cain and Abel in the sheepfold
11	Creation of Adam	Creation of Eve	Adam and Eve in Paradise	Fall
12	Lion and griffin		Lion and griffin	

Fig. 1. Scheme of the two doors made by Bonanno di Pisa. Left: the door from the cathedral of Pisa, Italy; right: the main door of the cathedral of Monreale, Sicily, Italy.

continuous movement without ever being greased, they have worn down and thinned slightly. This results in the audible creaks and resistance experienced during the opening and closing of the door. The iron ferrules at the bottom, on which the entire weight of the door is supported by gravity, were in good condition, as were the metal blocks on which they rotate.

In the lower part of the wings, where environmental degradation factors such as moisture, dirt and dust have been greater over the centuries, the wood has shown signs of wear. In this area, moderate traces of xylophagous insects have been found both on the vertical conifer boards up to 1 m above the ground and on the hardwood crossbeams. Various maintenance and reinforcement works have been carried out in the lower parts in the past, with the addition of wooden cross beams and patches.

1.1.2. Bronze elements

Bronze panels, frames, and rosettes were nailed onto the exterior of the two door leaves, hiding the wooden structure. The lost wax technique was used to cast all of these elements, including panels, plain frames, decorated frames, and rosettes. The panels were originally modelled entirely in wax, featuring figurines and inscriptions. The models were covered with clay and loam, and then left to dry. Once dried, the wax was removed through heat, leaving an empty mould that was then filled with molten metal. The surface required further
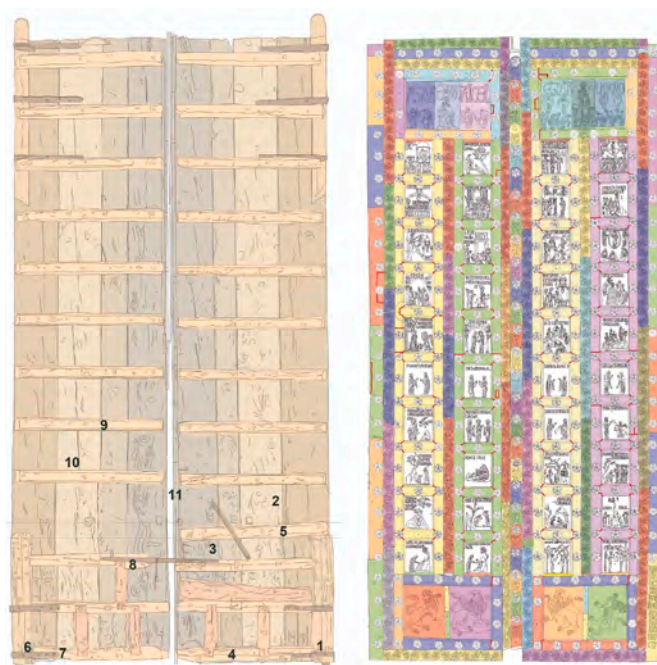

Fig. 3. Monreale. The wooden structure of the door with sampling locations (left) and the different metal elements applied onto it (right). Different colours distinguish the separate elements (© Carlo Usai). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

elaboration after casting (Fig. 4). The frames were cast in individual pieces, perhaps for easier transportation from Pisa to Monreale. They were then joined together by cast-ons from the backside and/or (less likely) welding, likely in Monreale, to form longer, cohesive elements that added rigidity and strength to the door. From a structural point of view, the stability of the bronze elements (frames, panels, rosettes and nails) was still good before the recent restoration works. In some areas, the vibrations caused by the opening and closing of the door had caused some of the panels to slide downwards, hiding part of their figures and highlighting their own upper edge, which should have been hidden by the frames.

Fig. 4. Monreale. Details of the decoration and surface elaboration of panel D6 (the three magi) (© M. Mödlinger/GAPAMET).

1.2. The door from Pisa

1.2.1. Wooden base

The door consists of two wings, each measuring approximately 470 × 150 cm. The supporting wooden structure consists of three vertical uprights, two lateral and one central, each with a section of approximately 22 × 8 cm, connected at the top and bottom by a pair of horizontal beams: the outermost beams are dovetailed, and the innermost beams are half-lapped. Additional horizontal elements connect the uprights at regular intervals along the entire height of the door. The uprights and horizontal beams are positioned to form a grid with dimensions suitable for fixing the individual bronze panels. The entire structure is constructed primarily of diffusely porous hardwood with differentiated heartwood. There are no signs of active or past insect or fungal decay on the wooden elements. Only a few tunnels of *anobium* beetles are present, almost certainly the result of insect migration from the panels that once covered the supporting structure, which were probably made of wood more susceptible to xylophagous attack.

1.2.2. Bronze elements

As the Monreale door, also the Pisa door consists of a wooden base onto which the different metal parts were nailed to. The panels each measure about 37–38 x 44–45 cm in rows 2–6 (20 panels), in the top row about 40 × 105 cm (a total of twice three panels each) and in the bottom row (four panels): 39-40 x 52–55 cm. To cover the borders of the panels, decorative frames were applied and joined together by cast-ons from the backside. Rosette and 'twisted' metal bars cover the joints. The rosettes, moreover, are arranged symmetrically in the corners, left, right, above, and below each panel on the flat, polished frame. As for Monreale, all metal parts were cast using the lost-wax technique. The removal of almost all surface corrosion allowed the precise work to be seen: the figures, animals, trees and building, all modelled separately in wax, were carefully arranged on a flat, smoothed wax plate so that the sharp edges between the different parts remained and could be more easily reworked after casting if necessary. In some cases, the back of the plate is slightly concave in the area where figures have been added, to reduce weight and use less metal for casting, or to correct some casting errors (Fig. 5).

After casting, the surface of the front side of the panels was heavily overworked with the help of chisels, files, ecc. Decoration, such as that of the dresses, was applied by punches and chisels (Fig. 6). The rosettes were cast with an iron nail in the mould, consequently surrounding it perfectly and providing a firm grip of the nail. However, sometimes the nail moved inside the mould and is therefore visible also on the rosette's surface. Also the spiral bars were cast using the lost-wax technique, as indicated by mould residues on their backside (Morigi and Banti,
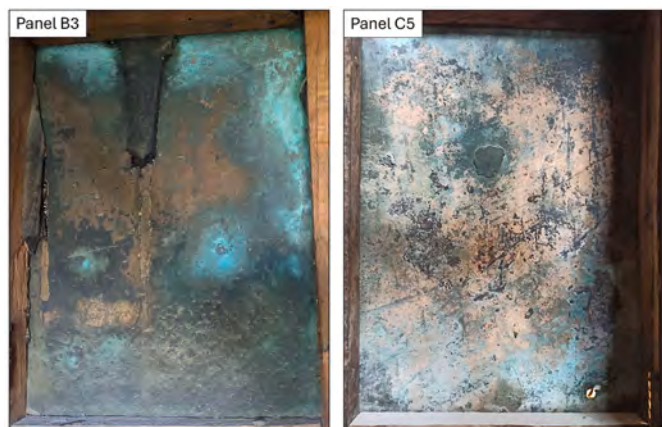
Fig. 6. Pisa, Italy. Details of panel A6 (Annunciation) (© M. Mödlinger/GAPAMET).

1999a). The plane frame elements are rather thin (0.4–0.7 cm) and in some areas joined together, or repaired, by cast-on with the same or a very similar alloy (see for example the analyses D5_11 to D5_15).

On the reverse of the panels, the original casting surface is still

Fig. 5. Pisa, Italy. Backside of panel B3 (left; Last Supper) and C5 (right; Massacre of the Innocents). (© M. Fera/Novetus/GAPAMET).

Fig. 7. Pisa, Italy. Details of panel B6 (Visitation) (© M. Fera/Novetus/GAPAMET).

visible, as are repairs in the form of cast-ons to fill in gaps. The most striking of these is the correction to the figure of Elisabeth in panel B6 (Fig. 7; see also (Morigi and Banti, 1999a)); on the backside, the artist, who carried out the repair and was responsible for the wax model, left his fingerprint on the backside, where we can see the remains of the repair. These corrections can also be seen on the radiographs taken by Alitalia. Other evidence of corrections can be seen on the back of panels B5, C5, D2, D6, and others.

Moreover, residues of the mould material are still preserved: homogenous sampling material, scarcity of fine binding fraction, a sedimentary origin of the clastic fraction from diverse parent rocks, were noted (Bianchetti et al., 1999). In total, six samples were taken, one each from the panels A4, B5, B6, C2, C6, and CD7 and analysed by means of optical microscopy (LOM), as well as Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), and Differential Thermogravimetry (DTG). From the latter analyses, a heating of over 550 °C of the mould material was assumed. All samples consist of very similar material; all noted minerals are, however, commonly found in Tuscany.

2. Conservation work

2.1. Monreale conservation work

The bronze door in Monreale underwent restoration at the end of the 17th century. Some frame elements in the lower part of the door and the inverted lion in the plinth area are dated to this period (Mende, 1994). However, evaluations, analyses, and further works carried out were first documented in 1978/1979. A report of the ICR (Istituto Centrale per il Restauro, Rome) confirms a general good condition of the metal parts and notes four different corrosion types, comprising all paratacamite. In 1988, first restoration works could finally be started by Ignazio Di Bella (Lima and Banti, 1999). These works included: a) removal of dust and dirt; b) mechanical removal of the upper encrusted layers of corrosion; c) cleaning and washing of the bronze surface with distilled water and 2% ammonia using brushes and scalpels (and protecting the wooden support of getting wet); d) stabilising treatment with a 2% aqueous solution of sodium sesquicarbonate; e) final treatment with distilled water until salts were removed; f) dehydration of the surface after each washing with jets of hot air; g) treatment of iron parts with *Feran* and wax (*Hoechst R 21*); h) treatment with benzotriazole; i) application of *Incralac* 5% in *Clorotene*, and a microcrystalline wax (*Hoechst R 21*). Despite this work, 40 years later the doors were in a very poor condition. Further restoration work was therefore required. Restoration of the door began in October 2022 and was completed by one of the authors in July 2023 (C.U.) under the supervision of the Superintendence (soprintendenza) for Cultural and Environmental Heritage of Palermo. In short, the works carried out included: the reparation of the hinges; surface cleaning and execution of different conservation treatments (cleaning, various surface treatments); replacement of missing metal parts; and the restoration of the wooden structure. The results of the work carried out will be published in the near future by the Superintendence.

2.2. Pisa conservation work

An initial assessment of the door was carried out at the end of the 1980s, identifying corrosion products and defects (eddy current analysis, IACS conductivity, microhardness, ultrasound, radiography) and the microstructure (three samples) (Guida et al., 1999a; Baracchini and Banti, 1999). Previous restorations are unknown, but from the remains of the plaster it has been established that at least some of the panels were reproduced in plaster before the 1980s. This probably happened in the 1960s and in the mid-19th century (Baracchini and Banti, 1999). The first restoration of the door was carried out between 1991 and 1993 by Morigi Restaurations (Morigi and Banti, 1999a, 1999b). All incrustations, polishing paste, wax and corrosion down to the first layer of cuprite were removed mechanically, the surface treated with

benzotriazol in alcohol (3%) and finally covered with a thin layer of Paraloid B.72 (Morigi and Banti, 1999b). Six missing rosettes were reproduced and patinated with liver of sulphur.

3. Methodology

3.1. Photographic documentation

To support the documentation of the analyses on the doors, a thorough photographic record of them was made using a methodological approach similar to that used for the bronze doors of San Marco, Venice and the doors from San Zeno, Verona (Mödlinger et al., 2023, Mödlinger et al., 2024a). The main goal was to establish a basis for precise measurements by capturing details of both the geometric features and surface textures. In addition to taking high-resolution close-up images of individual panels, both doors were documented using image-based modelling techniques, as described in (Mödlinger et al., 2024b).

For our documentation purposes the workflow consisted of the coverage of the entire objects by handheld photography utilising a Ricoh GR IIIx digital camera, equipped with a lens with a normal focal length (26.1 mm, 57° diagonal angle of view) and an RGB primary colour CMOS sensor (23.5 × 15.6 mm, 24.24 megapixels, pixel pitch 3.9 μm). The installation of the original door in Pisa in a museum presentation room required the use of artificial light sources. In addition to the museum lighting provided by rows of halogen spotlights installed on both sides of the object in the room, additional indirect illumination was achieved by 100 W LED spotlights with a colour temperature of 5600K directed at the ceiling and floor of the room. In Monreale the environmental natural dispersed light at the location at the western side of the Monreale Cathedral could be used for this purpose.

The images in Pisa were taken alternately with the measurements, using the scaffolding that had been erected for this purpose. The images were shot approximately vertically to the surface in horizontal rows with at least 60% overlap. In accordance with the measurement strategy, the height of the scaffolding platform was successively reduced from top to bottom and the images of the row at the according height were taken sequentially. In total, the object was covered with 1321 camera positions at a distance of about 95 cm. In Monreale the camera was mounted on a 5 m telescopic carbon pole, utilising an electronic gimbal for stabilisation. Due to a larger distance to the object (around 2 m) the larger area of this door was covered by 1255 approximately vertical images with sufficient overlap for further processing.

The door in Pisa is attached to a steel construction on the back for the museum presentation. This made it possible to access not only the constructive parts of the wooden frame but also the backs of many panels. The accessible areas were photographed in a very cramped space, so that a geometric model of parts of the wooden construction as well as views of the backs of some panels could be captured.

The data processing was carried out using Agisoft Metashape software (version 1.7.2). Scale was established by measuring specific distances on the object, and scaled poles (horizontal and vertical) were included in the acquired photographs to serve as reference scale bars during processing. The resulting digital surfaces were used to define a projection plane for the generation of an orthomosaic for each door. For Monreale a sampling distance on the object of 0.28 mm was achieved and a true orthophoto with a pixel size of 0.28 mm was exported. The smaller Pisa door was processed with an object sampling distance of 0.13 mm and a true orthophoto with this pixel size was generated.

3.2. Chemical analyses and principal component analysis (PCA)

The chemical composition of the metal parts was determined using an Oxford Instruments portable ED-XRF analyser, specifically model X-MET5100 with a high-resolution detector, 45 kV and max 50 μA Rh target X-ray tube. Measurements were made at 40 kV voltage, 10 μA current and 60 s acquisition time with spot measurements of

approximately 9 mm in diameter. Quantitative analysis detected alloying elements such as Cu, Sn, Zn and Pb, while other elements (Fe, As, Ni, Sb, Ag) were at first only qualitatively identified due to surface corrosion layers (Heginbotham et al., 2010, 2015) but later considered quantitatively for the PCA, based on the metallographic results. Sulphur was not detectable by this method. Calibration standards were made from alloys of different chemical compositions produced by the researchers (Mödlinger et al., 2023). The metal panels of each door were analysed in 5–10 (panels) or up to five (frame elements and other smaller metal elements) different areas to determine the average chemical composition of each panel.

Only after we carried out chemical analyses, the door in Monreale was restored in autumn 2022 under the supervision of the Superintendence (*soprintendenza*) for Cultural and Environmental Heritage of Palermo. The results of the restoration will be published by the *soprintendenza*. At the time analyses were carried out, the surfaces were severely degraded, with a patina of varying thickness (up to 2 mm in some areas) mainly consisting of bronze's corrosion products, which bonded with atmospheric dust to form thick and hard ochre crusts, obscuring many of the details of the figures and distorting the overall appearance of the bronze. The higher up the doorway, the more apparent the phenomenon became. Nevertheless, the crust provided a protective layer for the underlying metal, albeit an unsightly one. Furthermore, certain regions showcased active corrosion, identified by sublime efflorescence (copper chloride), resulting from the metal's interaction with salt from the nearby sea. For analyses, these heavy corroded areas were avoided whenever possible. Consequently, the XRF-analyses are well comparable with SEM-EDS analysis on metallographic samples from selected panels carried out by some of the authors (M.M.; G.G.; these results will be published by the *soprintendenza* in the near future).

A univariate and a multivariate approach were employed in order to achieve the desired results. For each panel and each variable, a mean, standard deviation, and variance were calculated and are presented in Table S1. This analysis revealed a notably low degree of variability for each panel (except for: Pb and Fe for panel CD and Zn for panel C7 of the Monreale door; Fe of panel A6 and Sb for panels A1 and A2 of the Pisa door), which suggests a good consistency and reliability in the measurements. A multivariate analysis was therefore performed on the data matrix according to a previously described protocol (Mödlinger et al., 2024a). The anomalous variance values were elucidated through an investigation of the correlations between the variables and the points of analysis, which were conceptualised as a multivariate system. Furthermore, the majority of decorative elements, including plain frames, decorated frames and rosettes, that were excluded from the univariate analysis, preventing a comprehensive chemical comparison between panels and decorative elements were included in a Principal component analysis (PCA). PCA was indeed capable of capturing relationships between multiple variables simultaneously, thereby revealing interactions and dependencies that a univariate approach might fail to identify. The PCA purpose is to extract as much information as possible from the multivariate data structure by representing it as linear combinations of variables. It transforms the original data set into a new geometric space where the x-axis represents the first principal component (PC1), the y-axis represents the second principal component (PC2), the z-axis represents the third principal component (PC3), and so on. Each axis is aligned with the largest variance in the data. This rotation allows a meaningful representation of the data set in terms of its maximum variance. The results of the PCA are presented in two graphical representations: loadings and scores. The loadings matrix shows the importance of each original variable within each eigenvector (new axis of the principal component space), while the scores matrix shows the projections of the samples in the newly defined space. The analysis was performed using CAT (Chemometric Agile Tool) software after centering and autoscaling the raw data (Heginbotham et al., 2010).

3.3. Wood analyses

The wooden structures of both portals were subjected to observations and studies in order to verify (Mende, 1994) the species composition (Boeckler, 1953), the feasibility of dating the elements using dendrochronology, and (Buccolieri et al., 2023) the presence of ongoing biotic attacks affecting the wooden structures.

For the Monreale door, where it was possible to collect micro-fractions, 11 structural elements were sampled: 6 from the left panel and 5 from the right panel (Table 1, section 4.3). Sampling was carried out using surgical scalpels, operating in the most concealed areas and taking advantage of cracks and splits in the wood where possible. The samples were subsequently prepared in the laboratory, cut into thin slices (approximately 50 μm), oriented according to the three anatomical directions, and examined under a transmitted light optical microscope (Olympus CX 41) at 40X, 100X, and 400X magnifications. The species were identified by comparing the observed structures with the anatomical descriptions given in the main texts on wood anatomy, according to the relevant UNI standard (Guglielmo, 1981; Nardi, 1994; Norma UNI 11118, 2004; Schweingruber, 1990).

The eight vertical boards of the door, being made of coniferous wood, would have been excellent material for dendrochronological investigations aimed at dating the timber. Unfortunately, unlike other doors analysed (Mödlinger et al., 2023), the cross-sections of the boards here were inaccessible, and the longitudinal sections were very rough, covered with patinas and dust. This made it impossible to measure the widths of the rings and thus to attempt to date the wood.

For the Pisa doors, micro-invasive sampling was prohibited, so observations were made on the wood on the back of both wings using a Dino-Lite portable microscope. The Dino-Lite was connected directly to a laptop with a resolution of 2592×1944 pixels and a magnification of 200×, allowing us to assess the main anatomical features of the wood and identify the species.

In this particular case, the main objective was to confirm and possibly extend previous studies on the species composition of the woods used, taking advantage of the accessibility of the door's supporting structures, which are currently free of the coverings and panels that covered the back of the door at the time of the initial studies. The wooden structure of the Pisa Door precludes any dendrochronological study, as it is made up of elements with small cross-sections made from wood species unsuitable for this purpose.

4. Results and discussion

4.1. Photographic documentation

For documentation and analysis purposes, as well as for dissemination, the orthomosaics were processed in a geographic information system (GIS), visualised and exported as true-to-scale images (Figs. S1 and S2).

Table 1
Micro-fragments collected from Bonanno's door in Monreale, their localization and the identified wood species. Right and left refer to the door as seen from the front. For the exact location of the various samples, see Fig. 3.

Sampling no.	Specie	Name
1	*Castanea sativa* Mill.	Sweet chestnut
2	*Abies alba* Mill.	Silver fir
3	*Abies alba* Mill.	Silver fir
4	*Castanea sativa* Mill.	Sweet chestnut
5	Gen. *Ulmus*	Elm
6	*Castanea sativa* Mill.	Sweet chestnut
7	*Castanea sativa* Mill.	Sweet chestnut
8	*Castanea sativa* Mill.	Sweet chestnut
9	*Abies alba* Mill.	Silver fir
10	Gen. *Ulmus*	Elm
11	*Celtis australis* L.	European nettle tree

Due to the very different surface conditions of the two doors discussed here, different, individually adapted strategies were necessary for the recording. The corroded and dirty surface of the door from Monreale, before the restoration, did not present any significant problems for a pictorial recording and a detailed reconstruction of the 3D surface (Fig. S3). For reasons of processing time, a surface with a resolution was generated that best met the objectives of creating an orthophoto of the entire object. The highly metallic, shiny surface of the restored door from Pisa, which is on display in a museum, required a shorter shooting distance, and therefore a larger number of images (with smaller coverage). This largely avoided shiny areas on flat surfaces, and the high resolution of the images and the micro-details they captured meant that geometric reconstruction was largely possible without problems. However, on concave sculptural figures and decorative elements, shiny spots could not be avoided. A visual comparison shows errors and artefacts in the generation of the detailed surface on the door of Pisa compared to the door of Monreale (Fig. 8, surface relief visualization on the left).

A setup with cross polarisation was not feasible on site, as the loss of light on the reflective metallic surface proved to be too great. Nevertheless, it was possible to obtain the geometry to a sufficient extent so that the generation of an orthomosaic in the desired quality was possible (Fig. 8, detail of the orthomosaic of the same section on the right).

4.2. Chemical analysis and principal component analysis (PCA)

4.2.1. Chemical analysis

The chemical results obtained for the doors of Monreale are corroborated by chemical analyses conducted by SEM-EDXS by some of the authors (M.M.; G.G.) on metallographic and drilling samples from panel CD1 (Monreale) for the *Soprintendenza per i Beni Culturali e Ambientali di Palermo* (soon to be published by the *Soprintendenza*). The comparison also showed that even though the doors are heavily corroded, the amount of Cu, Sn, and Pb measured by XRF matches well

(± 0.5 wt%) the SEM-EDXS results. Selected metal elements of both doors have already been analysed in the past; the alloy of the door from Pisa was found to be almost identical to that from Monreale (Guida et al., 1999b).

This was also confirmed by our most recent analyses: both doors were made of leaded tin-bronze. They both contain about the same amount of Sn (9–18 wt%, Fig. 9). Notably, some metal parts from Monreale contain less than 9 wt% Sn: these are usually parts containing also Zn, and are likely connected to more recent periods, such as several rosettes and the central door section covering the gap between the two door leaves, which is also stylistically completely diverse (see below). Also, several undecorated sheets on the left of some C-Panels (C2, C3, C4, C9, C12) contain >25 wt% Zn; some additionally added "covers" to the frames in panels of row 11 (A11, B11, C11, D11, all below) and row 2 (panels B2 and D2, top), as well as some rosette (below 5 wt% Zn), contain noteworthy quantities of Zn, and were likely not part of the original door made by Bonanno. Only two of the analysed rosettes from the Pisa door contain significant amounts of Zn; they are recent copies. Opposite to the Sn, the Pb-amounts vary notably between the two doors: while in Monreale usually only 1–5 wt% Pb were used, the Pb amounts measured in Pisa are significantly higher: most of them are found between 6 and 14 wt%. This is also similar to the more recent, central door section covering the gap between the two Monreale door leaves: here, Pb-amounts between 2 and 17 wt% were measured, but also about 1–9 wt% Zn. No clear grouping of these elements is visible.

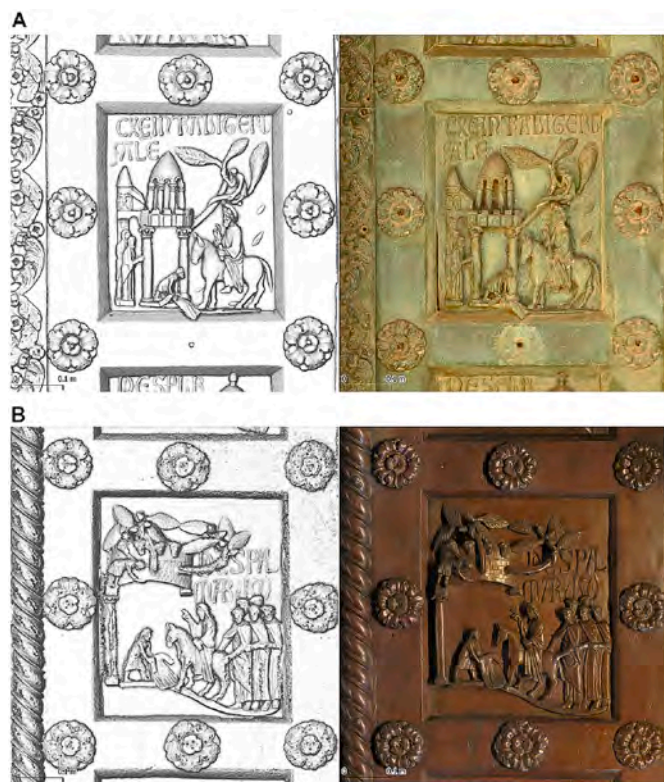Monreale's large central door leaf, highly decorated and in a rather

Fig. 8. A: Monreale, Italy, B: Pisa, Italy. Details of processed and visualised digital surface (left) and the corresponding orthophotos (© M. Fera/Novetus/GAPAMET).
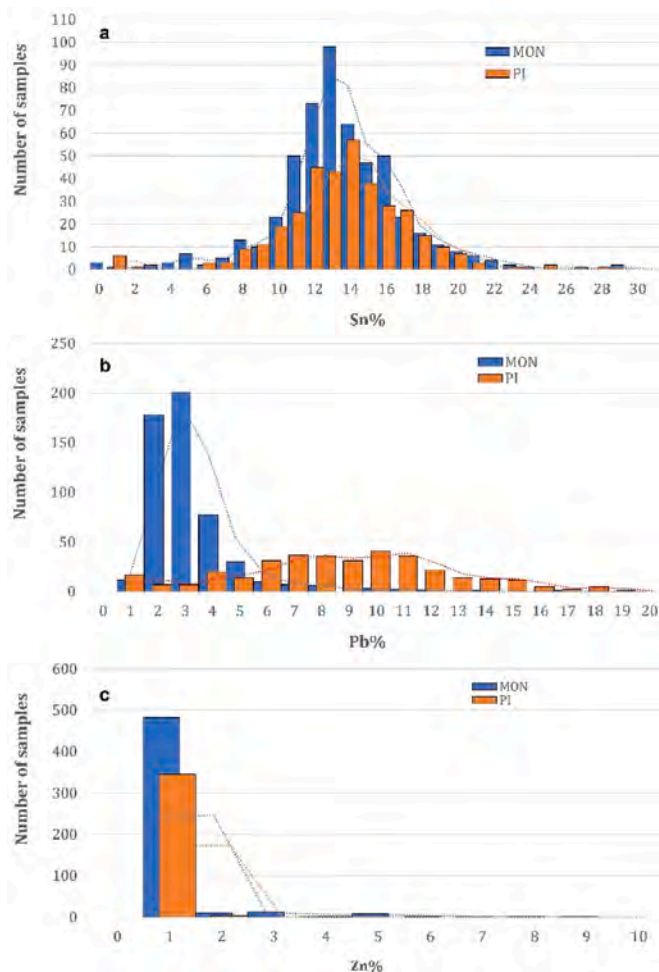

Fig. 9. Frequency distribution of the main alloying elements from the XRF analyses of the two doors analysed (MON=Monreale; PI=Pisa): **a)** Sn; **b)** Pb; **c)** Zn.

refined manner, in a different style from the rest of the door, is not related to Bonanno's intervention. Chemical analyses confirm this assumption, showing that these parts are made of a quaternary alloy, and not, like the rest of the metal parts of the door, of leaded tin bronze. Likely, these metal parts were not cast in Pisa in Bonanno's workshop, but at a later point in Sicily, perhaps in Palermo, to close the relatively wide central gap between the two wings when they are closed.

Metallographic analyses of panel A9 from Monreale show that the panel was cast, annealed and finally cold worked, while the part of the letters is an as-cast (Guida et al., 1999b). This was also confirmed by analyses of some of the authors (M.M.; G.G.) on another panel from Monreale. Metallographic analyses were also carried out on the doors from Pisa (Lima and Banti, 1999): three samples were taken for metallographic analyses (spiral element, bottom right corner, left wing (sample a); frame below panel B5 (sample b); panel D6, bottom right corner (sample c). Sample (a) shows a recrystallized microstructure with light deformation, α+δ eutectoid of the Cu-Sn system still present; sample (b) shows a semi-recrystallized microstructure with light deformation (slip lines) and partly visible dendritic structure, pointing to only slight/short annealing; Sample (c) shows also a semi-recrystallized microstructure with light deformation (slip lines) and partly visible dendritic structure. Hardness measurements carried out by the same authors show for instance for panel A7 hardness values of 182 HV, while in the back values reach a maximum of 129 HV, indicating the impact of the elaboration of the front side's surface.

4.2.2. PCA

Due to the large amount of data obtained from the two doors, a principal component approach was adopted: the data were arranged in a matrix of 884 rows (analysis points) and 4 columns (major alloying elements, Fig. S4a). In order to ascertain the number of statistically significant principal components, the Broken Stick model was employed (Johnson and Wichern, 2013). However, the scree plot of the analysis resembled a straight line (not visible), which could be indicative of a lack of significant variance structure in the data. This may be attributed to two factors: poor distinction between the eigenvalues of the principal components and high dimensionality of the data, which is characterised by a considerable amount of noise (Johnson and Wichern, 2013). Accordingly, in light of the metallographic findings, it was deemed appropriate to consider the minor elements on a quantitative basis. The principal component analysis (PCA) entailed the examination of a

comprehensive data set comprising 884 rows and 9 columns, encompassing all alloying elements. In accordance with the Broken Stick model, the initial three principal components were chosen. Fig. S4b shows the biplot of the entire data set obtained from the XRF measurements.

The data are arranged in a single macrocluster (both blue and orange points, defining Monreale and Pisa door respectively, partially overlap), with some anomalies located at a considerable distance from the main cloud. These also preclude the possibility of distinguishing the average composition of the individual doors. The points situated to the left of the principal cloud (III and IV quadrants) are evidently outliers and thus excluded from further consideration. The Monreale door points iron_1 and iron_2 correspond to iron bars. The points designated B7_17 and C6_13 of the Pisa door, originating from the C6 and B7 panels, respectively, exhibit an anomalous Pb content (ranging from 52 to 99 wt%), indicative of a soldering spot on the panel resulting from a subsequent repair. The plot resulting from the principal component analysis (PCA) of the raw data, excluding the anomalous values, is presented in Fig. 10.

The presented graphs confirm the consistency in composition of the two doors, with the main cloud still present and points that deviate from the average composition of the doors located in the upper quadrant, exhibiting a variation in coordinates along PC2. This is predominantly ascribed to the variables Sb and As. The majority of these analytical points (A1_5, A1_6, A1_7, A7_11, A7_12, B1_6, B2_1, B2_2, B2_3, B2_4, B2_5, B2_6, B2_7, B2_8, B2_9, B2_10, B2_11, B2_12, B3_10, B7_11, B7_12) originate from the Pisa door and present an average Sb content between 2 and 7.5 wt% (vs 0.9 wt% average of the door). The majority of XRF measurements corresponding to these points were obtained from either the frame structure or decorative elements of the framing system, including rosettes and 'twisted' metal bars. They display a composition which is compatible with the use of a different alloy. Also the panel B2 displays a composition consistent with that of a quaternary alloy (78.8 wt% Cu, 10.1 wt% Sn, 7.2 wt% Pb and 2.6 wt% Sb), which diverges from the average composition of the entire door. Additionally, one point from the Monreale door (23_3) falls into this category. Given its known attribution to a more recent decorative element, this observation prompts the question of whether panel B2 may also represent a more recent element, a reconstruction of the original panel, or a consequence of Bonanno's selection of an alternative alloy. Seemingly, an alternative alloy was selected, as the arsenic content is significantly higher (up to 1.5 wt % vs. LOD) compared to that present in the recent decorative
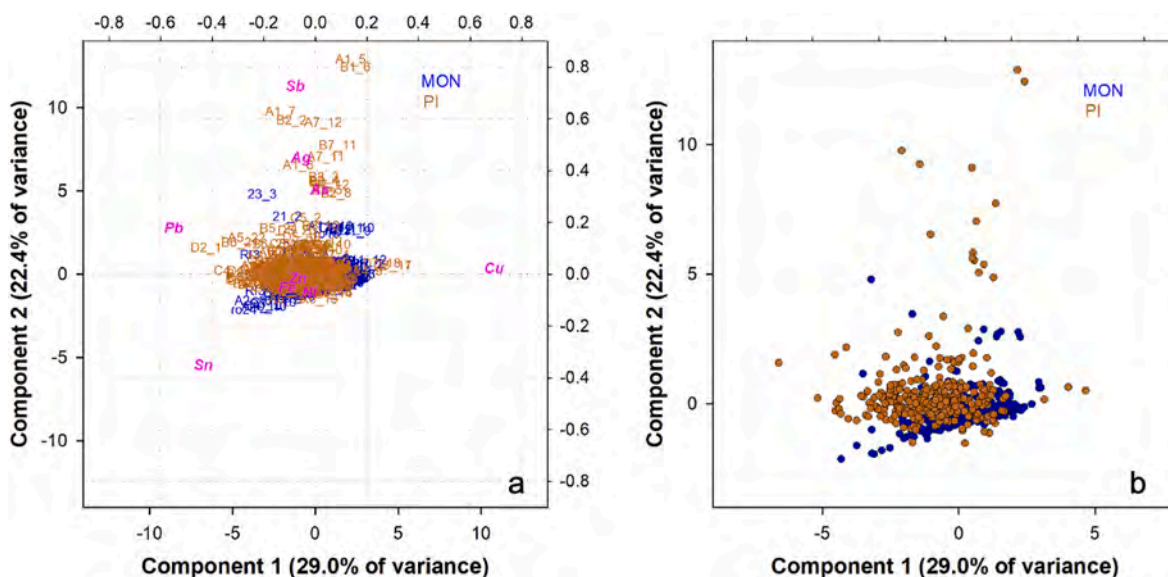

Fig. 10. PCA computation on the matrix of the XRF analyses without anomalies carried out on the doors (PC1 vs PC2, total explained variance of 51.4%): MON-=Monreale; PI=Pisa. a) biplot; b) score plot.

element of the Monreale door.

A more comprehensive analysis was subsequently conducted, focusing exclusively on the panels comprising the doors, with the objective of further investigating any compositional anomalies or similarities. Fig. 11 illustrates the findings of the PCA conducted on the panels alone.

The graphs illustrate the presence of two macroclusters. The larger cloud, closer to the centre point, encompasses the majority of the panels from Pisa and a portion of those from the Monreale door. The smaller cloud, situated towards the lower right (II quadrant), exhibits a distinctive composition, characterised by a higher Fe and Zn content and a lower Pb content in the alloy. This is evident from the observation that points of analysis exhibiting a lower content of these elements are located far from the variables, while those with a higher content are situated closer to them. A detailed examination of each variable, corresponding to a single element, reveals that the panel elemental composition of each door is, with few exceptions, consistent (Fig. 12). The Pb content, however, deviates from this pattern.

The univariate analysis indicates that the concentration of Pb is the sole factor responsible for differentiations in the panel composition. A normal distribution curve with a peak at 2–3 wt% is evident in the Monreale door, whereas a quasi-uniform distribution curve is discernible in the Pisa door, spanning a range of 4–18 wt% of Pb, when compared to the other door. Additionally, several points from the Pisa door are situated at a considerable distance from the primary cloud (upper left or IV quadrant). These points (A5_22, B5_24, B6_21, B6_25, C5_2, C5_20, D5_20, D5_23), some of which have been previously discussed (panel B2, points B2_1, B2_2), exhibit a notable Sb content that exceeds the average for the door (0.9 wt% of Sb).

The two doors exhibit a high level of production of decorative elements. Consequently, it was resolved to compute individual PCA for each door with a view to identifying clustering of decorative elements (with a particular focus on panels and frames) or possible anomalies in the alloy composition (differences in the average alloy composition between panels depicting scenes from the Old or the New Testament). Fig. 13 displays the PCA computation on the Monreale Door.

As previously discussed, the composition of the Monreale door is notably homogeneous, as evidenced by the PC1 vs. PC2 graph. The XRF points of analysis are concentrated on a main macro cluster located at the centre of the axes, with some points distributed towards the variables Sb, Zn, Ag and Pb, and some towards Fe and Sn. It is evident that point 23_3 is an outlier, representing a more recent decorative element
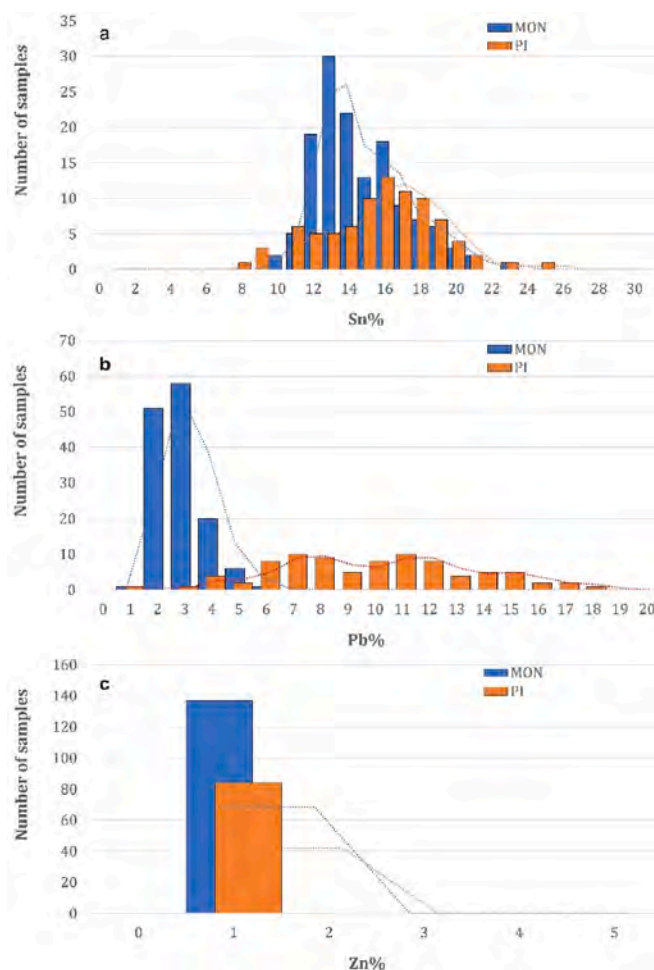

Fig. 12. Frequency distribution of the main alloying elements from the XRF analyses of the panels of two doors analysed (MON=Monreale; PI=Pisa): a) Sn; b) Pb; c) Zn.

(central part, left wing). Similarly, point 21_2 also falls into this category. However, the second rosette from the top left of panel A11 (point ro_24) and the points A2_10 and A10_10 (both plain frames), represent
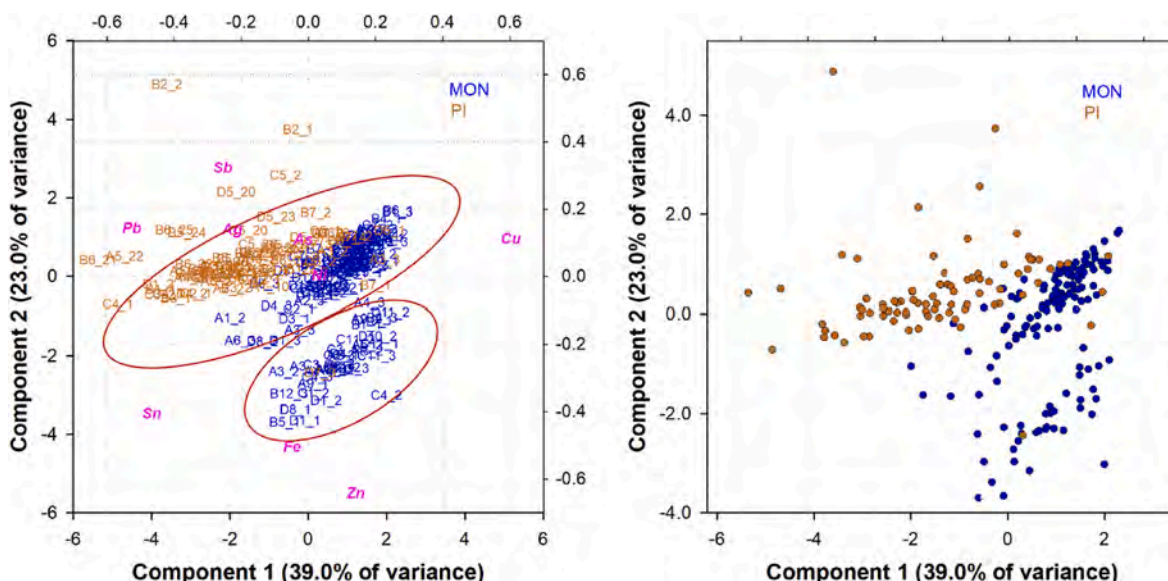

Fig. 11. PCA computation (PC1 vs PC2, total explained variance of 62.0%) on the panels of the doors: MON=Monreale; PI=Pisa. a) biplot; b) score plot.
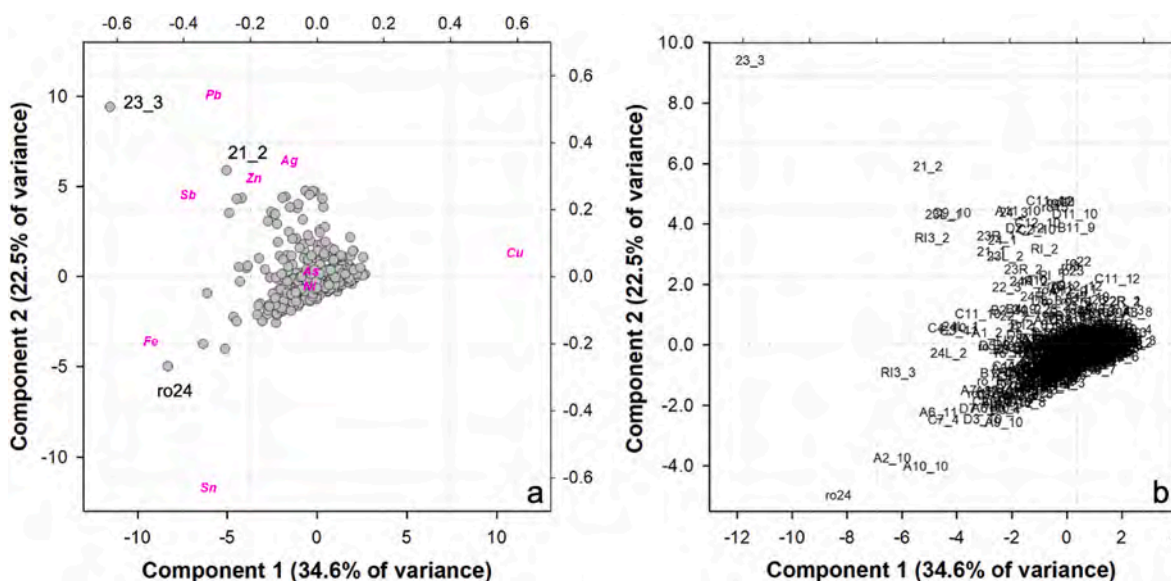
Fig. 13. PCA computation (PC1 vs PC2, total explained variance of 57.1%) on the XRF analysis on the Monreale door: a) biplot; b) score plot.

an anomaly that requires an alternative explanation. The values obtained from these analyses are the result of contamination from the iron structure (nails, bars) that was applied to reinforce the door as their Fe content varies between 3.5 and 5.9 wt %. It is noteworthy that the PC1 vs. PC3 graph (total explained variance of 52.8%, not visible) depicts a supplementary minor cluster situated proximate to the variable Zn. This cluster encompasses a few frames and some of the plain frames (B2_10, C2_10, C3_11, C4_10, C9_10, C11_10, C12_10, D2_12, see Fig. 14) that exhibit a Zn content markedly elevated in comparison to the remainder of the objects (approximately 30 wt% on average). Likely, this can be attributed to a replacement procedure conducted during previous restoration works.

A more detailed examination of the panels (in red) and frames (in black) is provided in Figs. 15, which illustrate the principal component analysis (PCA) and the univariate analyses carried out for each major alloying element.

The results of both analyses corroborate the previous interpretation,

namely that the composition exhibits a consistency that is evident in the PCA (both biplot and score plot), with all points arranged in one cluster distributed along the PC1, which is mostly explained by the variables Cu and Sn. It can thus be postulated that the panels and frames originate from a single alloy, as evidenced by the overlap observed in the frequency distribution plot for all the major elements under consideration. The principal component analysis (PCA) identifies points that deviate from the mean composition of the frames. As previously discussed, points B2_10, C11_10, and D2_10 are replacement parts. Points A1_2, B11_9, and D11_10 exhibit partial contamination with iron from the reinforcing frame, though to a minor extent.

A principal component analysis (PCA) was also conducted on the Pisa door, and the resulting data are presented in Fig. 16.

The majority of the XRF data are clustered in a single group around the centre point, which suggests a narrower window of compositions. Furthermore, all anomalies identified in the graph have been previously discussed. B7_17 and C6_13 are identified as soldering spots resulting
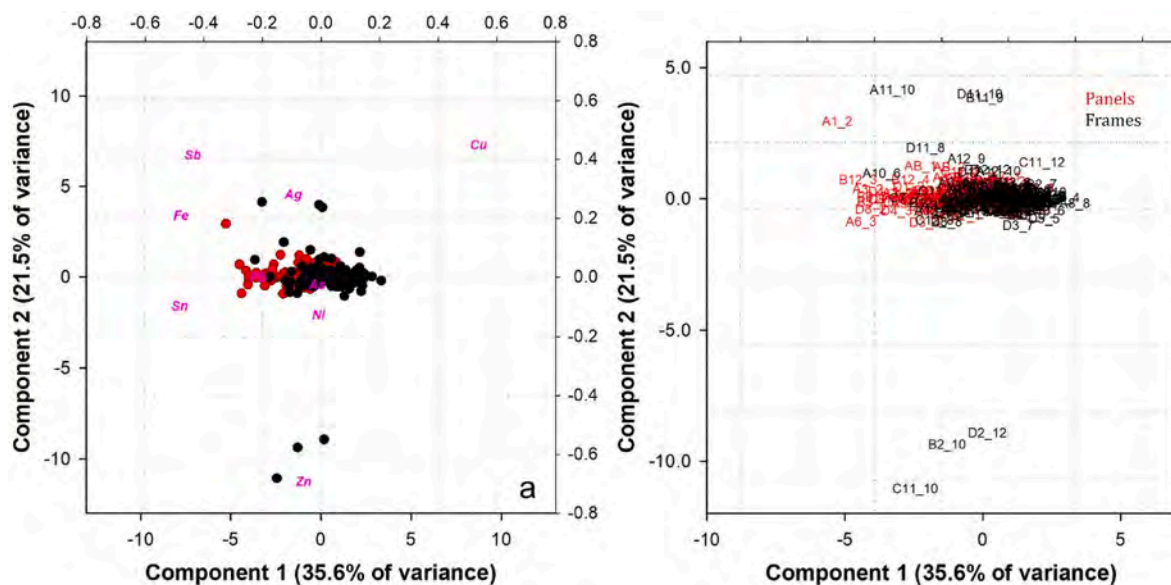

Fig. 14. PCA computation (PC1 vs PC2, total explained variance of 57.1%) on the XRF analysis of panels (red) and frames (black) on the Monreale door: a) biplot; b) score plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
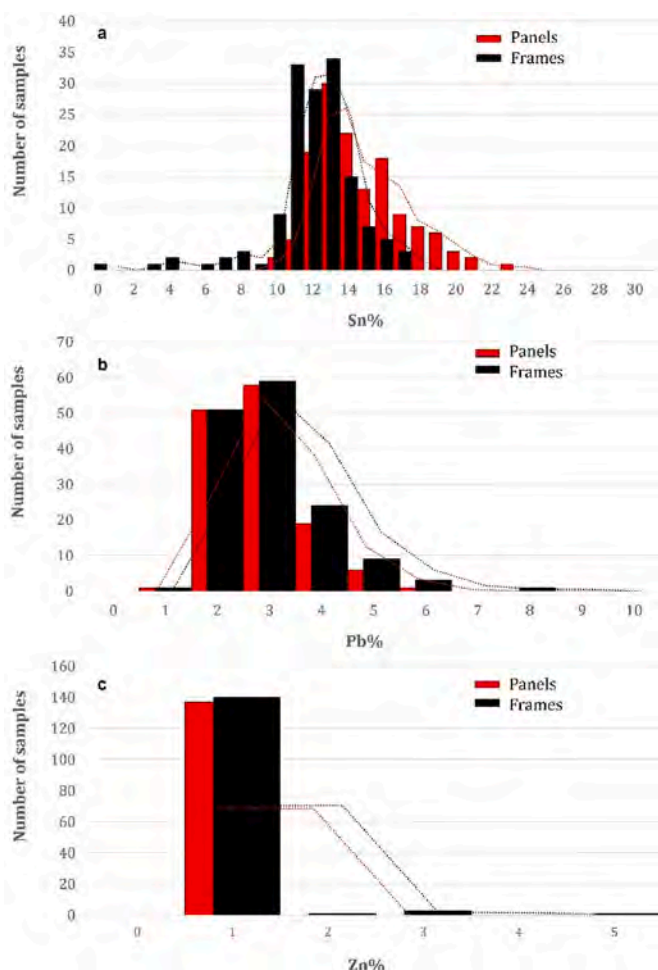
Fig. 15. Frequency distribution of the main alloying elements from the XRF analyses of the panels (red) and the frames (black) of the Monreale door: a) Sn; b) Pb; c) Zn. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

from repairs. Points A1_5, A1_6, A1_7, A7_11, A7_12, B1_6, B2_1, B2_2, B2_3, B2_4, B2_5, B2_6, B2_7, B2_8, B2_9, B2_10, B2_11, B2_12, B3_10, B7_11, B7_12 are consistent with the use of a quaternary alloy rich in Sb. A further computation was thus performed, considering only the panels (in red) and frames (in black), as was done for the Monreale case (Fig. 17).

The data presented in Figs. 18 enables a more detailed analysis of the compositional differences between the panels and frames. A macro cluster is displayed in the graph and is distributed along an imaginary line that connects the variables Cu and Sn, Pb. This demonstrates that the composition of the panels and frames of the door is connected to the amount of Sn and Pb in the alloy. Moreover, the macrocluster is sub-divided into an upper section, which predominantly comprises the frames, and a lower section, which encompasses the panels. Additionally, the frequency distribution plots illustrate a differentiation in the mean composition of the two objects (Fig. 18).

The Sn frequency plot displays a bimodal distribution, which models both the panels and the frames. This suggests the presence of two dominant sets of data points. However, the two peaks are not in alignment and exhibit a discrepancy in Sn content, with the panels displaying a lower concentration (12 wt % compared to 16 wt % for the frames).

Some of the measured points on both panels and frames deviate from the main cluster towards the variables Ag, As and Sb, indicating an enrichment of these elements in the alloy. The following measurements are excluded from the discussion: A5_22, B5_24, B6_25, C5_2, D5_20; B2_1, B2_2 (panels) and A1_5, A7_11, A7_12, B1_6, B3_10, B7_11, B7_12 (frames). The Sb content of points B7_1 and B6_21 is higher than the average composition of the door. B6_21 has a higher Sb content due to the measurement point being taken in the letters of the plate inscription. Points B7_1 and B7_2 show a composition of a quaternary alloy, indicating that a Cu-Sn-Pb-Sb alloy was used for the plate B7.

4.3. Wood analysis

The analyses on the Monreale door revealed a mixed composition of softwoods and hardwoods, confirming the initial deductions made through visual observations (Table 1).

The large vertical boards are made of white fir (Fig. 19), a wood traditionally used for this type of application, as well as for beams and marine masts due to the considerable heights it can reach (up to 60 m). The white fir is widespread in Europe and Italy at altitudes between 500 and 1900 m. There is another closely related endemic species, the
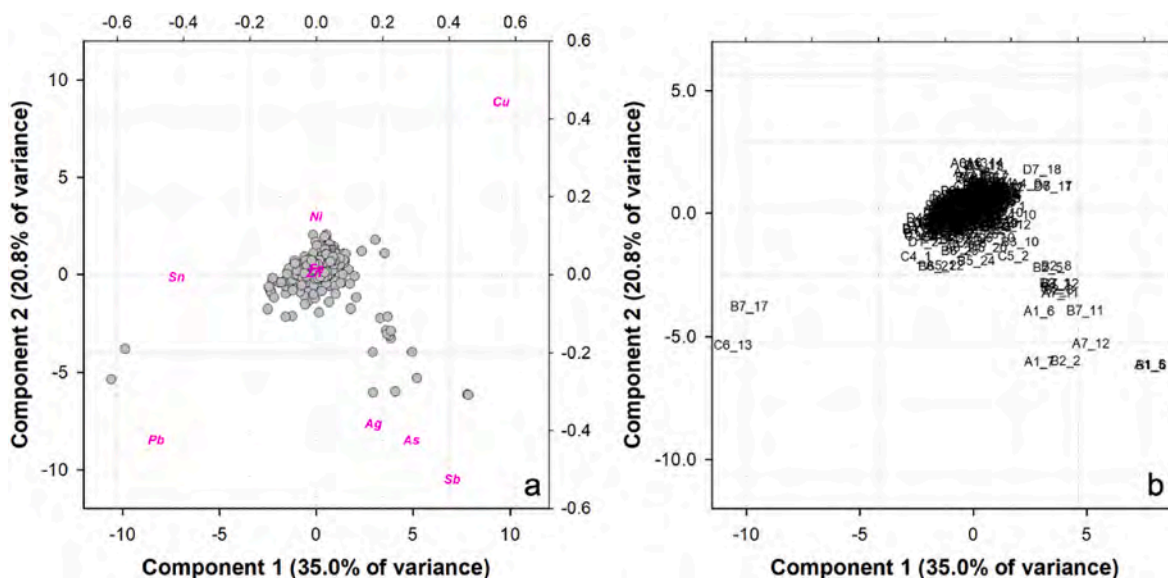

Fig. 16. PCA computation (PC1 vs PC2, total explained variance of 55.8%) on the XRF analysis on the Pisa door: a) biplot; b) score plot.
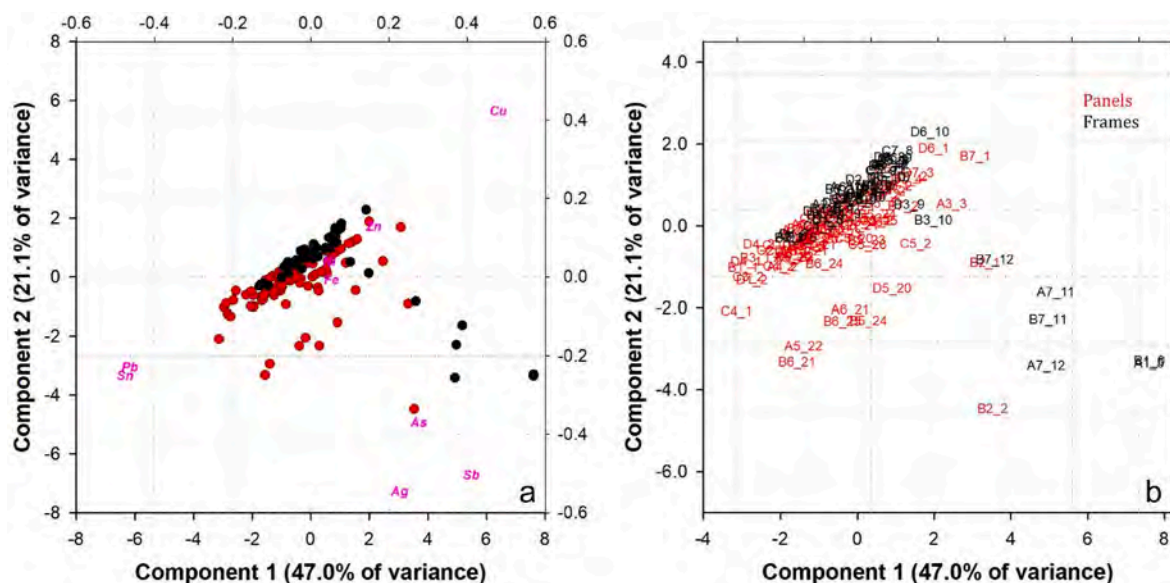
Fig. 17. PCA computation (PC1 vs PC2, total explained variance of 68.1%) on the XRF analysis of panels (red) and frames (black) on the Pisa door: a) biplot; b) score plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
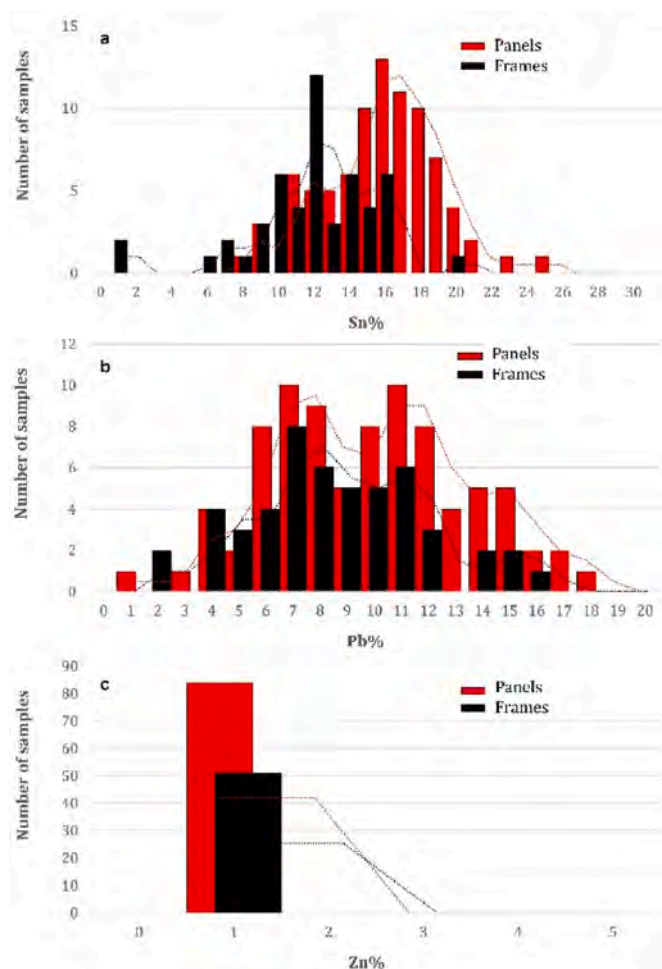

Fig. 18. Frequency distribution of the main alloying elements from the XRF analyses of the panels (red) and the frames (black) of the Pisa door: a) Sn; b) Pb; c) Zn. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Sicilian fir (*Abies nebrodensis (Lojac.) Mattei*), exists in Sicily. This species was thought to be extinct for a long time. Anatomically, it is impossible to distinguish between the two firs, but the generally smaller size of the Sicilian fir makes it unlikely to have been used. It is worth noting that, due to the excellent technological characteristics of this wood, the transport and trade of white fir has been very active since ancient times. It is well known that much of the white fir found in the archaeological excavations of Pompeii and Herculaneum came from the Alps, present-day Austria, or Central Europe (Kuniholm et al., 2002).

The investigated crossbeams and the wooden elements constituting the lower pivots of the two panels were all made of chestnut elm (Fig. 19, below and Fig. 20).

In both cases, these woods were and still are, chosen for their excellent mechanical properties, remarkable stability, and durability; they are used in particular in carpentry for the construction of beams, structures in general, and carriage work. Finally, it is worth mentioning the use of a less common type of wood, such as nettle, which is used for the element that forms the stop between the two panels. With a density of 960 kg/m3, this wood also has excellent mechanical properties and shock resistance. In the past, it was used to make carriages, agricultural and sports implements and fine whips (Fig. 20 below).

Regarding the Pisa door, on-site observations with the Dino-Lite confirmed that the entire structure is essentially made of elm wood. Some anatomical features that can be observed even at low magnification, such as the dark parenchyma rays that stand out in radial sections and the wavy bands of axial parenchyma that form a characteristic pattern in transverse or subtransverse sections, make the identification of this species quite easy even without the need for micro-sampling (Fig. 21).

There are a few exceptions to the predominance of elm wood: some of the horizontal joints between the uprights are occasionally made of chestnut wood and, exceptionally, even of pear wood (*Pyrus communis* L.) (Nardi Berti, 1986). The entire structure of the Pisa door is intact and has not suffered any significant attack from decaying agents, thanks to the use of durable woods, mainly elm and chestnut, and to the careful workmanship that has removed all the sapwood (the outer, lighter part of the trunk), which is easily attacked by xylophagous insects.

5. Conclusions

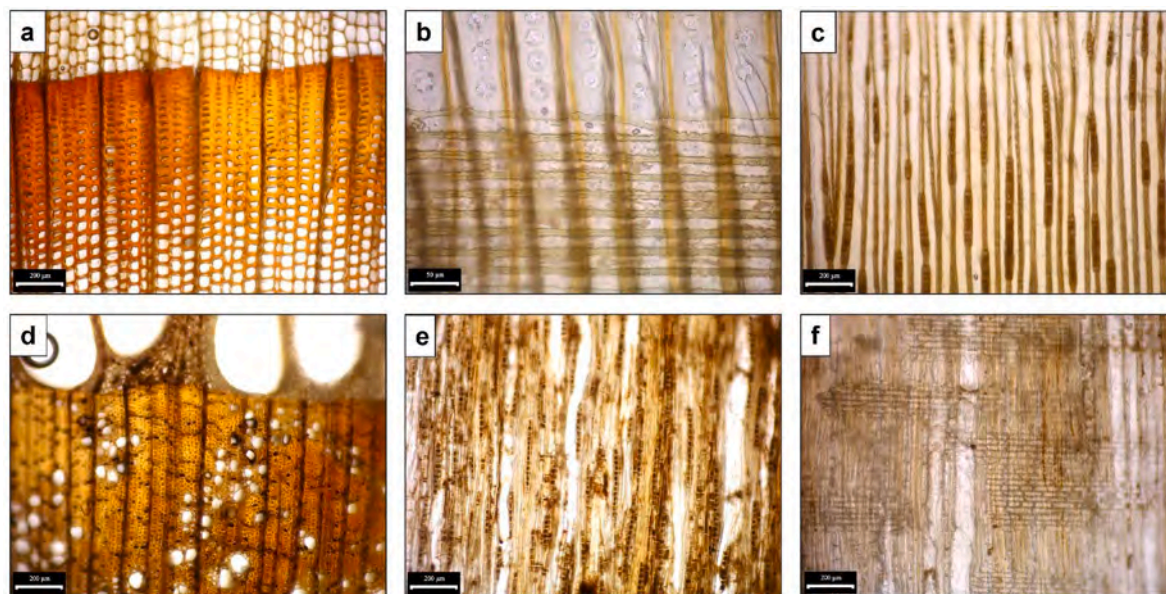Given the iconographic similarities between the two doors, it has

Fig. 19. Monreale, Italy. Analyses of wood samples from the door. Top row, from left: transverse section (100X), radial section (400X), and tangential section (100X) of sample 3. Identified species: white fir. Below, from left to right: transverse section (100X), radial section (100X), and tangential section (100X) of sample 7. Identified species: chestnut.
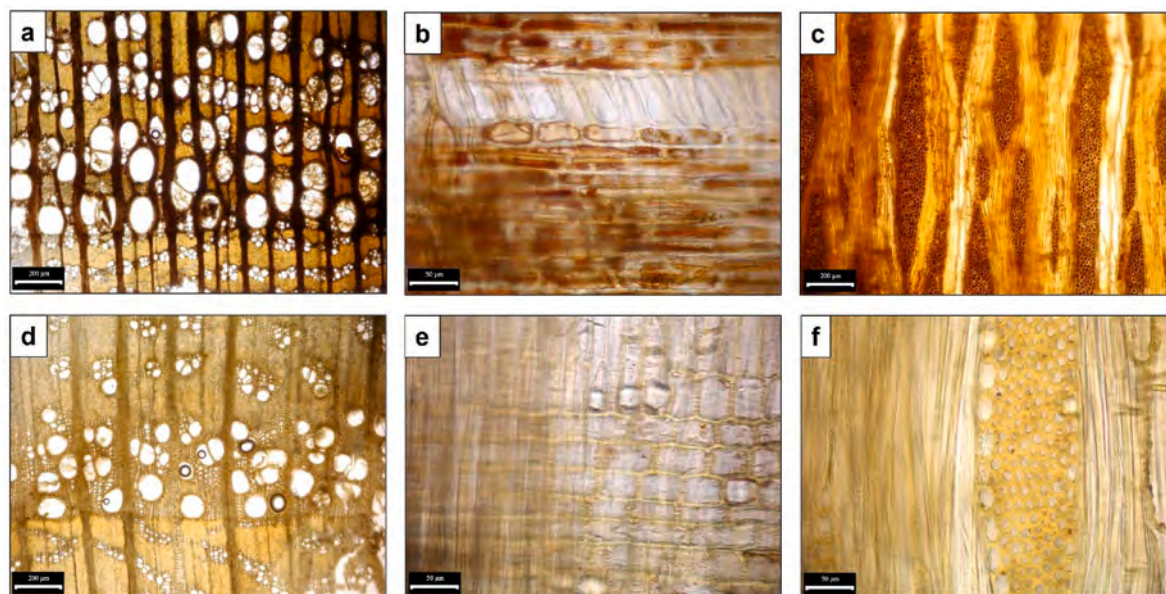

Fig. 20. Monreale, Italy. Analyses of wood samples from the door. Top row, from left: transverse section (100X), radial section (400X), and tangential section (100X) of sample 5. Identified specie: elm. Below, from left: transverse section (100X), radial section (400X), and tangential section (400X) of sample 12. Identified species: European nettle tree.

long been thought that both the signed door in Monreale and the unsigned door in Pisa must have come from the workshop of Bonanno of Pisa. However, the alloys used for the production of the two doors are so different that it is likely that the doors were not made at the same time. The Monreale door, dated 1185, is probably younger than the surviving Pisa door, which must have been made around the same time as the lost Pisa door in 1179. Furthermore, material analysis has shown that the centrepiece of the Monreale door was made later and is unlikely to have come from the Bonanno workshop.

The metal parts of the Monreale door are made of leaded tin bronze and contain approximately 80–90 wt% Cu, 9–18 wt% Sn, and 1–5 wt% Pb. The last component is most likely oxidation products from the iron nails of the door. The central leaf is not related to the Bonanno castings,

as indicated by a different style and chemical composition (a quaternary alloy of Cu, Sn, Zn and Pb); neither are several undecorated elements with high Zn content and smaller additional protective elements in front of some panels. Like the Monreale door, the Pisa door was made of leaded tin bronze. However, the Pisa doors contain 6-14 wt% Pb and thus more than the Monreale doors, while the Sn amounts are quite similar at 10–18 wt%. Most of the frames and decorative elements from the Pisa door exhibit a compositional arrangement that indicates the utilisation of an alternative quaternary alloy with a high Sb content (2–7.5% by weight), analogous to that employed in the production of the B2 and B7 panels. This observation leads to the hypothesis that the alloy was derived from copper-antimony bearing minerals. Cu contents range from 63 to 87 wt% (both frame elements and panels) for Pisa and 60–90
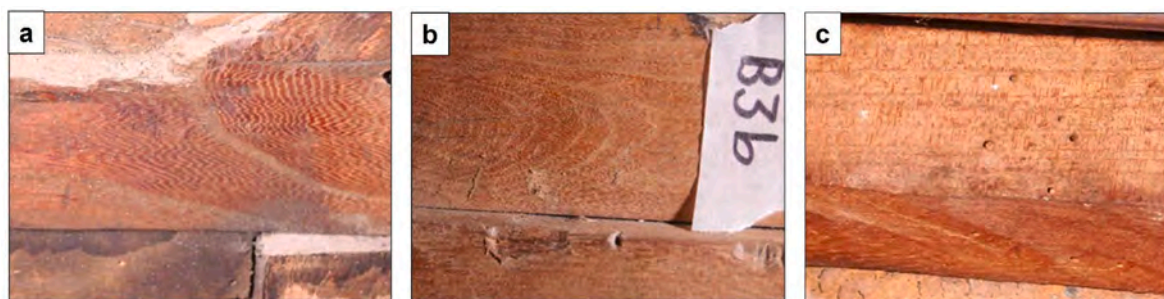
Fig. 21. On the left and in the centre are two sub-transverse surfaces showing the characteristic wavy light lines due to the particular distribution of axial parenchyma. On the right is a radial surface highlighting the parenchyma rays, visible as thin and short dark lines.

wt% for Monreale (again including frame elements, panels and recently added, non-original parts). There is no difference in the average alloy composition between panels depicting scenes from the Old or the New Testament.

The wood of the two doors has remained structurally intact thanks to their sheltered location from meteorological phenomena, the choice of wood species that are resistant or highly resistant to decay, and the careful machining of the structural elements, which has eliminated all traces of sapwood. The portals have thus been constructed with great skill, taking advantage of the characteristics of the wood species that are particularly suitable for this purpose. It is significant that for both doors, despite the very different geographical and cultural contexts, the most mechanically stressed supporting elements are essentially made of the same two species: chestnut and elm. For both doors, but for different reasons, it was not possible to carry out dendrochronological studies to date the wood, and therefore it was not possible to determine with certainty the date of construction of the wooden structures.

The chemical analyses carried out on Bonanno's door, as further analyses on contemporary doors, are also available on the project's open-access database at https://gapamet.imareal.sbg.ac.at/en. By mid 2025, the high-resolution photographic documentation of both doors will be also available under the same URL.

Links

XRF-results of Bonanno's door in Monreale, Italy: https://gapamet.imareal.sbg.ac.at/api/attachment/XRF_MONREALE_main.xlsx.

XRF-results of Bonanno's door in Pisa, Italy: https://gapamet.imareal.sbg.ac.at/api/attachment/XRF_PISA.xlsx.

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CRediT authorship contribution statement

M. Mödlinger: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **M. Bassi:** Writing – review & editing. **J. Bontadi:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **M. Fellin:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **M. Fera:** Writing – review & editing, Writing – original draft, Visualization, Software, Investigation, Formal analysis, Data curation. **M. Negri:** Writing – review & editing, Formal analysis, Data curation. **C. Usai:** Writing – review & editing, Writing – original draft, Visualization. **J. Utz:** Writing – review & editing, Writing – original draft, Supervision. **G. Ghiara:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jas.2024.106130.

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