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Original article

# First insights on the mineral composition of “stucco” devotional reliefs from Italian Renaissance Masters: investigating technological practices and raw material sourcing

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## ABSTRACT

The production of devotional reliefs particularly flourished in 15th century Florence, where models from Renaissance Masters actually became the object of a serial-production. One of the materials mostly used to this purpose was the so-called “stucco”. This preliminary work focuses on the multiscale structural and compositional analysis of micro samples from 22 representative stucco low reliefs attributed to the workshops of renowned Masters. The identification and characterisation of main mineralogical phases showed that the material used to make these reliefs consists in a gypsum-based plaster. Data from both X-ray diffraction and Particle induced X-ray emission allowed to gather also information on secondary mineral phases (sulphates, carbonates and clay minerals, together in few weight percentage maximum) and trace elements. Through an extensive comparison of all the mineralogical and compositional data collected on the corpus of artworks, first insights on workshop practices and raw material used have been enlightened.

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## 1. Introduction

Besides the recurrent use for architectural decorations and mouldings, many different objects kept in museums are catalogued under the generic term of “stucco”. It is for instance the case of numerous devotional polychrome reliefs produced during the Italian Renaissance (mainly in the 15th century Florence), by the workshops of Masters such as Ghiberti, Donatello, Luca della Robbia, Desiderio da Settignano and Antonio Rossellino. These artworks were intended to satisfy an increasing demand for domestic devo-

tional objects from wealthy and rising middle class families [1–3]. Several fine examples of these objects (Fig. 1), generally representing iconographic variations of the Madonna and Child or related religious subject, are nowadays displayed or stored in museums, private collections as well as sold on the art market [4,5]. Such a large number of reliefs (more than 70 catalogued just in French public collections) [3] were most likely obtained by moulding from an original model, generally in marble, bronze or terracotta, or from one of its direct replicas. These reliefs were then reproduced in series, probably by casting several replicas obtained with stucco mixture or other mould materials (e.g. the above-mentioned terracotta and cartapesta) [1,6,7]. They were subsequently gilded, painted, framed and then sold on a large scale, influencing analogous productions in the rest of Italy [7,8]. The standing hypothesis is that most of these reliefs were produced in Florence either in

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**Fig. 1.** Three examples of studied stucco devotional reliefs: a: after Antonio Rossellino, Madonna and Child (called “Madonna of the Candelabra” (Louvre Museum, Inv. Camp. 20); b: after Benedetto da Maiano, Madonna and Child (Strasbourg Fine Arts Museum, Inv. 507); c: after Donatello and others, The Nativity (Lyon Fine Arts Museum, Inv. D 488) ©Louvre Museum and C2RMF.

the own sculptors workshops or in other production workshops [1,8]. Furthermore, even if these sculptors were mostly active in Florence and surrounding areas, some of them were reported to be also active in other parts of Italy [1,3,9]. Doubts on manufacturing centres still stand also due to the possibility that other workshops, starting from a known original, replicated/copied the same model. This situation of debated authorship and multiple replicas of the same models became even more complex when, during the second half of 19th century, these objects became highly demanded from academies, collectors and art dealers. As a consequence to that, some scholars claim that several late copies, or even forgeries, could have been introduced to enlarge this lucrative market and eventually ended up in private or public collections [1,4,7,9–11].

Talking about the constitutive material of these artworks, the so-called “stucco” was particularly suitable for this kind of serial production because of easy manufacturing and relatively inexpensive raw materials. As a matter of fact, the term “stucco” generally defines a class of composite materials used in monuments and artworks for the creation of rendering sculpture and ornamentation [12–14]. Reading both ancient treatises and scientific literature on the topic, it is clear that there was not a single recipe for this kind of material: variations occurred according to geographic areas, material availability and applications [9,15–18]. These materials, also generically referred to as plasters, are formed by a lime- and/or gypsum-based binder creating a matrix, which can contain mineral fillers/aggregates (e.g. calcite, marble powder, sand, brick fragments, etc.) and variable quantities of organic additives (e.g. glue, resins, oils, fibres, etc.) [12,14,19]. The above-mentioned devotional reliefs were most likely made with a form of gypsum-based plaster also called, in Italian, “gesso”. Gypsum plasters are in fact considered ideal mould making materials. Gypsum is obviously their main constituent. This mineral (calcium sulphate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )) occurs widely in Tuscany and its noble fine grained form is known as alabaster. By heating gypsum to a temperature of about  $120^\circ\text{C}$ , part of the water is lost and bassanite ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) is obtained. This latter form, once ground and mixed with water, allows to obtain again  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  that forms a solid matrix [12,14,19,20]. On the one hand, literature dedicated to the most common architectural stucco and plasters has been quite prolific [12,17,18], on the other hand, only few organized studies dealt with this specific kind of stucco artworks [1,7,11,21]. Most of them focused on art history and conservation issues, while just few scientific works report on the analysis of at best some artworks. Therefore, despite the wide diffusion of these objects, exact details about their constitutive materials and manufacturing processes are nowadays fragmentary and not exhaustively investigated.

### 1.1. Research aims

A systematic study has been carried out to shed more light on the Renaissance production of stucco devotional reliefs focusing on the crucial period of the 15th century, especially in the Florentine area. As potential indicators for different centres of production and eventually of late copies, three main related issues had to be solved:

- the identification and characterization of materials constituting the “stucco”;
- the provenance of the raw material;
- the understanding of manufacturing techniques adopted.

This paper presents the first outcomes about the study of the constitutive mineral materials used to produce 22 representative artworks from Renaissance masters. To this aim, the first objective was to identify and characterise the binder and to determine the presence of eventual mineral fillers in the stucco mixture used. A multianalytical approach by means of Field Emission Gun Scanning Electron Microscopy (FEG-SEM) and X-ray Diffraction (XRD) provided the identification, the structural and morphological characterization of mineral phases. For deeper insights, compositional data on both major, minor and trace elements were obtained by using particles induced X-ray emission (PIXE).

## 2. Materials: micro samples from historical stucco reliefs

A total number of 22 reliefs have been selected and sampled as a starting point for the study. The studied reliefs are displayed or stored at the French Louvre Museum in Paris, Fine Arts Museum of Strasbourg, Fine Arts Museum of Lyon and the Renaissance Museum of Ecoen. They were chosen considering their relevance and their representativeness both from the point of view of the supposed dating (ranging from early 15th to 16th century), the stylistic features and the attribution to different workshops. Detailed information are reported in Table 1 where artworks are ordered according to workshops attribution. Amongst these reliefs, 18 are catalogued as coming from the workshops or “after” original models of Ghiberti, Donatello, Luca della Robbia, Desiderio da Settignano, Mino da Fiesole, Antonio Rossellino and Benedetto da Maiano. Three other reliefs, without precise authorship or attribution to a workshop, have been studied as well. They are considered stylistically compatible and then catalogued as made during the 15th century (Inv. 244 and Inv. 246) and 16th century (RF 564). Out of the 22 artworks, 17 are low reliefs, while 5 are high reliefs.

**Table 1**

List of the 22 stucco reliefs studied and sampled for analysis in this work. The artworks have been regrouped by artist/workshop and then listed according to chronological order. For each artwork, attribution details and dimensions (H, height; W, width; D, depth) are also reported when available. In the right part of the table, results of the XRD analysis and FEG-SEM examinations are reported. Inventory numbers correspond also to samples codes.

| Workshop                   | Date                                  | Attribution | Artwork<br>(Dimensions in cm)                       | Sample<br>(Inventory number) | XRD<br>Secondary crystalline phases <sup>a</sup> | FEG-SEM<br>Gypsum crystals shapes                                  |
|----------------------------|---------------------------------------|-------------|---|------------------------------|--|--|
| Ghiberti<br>Lorenzo        | Florence, 1378–1455                   | Workshop    | Madonna and Child (H. 64; W. 55; D. 205)            | RF 786                       | dolomite, celestine                              | prismatic, rounded shaped  |
|                            |                                       | Workshop    | Madonna and Child (H. 65; W. 44)                    | Inv. 239                     | anhydrite, calcite, dolomite                     | massive, tabular, not well formed                                  |
| Donatello                  | Florence, 1386–1466                   |             | Madonna and Child, holding pomegranate              | RF 896                       | anhydrite  | prismatic, tabular   |
|                            |                                       | After       | Madonna and Child, type Pazzi (H. 68; W. 52)        | Inv. 242                     | anhydrite, dolomite                              | prismatic, rounded, not well formed                                |
|                            |                                       | After       | The Nativity (H 77, W79, D 10)                      | RF 1191                      | calcite, dolomite                                | prismatic, lammellar, swallow tails, contact twins, rounded shaped |
| Luca Della<br>Robbia       | Florence, 1399/1400–1482              | After       | The Nativity (H: 76 W: 76, D: 9)                    | D 488                        | anhydrite, calcite, dolomite                     | prismatic, tabular, needle, lamellar                               |
|                            |                                       | After       | Madonna and Child, type Massimo (H. 67; W. 50)      | Inv. 247                     | anhydrite, dolomite                              | prismatic, tabular, lamellar                                       |
|                            |                                       | After       | Madonna and Child, type Turin (H. 62; W. 38; D. 40) | RF 897                       | anhydrite, calcite, dolomite                     | needle like, lamellar, rounded                                     |
| Desiderio da<br>Settignano | Settignano, 1430–Florence, 1464       | After       | Madonna and Child, type Turin (H. 62; W. 40)        | Inv. 586                     | anhydrite, dolomite                              | massive, rod shaped  |
|                            |                                       | After       | Madonna and Child, type Turin                       | D 489                        | anhydrite, calcite, dolomite                     | lamellar, prismatic  |
|                            |                                       | After       | Madonna and Child, type Turin                       | D 489                        | anhydrite, calcite, dolomite                     | lamellar, prismatic  |
| Mino da Fiesole            | Papiano 1427, Florence 1484           | After       | Bust of woman, Virgin of Annunciation, type Kress   | RF 588                       | anhydrite, calcite, dolomite                     | prismatic, lamellar  |
| Antonio<br>Rossellino      | Settignano?, 1427/1428–Florence, 1479 | After       | Madonna and Child, Vienna                           | Camp. 16                     | nd   | prismatic  |
|                            |                                       | After       | Madonna and Child, type St. Maria Nova              | Camp. 19                     | anhydrite, calcite, dolomite                     | massive, prismatic, tabular  |
|                            |                                       | After       | Madonna and Child, type St. Maria Nova              | Inv. 362                     | anhydrite, calcite                               | prismatic  |
|                            |                                       | After       | Madonna and Child, called Madonna of the Candelabra | Camp. 20                     | calcite, dolomite                                | tabular, prismatic, (not well formed)                              |
|                            |                                       | After       | Madonna and Child, called Madonna of the Candelabra | 1937–4                       | anhydrite, calcite                               | lamellar   |
| Benedetto da<br>Maiano     | Florence?, 1442–1497                  | Workshop    | Madonna and Child, called Madonna of the Candelabra | DS534                        | anhydrite, calcite, dolomite, celestine          | tabular, prismatic, massive  |
|                            |                                       | Workshop    | Madonna and Childt, type Kress (H 115 m; L. 65)     | RF 1169                      | calcite  | massive, rod shaped  |
| Florence 15th<br>century   | Maiano, 1442–1497                     | After       | Madonna and Child, type Scarperia                   | Inv. 507                     | calcite  | lamellar, swallow tails  |
|                            |                                       |             | Madonna and Child                                   | Inv. 244                     | anhydrite, calcite, dolomite                     | prismatic, needle  |
| Florence 16th<br>century   | 15th century                          |             | Madonna and Child                                   | Inv. 246                     | anhydrite, dolomite                              | tabular, prismatic, needle   |
|                            | 16th century (1st half)               |             | Madonna and Child carried by angels                 | RF 564                       | calcite, celestine, dolomite                     | lamellar, swallow tails  |

<sup>a</sup> Formula and ICDD files: anhydrite, CaSO<sub>4</sub> (01-080-6360); calcite, CaCO<sub>3</sub> (01-071-3699); dolomite, CaMg(CO<sub>3</sub>)<sub>2</sub> (01-071-3697); celestine, SrSO<sub>4</sub> (00-005-0593).

Prior to the sampling, a careful survey was performed in order to prevent any risk and to minimize the quantity of sample collected from the reverse and non-decorated side of the objects. In fact, almost all of these reliefs are painted and/or gilded and some of them were mounted in wooden frames limiting accessible areas for sampling. When possible, the sampling areas were selected close to visible cracks or in areas that already presented conservative issue avoiding any risk of damage. At the same time, it was necessary to be careful not to sample material used for restoration or conservative purposes that could mislead the following analysis. Micro samples (approximately 100 mg of powder and few mm<sup>2</sup> size flakes) were taken by using a tungsten carbide micro-drill and a scalpel. In Fig. 1 (Annexes), an example of sampling points is shown for one of the studied reliefs. Sometimes visible differences in the material seem to suggest a stratigraphy of different plaster layers due to different mixtures used for specific needs of the manufacturing procedure. On some artworks (RF 1191, D 488, 1937–4, DS 534, Inv. 507, Inv. 244), sampling was repeated in different area and at different depths of the object: first, to check whether a single sample can be considered as representative for the material of the

whole artwork and second, to verify the actual presence of several layers of stucco.

### 3. Methods

A multianalytical protocol was carried out in order to have both structural and compositional characterization of the samples. Non-destructive techniques were chosen. The few mm<sup>3</sup> flakes with a fresh fracture surface were firstly examined by means of optical microscopy to assess their colour, heterogeneity, presence of contaminants or to isolate the presence of organic fibres often used during manufacturing processes [12,16,19]. FEG-SEM was used to study and record microstructures of the stucco binder and other eventual mineralogical phases. On the other hand, pellets (5 mm diameter) were prepared with powders to obtain simultaneously bulk elemental analysis of major, minor and trace elements by means of PIXE measurements. XRD measurements were performed on small quantity of powder dispersed with ethanol on a micro-scope slide.

### 3.1. Experimental set up

#### 3.1.1. Field emission gun – scanning electron microscope

Fracture surfaces were coated with a 1.6 nm Pt film and examined with a FEG-SEM JEOL 7800F in secondary electrons (SE) mode at a voltage of 2 kV and current of 0.1 nA. For a first recognition of the mineral phases, qualitative EDX analyses were also performed at a voltage of 7 up to 10 kV.

#### 3.1.2. X-ray diffraction

The X-ray diffraction pattern were acquired with a Bragg-Brentano (Cu K $\alpha$ 1,  $\lambda = 1.5406 \text{ \AA}$ ) PANalytical XPert Pro diffractometer between  $4^\circ$  and  $60^\circ$  with a  $0.02^\circ$ , 1.4 s step and 52 min acquisition time. The databases of the International Centre for Diffraction Data (ICDD) and the Crystallography Open Database (COD) were browsed to identify the phases.

#### 3.1.3. Particle induced X-ray emission

The measurements of elements from Na to U were performed at the AGLAE 3 MeV proton external beam of the C2RMF laboratory in Paris. This micro-probe relies on a 5 EDX-SDD detectors system for major and trace elements analysis. The system was particularly conceived for the analysis of cultural heritage samples [22,23]. Analyses were performed by scanning over selected area of  $1 \text{ mm}^2$  with a beam size of  $25 \text{ }\mu\text{m}$ . Secondary filters of  $50 \text{ }\mu\text{m}$  Al and  $200 \text{ }\mu\text{m}$  Mylar were used to filter the more important contribution of some elements (particularly major contributions of the matrix) and enhance the detection of minor and trace elements. The spectra obtained were quantitatively analysed to obtain data on elemental composition by means of the GUPIXWIN (version 2.2.3) and TRAUPIXE programs [24]. A set of reference standards for calibration were used with the pivot procedure normalization between major and trace elements concentrations by using Ca as pivot. To adjust the processing parameters, the Dr-N (Diorite) geo-standard provided by CRGP was used. Four gypsum certified reference samples by DOMTAR $\text{\textcircled{R}}$  were used as references for CaO/SO $_3$  ratio. In the following, the C and H $_2$ O contributions will not be taken into account. Precision is below 1% for major elements and 5% for traces according to uncertainty calculation [25].

Bulk chemical analysis was performed on an average area of  $1 \text{ mm}^2$  on the pellets made with the powders issued from micro drilling and exempt of large grains according to elemental mapping. Nevertheless, the representativeness of these measurements had to be questioned since both chemical and microstructural heterogeneity of gypsum-based materials, can slightly bias results [26,27]. To verify this assumption results from both different samples of the same artworks and repeated measurements on the same samples were compared. Indeed, concentration values obtained by repeated analyses on different areas of the same sample (Table I Annexes) (e.g. RF 896, RF 588, Camp. 16, Camp. 19, Camp. 20, RF 564) appear quite homogeneous for major element with some wider variation for trace elements. The same can be said of values measured on samples taken from different parts of the same artwork (Table II Annexes) (e.g. RF 1191, D 488, Inv. 507, 1937-4, D5534, Inv. 244). To facilitate the reading of results in the following, average values will be reported (see Table 2 in Section 4).

## 4. Results

### 4.1. FEG-SEM-EDX

By means of OM samples observation, various aspects were examined. Colour, heterogeneity (e.g. presence of black or red to brown grains), presence of contaminants and organic fibers, have been taken into account. The overall examination of these aspects

alone did not allow so far to pull out features or patterns related to specific artworks or workshops. Hence, the investigation was carried out by means of FEG-SEM.

The main and recurrent features were synthetically reported for all the samples in Table 1. Considering the large variability observed from one sample to another, and even in different areas of the same sample, a selection of the most representative SE images was reported in Fig. 2. EDX qualitative analysis allowed identifying the ubiquitous presence of crystals characterised by high contents of Ca, S and O compatible with gypsum matrix. A wide variety of different microstructures, crystal arrangements and morphologies of the gypsum binder were observed in SE images. Crystal habits vary from acicular, as recurrently described in literature [14,19,27], columnar to tabular (Fig. 2a) or in some case in massive form (Fig. 2b). Sometimes prismatic subhedral crystals are visible (few to  $10 \text{ }\mu\text{m}$  length), while other samples present smoothed morphologies (Fig. 2c). Swallow tails and lamellar habits are also often observed (Fig. 2d). In other cases, crystals exhibited hexagonal plates or lenticular habit, or were found to be globular, short and rounded (Fig. 2e). As additional information, it has to be stressed out that probable rests of organic coating or additives residues were occasionally observed and biological contaminants (fungal filaments and spores) found in six samples, presumably because of the conservative history and storage conditions of the artworks (Fig. II Annexes).

### 4.2. XRD

The XRD mineralogical identification allowed to confirm what observed by FEG-SEM. Diffraction patterns outcomes pointed out that the main mineral phase present in all the analysed samples is gypsum CaSO $_4 \cdot 2\text{H}_2\text{O}$ . With respect to the secondary mineral phases detected, results for each samples were reported in Table 1. In particular, the presence of anhydrous Ca-sulphate (anhydrite, CaSO $_4$ ) was determined in 15 samples, calcite (CaCO $_3$ ) in 15 samples mainly associated with dolomite (CaMg(CO $_3$ ) $_2$ ). In addition, celestine (SrSO $_4$ ) was detected in 3 samples. No silicates were detected. All the secondary phases detected are present in low percentage (ranging from traces to low proportion).

### 4.3. PIXE

In all the samples, CaO and SO $_3$  were found to be by far the major constituents, representing a total value higher than 95wt% (see Table 2). The theoretical stoichiometric ratio CaO/SO $_3$  is of 0.70 for pure gypsum. Among the studied samples, calculated ratio varies from 0.74 to 0.80 due to the above-mentioned secondary mineral phases in variable amounts. Systematic excess of CaO has to be considered as related to the presence of calcite or dolomite. No direct correlation between CaO, MgO and SrO has been found.

Besides, SiO $_2$  (0.5 to 3%wt) and Al $_2$ O $_3$  (0.1 to 1%wt) were found to be the main minor oxides, despite no associated mineral phases were observed by XRD. Concerning trace elements, Sr, Ti and Mn were mainly taken into account due to their possible correlation with the above-mentioned secondary mineral phases and minor elements.

## 5. Discussion

Some main features were found to be recurrent in all the artworks studied. The material of all the reliefs analysed mainly consists in a gypsum-based plaster as confirmed by both FEG-SEM examinations, XRD phases' identification and PIXE elemental analysis. This corroborates the hypothesis, that the stucco mixture used

**Table 2**

Summary of the calculated average compositions in major, minor oxides, and selected trace elements obtained by PIXE measurements on micro samples of stucco devotional reliefs regrouped by workshop. Artists' names are given as references for the models. According to Tables I and II (Annexes), in brackets are reported the number of repeated measurements performed when is the case, while number followed by a star indicate the number of micro samples of the same artworks analysed.

| Sample                       | Na <sub>2</sub> O | MgO   | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | Cl    | K <sub>2</sub> O | CaO   | Fe <sub>2</sub> O <sub>3</sub> | Sr    | Ti    | Mn    | CaO/SO <sub>3</sub> |  |
|------------------------------|-------------------|-------|--------------------------------|------------------|-------------------------------|-----------------|-------|------------------|-------|--------------------------------|-------|-------|-------|---------------------|--|
|                              | (wt%)             | (wt%) | (wt%)                          | (wt%)            | (wt%)                         | (wt%)           | (wt%) | (wt%)            | (wt%) | (wt%)                          | (ppm) | (ppm) | (ppm) |                     |  |
| <i>Ghiberti</i>              |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| RF 786                       | 0.060             | 0.32  | 0.26                           | 0.95             | 0.29                          | 54.8            | 0.05  | 0.09             | 42.6  | 0.14                           | 2732  | 137   | 22    | 0.78                |  |
| Inv. 239                     | 0.075             | 0.36  | 0.36                           | 0.95             | 0.29                          | 53.5            | 0.08  | 0.23             | 43.2  | 0.17                           | 4440  | 120   | 20    | 0.81                |  |
| RF896 (3)                    | 0.056             | 0.60  | 0.24                           | 0.75             | 0.31                          | 54.2            | 0.06  | 0.13             | 42.6  | 0.11                           | 3430  | 87    | 56    | 0.79                |  |
| <i>Donatello</i>             |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| Inv. 242                     | 0.038             | 0.32  | 0.17                           | 0.55             | 0.32                          | 54.7            | 0.04  | 0.06             | 42.7  | 0.18                           | 3580  | 88    | 16    | 0.78                |  |
| RF1191 (3*)                  | 0.040             | 0.37  | 0.70                           | 2.40             | 0.20                          | 52.6            | 0.05  | 0.19             | 42.2  | 0.36                           | 5345  | 240   | 74    | 0.80                |  |
| D488 (2')                    | 0.177             | 0.43  | 0.60                           | 1.89             | 0.24                          | 54.5            | 0.19  | 0.24             | 40.5  | 0.62                           | 2023  | 214   | 59    | 0.74                |  |
| <i>L. della Robbia</i>       |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| Inv. 247                     | 0.073             | 0.61  | 0.67                           | 1.66             | 0.27                          | 53.2            | 0.09  | 0.34             | 42.1  | 0.30                           | 2629  | 391   | 44    | 0.79                |  |
| <i>D. da Settignano</i>      |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| RF897 (2)                    | 0.011             | 0.68  | 0.26                           | 0.98             | 0.29                          | 53.6            | 0.05  | 0.22             | 42.7  | 0.16                           | 3532  | 105   | 51    | 0.80                |  |
| Inv. 586                     | 0.013             | 0.32  | 0.20                           | 0.60             | 0.31                          | 54.7            | 0.04  | 0.07             | 42.7  | 0.07                           | 2919  | 214   | 15    | 0.78                |  |
| D489                         | 0.040             | 0.38  | 0.15                           | 0.45             | 0.26                          | 55.3            | 0.05  | 0.06             | 42.5  | 0.09                           | 1959  | 62    | 29    | 0.77                |  |
| <i>M. da Fiesole</i>         |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| RF588 (5)                    | 0.016             | 0.29  | 0.13                           | 0.47             | 0.25                          | 55.5            | 0.06  | 0.09             | 41.9  | 0.07                           | 7118  | 52    | 254   | 0.76                |  |
| <i>A. Rossellino</i>         |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| Camp. 16 (4)                 | 0.007             | 0.48  | 0.16                           | 0.46             | 0.32                          | 55.0            | 0.05  | 0.10             | 42.4  | 0.12                           | 2874  | 32    | 46    | 0.77                |  |
| Camp. 19 (4)                 | 0.040             | 0.41  | 0.29                           | 0.91             | 0.30                          | 54.6            | 0.07  | 0.16             | 42.0  | 0.20                           | 3431  | 149   | 52    | 0.77                |  |
| Inv. 362                     | 0.103             | 0.70  | 0.95                           | 2.75             | 0.29                          | 52.2            | 0.08  | 0.29             | 41.7  | 0.39                           | 2994  | 296   | 102   | 0.80                |  |
| Camp. 20 (3)                 | 0.047             | 0.46  | 0.29                           | 0.97             | 0.33                          | 54.3            | 0.05  | 0.20             | 42.3  | 0.12                           | 2861  | 156   | 32    | 0.78                |  |
| 1937-4 (2*)                  | 0.087             | 0.60  | 0.48                           | 1.78             | 0.26                          | 54.7            | 0.07  | 0.15             | 40.9  | 0.25                           | 1385  | 167   | 53    | 0.75                |  |
| DS534 (3*)                   | 0.036             | 0.65  | 0.39                           | 1.16             | 0.21                          | 54.2            | 0.03  | 0.20             | 42.5  | 0.17                           | 2984  | 169   | 22    | 0.78                |  |
| <i>B. da Maiano</i>          |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| RF1169                       | 0.048             | 0.21  | 0.09                           | 0.68             | 0.35                          | 54.3            | 0.05  | 0.05             | 43.9  | 0.06                           | 1645  | 72    | 18    | 0.81                |  |
| Inv. 507 (2*)                | 0.054             | 0.08  | 0.12                           | 0.71             | 0.36                          | 53.7            | 0.11  | 0.13             | 44.1  | 0.20                           | 1684  | 92    | 271   | 0.82                |  |
| <i>Florence 15th century</i> |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| Inv. 244 (2*)                | 0.072             | 0.21  | 0.11                           | 0.38             | 0.34                          | 54.5            | 0.08  | 0.12             | 43.3  | 0.15                           | 1973  | 72    | 30    | 0.79                |  |
| Inv. 246                     | 0.154             | 0.43  | 0.23                           | 0.73             | 0.31                          | 53.7            | 0.10  | 0.25             | 43.5  | 0.16                           | 2496  | 118   | 33    | 0.81                |  |
| <i>16th century</i>          |                   |       |                                |                  |                               |                 |       |                  |       |                                |       |       |       |                     |  |
| RF564 (4)                    | 0.041             | 0.08  | 0.11                           | 0.49             | 0.35                          | 55.8            | 0.05  | 0.05             | 42.6  | 0.09                           | 2072  | 55    | 38    | 0.76                |  |

was composed by a gypsum plaster (gesso) quite free from additional fillers if compared to an architectural plaster or a stucco s.s. as described by Vasari [9,28]. The latter one is in fact generally richer in aggregates due to its specific applications. Based upon present results, two main aspects will be discussed considering their implications for a deepened understanding of technological processes and workshop practices adopted to produce these devotional reliefs.

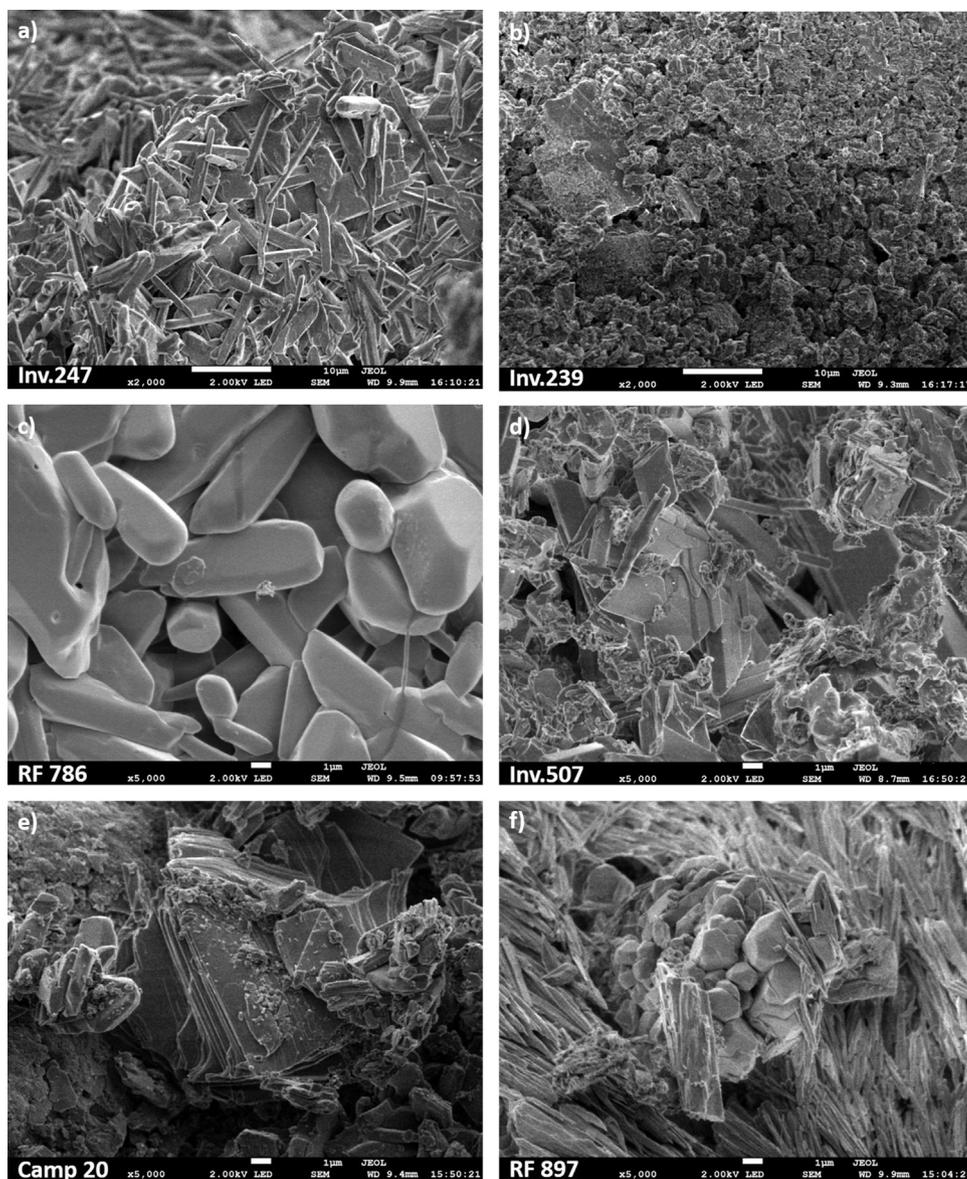
### 5.1. First investigation on materials and practices of 15th century Florentine workshops through microstructures, secondary mineral phases and chemical composition

The examination of gypsum microstructures is a first step to obtain information on material used, recipes and practices used. A large intra- and intervariability was found for artworks attributed to the same workshop and to different ones. All the samples were found to be composed by crystals that largely differ in shape and size. Wide variations were also observed within the same micro-sample (Fig. 2f).

Several are the parameters that can explain this variability. This could be due to the use of different materials, but especially to different processing adopted. For instance different calcination conditions (size and temperature of the kiln, size of the raw gypsum blocks, uniformity of heating temperature) [20,28], grinding and form of the semi-processed Ca sulphate hemihydrate or also hydration degree. As a matter of fact, the variability observed could be mainly explained by the use of different organic additives in the final plaster slurry to change setting, mechanical or aesthetic properties [12,16,19]. As described in the literature, naturally-grown mineral gypsum generally exhibits needle-like crystals while the presence in different proportions of organic additives could give

crystals with various shapes [12,28,29]. Other parameters involved in blending and pouring (influencing water/plaster mixing ratio and consequently differences in porosity), pH, setting time and crystallization speed, could affect crystals habits of newly formed gypsum and of remaining lumps [12,27,30]. At this stage, it is difficult to find characteristic and discriminant features based on the sole examination of the crystal microstructures.

Another way to obtain relevant indicators is to correlate secondary mineral phases and bulk chemical composition. As a first hypothesis, these minor phases could be considered as inherited from the raw gypsum used. In this sense, they could give indications of the level of refinement in materials selection in quarries and following processing (grinding and sieving). The second option is that they were intentionally added as mineral aggregates in the stucco mixture and that they could hence indicate specific processing. However, interpretation is complicated by the fact that some of the secondary mineral phases detected, can both naturally occur in common paragenesis of evaporitic rocks and be used as fillers. For instance, calcite (CaCO<sub>3</sub>) is very common in gypsum paragenesis, but could also correspond to the white marble powder often mentioned as aggregate. Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), can be naturally present in association with gypsum, but the use of magnesian plaster in architecture is also well known [9,12]. Celestine (SrSO<sub>4</sub>) turns out to be possibly present in association with all the three aforementioned minerals being common in sedimentary environments. The implications of secondary minerals in manufacturing processes can be even more deceitful in other cases. Typically, the presence of anhydrous calcium sulphate (anhydrite, CaSO<sub>4</sub>), could be both related to its natural occurrence in association with geological gypsum [20,27,31,32] and to manufacturing processes. Anhydrite occurrences in gypsum deposits are frequent, but its presence could also account for differences in the thermal processing/calcination



**Fig. 2.** SE images of most recurrent crystal morphologies observed in the analysed samples (samples codes are indicated in the left lower corner for each micrograph). From the top to the bottom: two general view of recurrent textures and microstructures observed, respectively: **a)** prismatic; **b)** massive rod shaped crystals; **c)** prismatic/short rounded rod-shaped crystals; **d)** swallow tails crystals; **e)** lamellar/tabular crystals surrounded by rounded and short ones; **f)** example of microstructural varieties of crystals within the same sample: in the same micrometric area both acicular, lamellar and rounded crystals are observable.

of the raw gypsum prior to obtain the hemihydrate form [20], leading to transformation of part of the raw gypsum in anhydrite. As a result, the presence of over burnt/heated gypsum ( $\text{CaSO}_4$ ) would not be unusual.

Calcite under the form of both spath, carbonated lime, or marble is reported in stucco recipes by ancient treaties and literature such as in Vasari [9]. Since for the moment no characteristic features of spathic calcite or marble fragment have been observed in our study, we have to assume that this contribution is mainly due to calcite impurities in the raw gypsum and not to the intentional addition of aggregates. Looking more in detail at samples from a same workshop, all the samples from the workshop of Desiderio da Settignano showed presence of anhydrite and dolomite, all the three samples from Donatello workshop present dolomite and the two from Benedetto da Maiano workshop calcite. Considering reliefs from Antonio Rossellino, calcite was found in all the samples except for Camp. 16, anhydrite in four out of the six samples while dolomite in three samples.

Bulk chemical composition of the stucco samples was then analysed. Fig. 3 shows results concerning minor elements highlighting (in Fig. 3a) the correlation between  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  (correlation factor equal to 0.9). The slope of the curve (2.9) is compatible to values of clay minerals (e.g. minerals of the illite group) [27,33]. An analogous direct correlation is shown in Fig. 3c and d between  $\text{Al}_2\text{O}_3$  vs  $\text{Fe}_2\text{O}_3$  and Ti (ppm) respectively suggesting their compatible relation with clay mineral phases probably associated to the evaporitic basin where raw gypsum was extracted. Intentional addition to the final “stucco” mixture using aggregates, such as brick fragments, sand, or others [12] seems less probable due to their low amount. In Fig. 3b,  $\text{Al}_2\text{O}_3$  vs  $\text{K}_2\text{O}$  diagram, shows two slightly different trends that could be based on the contents of  $\text{K}_2\text{O}$  in clay minerals impurities or to the presence of different clay minerals in variable proportions.

Despite the dispersion of the data representing calculated concentrations obtained by PIXE, few trends appear considering workshops represented by at least three artworks in our

data set (Ghiberti, Donatello, Desiderio da Settignano and Antonio Rossellino). In fact, the most part of the result seems to be quite closely regrouped with the exception of data from (Inv. 242) that are more widely scattered if compared to the values of other samples from Donatello workshop. The same observation can be inferred for the value of sample (Inv.362) if compared to the others belonging to A. Rossellino group.

Data from non-attributed reliefs (Inv. 244, Inv. 246, RF564) do not show so far any significantly strong difference if compared with those catalogued as being of Florentine production and related to a specific workshop.

5.2. Raw material provenance: comparison with geochemical data of Tuscany gypsiferous rocks

As a further step to find attribution criteria, trace elements contents measured by PIXE were taken into account to have

insights on the provenance of the raw material used. Gypsum deposits are widespread in Tuscany and ancient treaties often mention that alabaster and gypsum from the areas in the surroundings of Volterra and Siena supplied the Florentine artistic manufacturing [8,9,20]. However, to the best of our knowledge, few detailed works have been made on this topic. It has to be stressed out that the names of these two historical centres (which are located approximately within a 60 km range) could have been used as main reference for different occurrences in the same geographic area. Moreover, from a geological point of view, occurrences in the area of both centres can correspond to the same evaporitic basin, i.e. the so-called Volterra basin [34]. Other occurrences are reported across Tuscany as for instance in the Fine river basin (about 40 km west from Volterra towards the Tyrrhenian coast) or in other areas of the region [31,32,34]. All of these makes quite difficult to determine the actual exploitation of a certain quarry in this specific period and, therefore, many

- |                      |                             |                          |                           |
|----------------------|-----------------------------|--------------------------|---------------------------|
| □ Ghiberti (RF786)   | ○ L. della Robbia (Inv247)  | ◇ A. Rossellino (Camp16) | ◁ B. da Maiano (RF1169)   |
| ▣ Ghiberti (Inv239)  | △ D. da Settignano (RF897)  | ◊ A. Rossellino (Camp19) | ▷ B. da Maiano (Inv507)   |
| ▤ Ghiberti (RF896)   | ▲ D. da Settignano (Inv586) | ◈ A. Rossellino (Inv362) | ⊕ Florence 15th (Inv244)  |
| ▥ Donatello (Inv242) | ⊠ D. da Settignano (D489)   | ◉ A. Rossellino (Camp20) | ⊗ Florence 15th (Inv 246) |
| ⊕ Donatello (RF1191) | ☆ M. da Fiesole (RF588)     | ⊖ A. Rossellino (1937-4) | ✱ 16th (RF564)            |
| ⊗ Donatello (D488)   |                             | ⊘ A. Rossellino (DS534)  |                           |

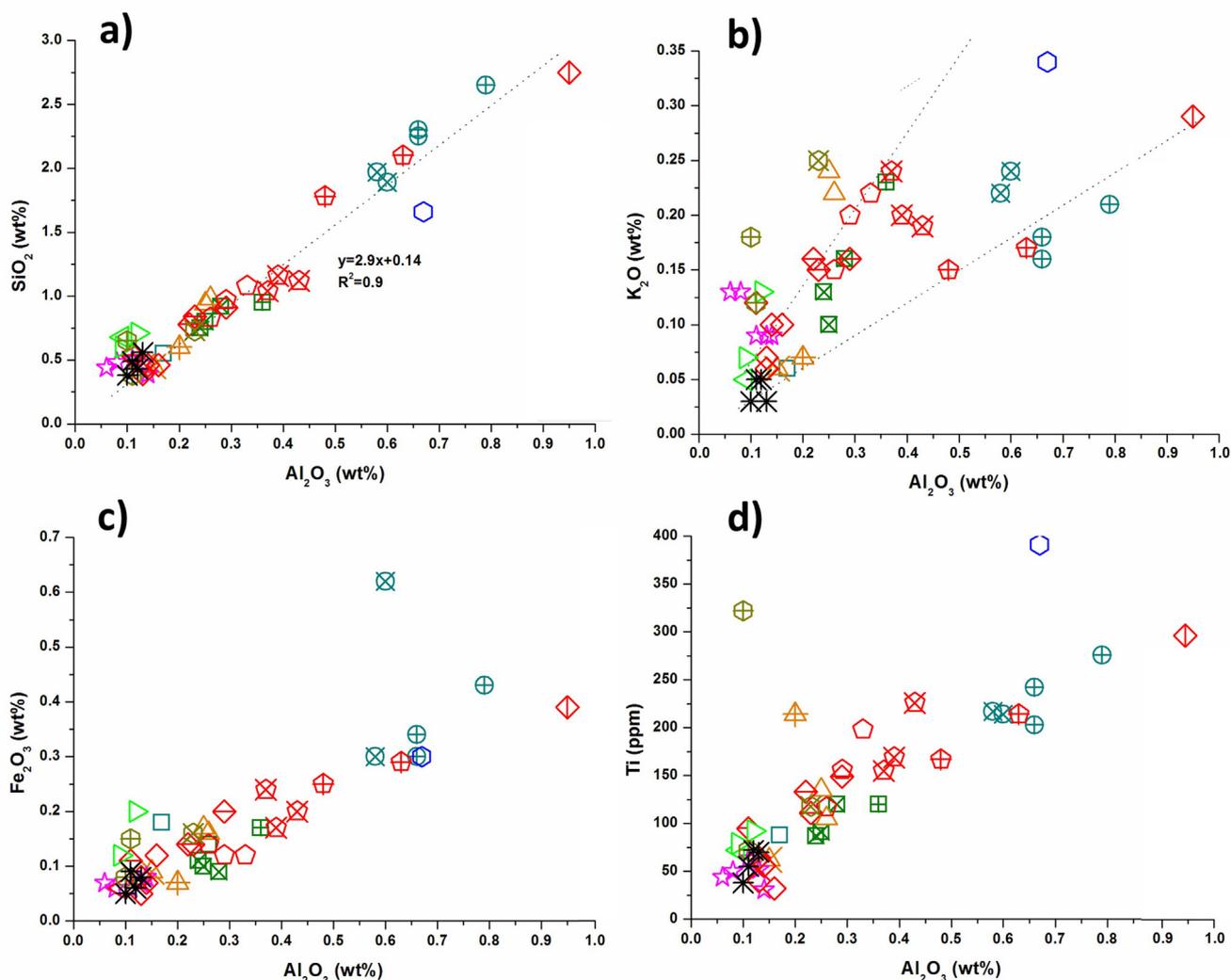


Fig. 3. Scatter plot of Al<sub>2</sub>O<sub>3</sub> (wt%) vs SiO<sub>2</sub> (wt%), K<sub>2</sub>O (wt%), Fe<sub>2</sub>O<sub>3</sub> (wt%), and Ti (ppm). Each point represent a PIXE elemental analysis. Artists' names are given as references for the models.

questions about the sourcing and selection of raw gypsum are still open.

A focus was made on few elements so far. In particular, Ti content is directly correlated to  $Al_2O_3$  (see Table 2 and Fig. 3d), but no trend related to artworks of the same workshops was observed so far. The same consideration can be extended for Mn content, which, as only notable difference, shows for some samples (in particular RF 588) a wider fluctuation of values. This is probably due to the presence in the analysed areas of an heterogeneous distribution of calcite, in which Mn can occur [27,35] or simply to the larger number of measurements performed. Since no correlation have been observed between MgO and Mn, it can be assumed that the latter one is not correlated with dolomite. No straightforward conclusion can be taken on calcite.

Among trace elements detectable in gypsiferous rocks and gypsum based materials, strontium is reported as particularly useful marker to obtain both origin and provenance information [26,32,34,36]. Sr concentrations calculated by PIXE measurements on samples from the 22 artworks analysed are reported in Fig. 4.

In the box charts, each point represent a PIXE measurement. For some artworks, only one analysis is available; statistic has to be improved but results give as well a first comparison. The box plots range from a lower value of 1385 ppm to higher value of 7118 ppm. Nonetheless, data fall into a narrow range if considering the same artworks.

A comparison of experimental results obtained was made with data from literature on geological gypsum of Tuscany from different depositional units. The latter ones were represented in Fig. 4 in

separate boxes: two boxes regroup data respectively on the aforementioned Volterra basin (in grey in Fig. 4) and on the Fine river one (in light grey). Other Tuscan occurrences were regrouped in a third box (in black) [32,34,36–40].

At this stage of the work, the comparison showed that the dispersion of data from the analysis of devotional reliefs samples matches, in the most part of the cases, with the albeit high variability of Sr distribution reported in literature for gypsiferous rocks of different lithofacies and quarries sites of Tuscany. Even if it is not possible to draw any definitive conclusions, most of the artworks, including the three non-attributed reliefs, are gathered in a range of values overall compatible with the values of Sr contents covered by literature data. The values from stucco reliefs' samples seems to be a little bit higher than the average of the geological samples, especially for sample RF1191 and RF588. However, some scattered high Sr values are also reported for geological samples, with a larger dispersion of values reached for the Volterra unit. Another aspect to be considered for further investigations is the variability within a single quarry and the differences in Sr that can be related to different lithofacies [36]. Other questions raise after these preliminary comparisons, showing how this topic is worth exploring in deeper. In fact, old treaties often talk generically about alabaster from Volterra and Siena but without detailed information. It would be interesting to increase analyses on geological materials presumed to be used during Renaissance. This could be useful to determine more precisely which kind of gypsiferous rocks were actually used and if it is possible to enlighten different sources and supplies of material according to historical period, workshops and series of devotional reliefs.

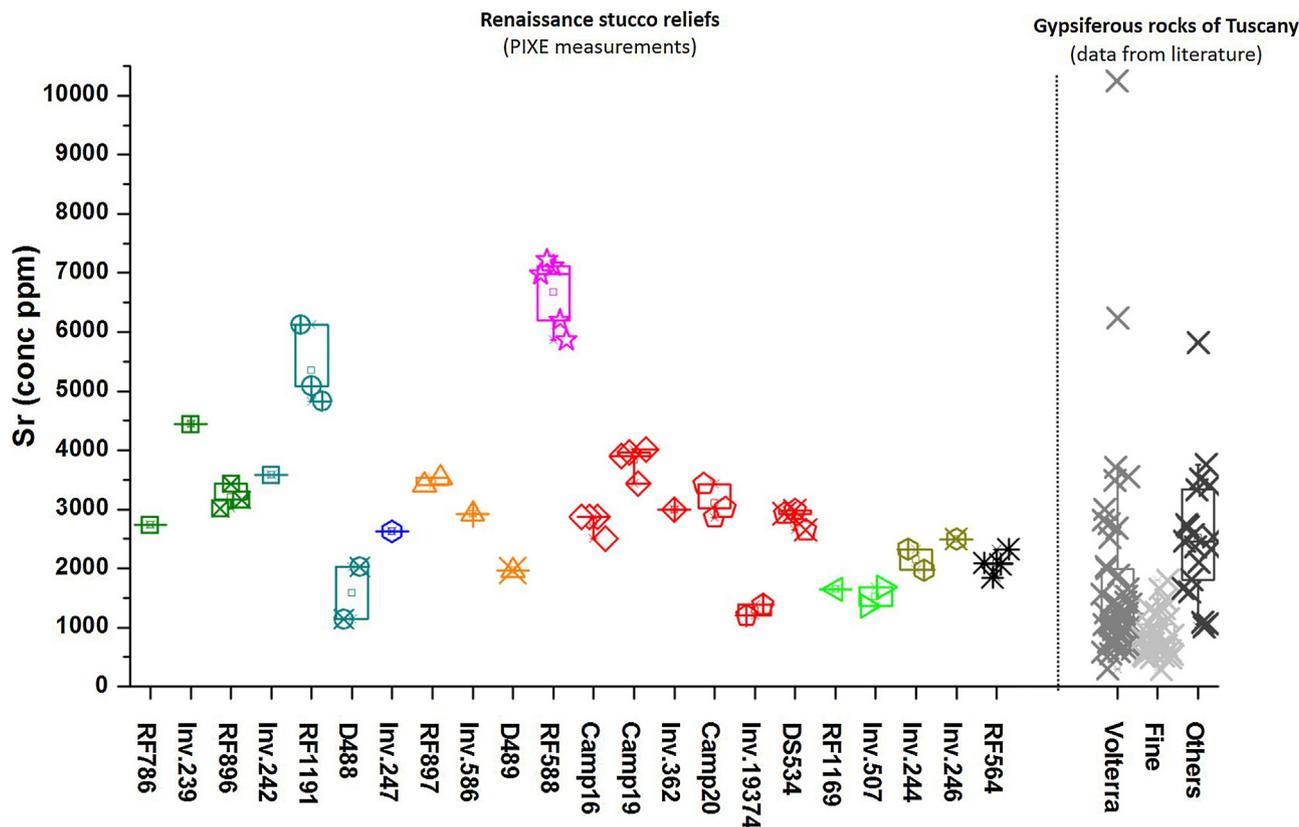


Fig. 4. Whisker plot of Sr contents (expressed in ppm) measured in reliefs samples. Artworks attributed to the same workshop are displayed with different colours while each box chart represents PIXE data from a same relief. The three box charts in the right part of the figure represent data from literature on Sr contents in gypsiferous rocks of Tuscany, respectively from units within the Volterra (grey), and Fine river (light grey) evaporitic basin. In black are regrouped data of other Tuscan occurrences (Dinelli et al., 1999, Barbieri et al., 1976, Cortecci et al., 1981 Bigazzi et al., 1996). Data from literature are shown as useful term of comparison to have first hints on geological sourcing of the raw materials.

## 6. Conclusions

The aim of this work was to provide a first identification and characterisation of the constitutive mineral phases of the material, generically classified as “stucco”, used in 15th century Florence to produce a significantly large number of devotional reliefs in the workshops of Renaissance masters. The multianalytical characterisation of a large number of these artworks represents itself a novelty. In fact, few information and studies about their constitutive materials are available, even if these objects represent a source of interest and issues for conservative and authentication purposes. Based on first results, two main research lines have been discussed; the aim is to find straightforward attribution criteria, not only based on stylistic considerations, but also related to and supported by evidences on both technological processes and raw material provenance.

As determined in all the samples, the stucco employed appears to be systematically a gypsum based plaster, probably elaborated with a recipe more similar to those typically used for plaster casts (gesso) than to the stucco for architectural applications. Considering gypsum microstructures, a large intra- and intervariability was found for artworks attributed to the same workshop and to different ones. Up to now, no satisfactory explanation can be given and further investigations will be needed by comparison with the results on the identification of organic additives. The identification and characterisation of the latter ones is in fact a crucial point for the study of this kind of composite materials. Due to the specific analytical protocol developed for the organic additives, a forthcoming work program will deal with this specific aspect.

The correlation between secondary mineral phases detected by XRD, and minor elements by PIXE, is not systematic, but some trends were observed. Main secondary mineral phases found are calcite, dolomite, and celestine; the presence of clay minerals can be assumed from the positive correlation between  $Al_2O_3$  and  $SiO_2$ . Given the overall low amount of these phases and oxides, it seems more plausible that they were present as impurities occurring in the raw gypsum used for the stucco binder rather than intentionally added as aggregates. The consistency of these results for all the samples is compatible with a common practice adopted to produce devotional reliefs in all the considered botteghe (workshops) of 15th century Florence. Nevertheless, slight differences, especially in  $K_2O$  and  $Al_2O_3$  allow to partially detaching some trends to investigate in deeper. Finally, first hints for the provenance of the raw gypsum used have been found. Scholars' leading hypothesis of Florence as the major centre of devotional reliefs' serial production, still in need to be confirmed by follow-ups, is supported by strontium contents, compatible with those reported in literature on geological gypsum of Tuscany. A further step will consist in compared analyses of the present samples with geo-referenced samples collected in Tuscany and other Italian regions; one of the most promising methods is the analysis of S, O and Sr isotopes [35,37,40].

In conclusion, even if at its early stage, this work is an important starting point for a better understanding of stucco devotional reliefs. Further investigations will hopefully yield more details on raw materials and technological processes involved in the production of these long-neglected objects even though with a key role in the arts and cultural life of 15th century Florence and Renaissance Italy.

## Authors' contributions

G.G., A.B., F.G. and P.L., envisioned the experiments concept. G.G. and P.L. conducted the FEG-SEM experiments; G.G. with the support from G.W. conducted XRD measurements. G.G. and

A.B. performed PIXE measurements. L.L. F.G. and G.W. were importantly involved in the interpretation of all the data and in the discussion with all the authors. M.B. provided access to the artworks and assisted the sampling campaign supervising the study due to its significance for art history. The bulk of the paper was written by G.G. with significant contributions from all the authors.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://www.sciencedirect.com> and <https://doi.org/10.1016/j.culher.2018.05.003>.

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