



Diagnostic characterisation of masonry and decorative materials of the apsidal area of the Cathedral of Cefalù (Sicily, Italy)

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Abstract The Cathedral of Cefalù (Sicily, Italy), a UNESCO World Heritage Site since 2015, was built during the Norman rule and is famous for its magnificent mosaic. The mosaic apparatus, located in the apsidal area of the Cathedral, recently underwent extensive conservation work. Besides the mosaic *tesserae*, this area of the Cathedral was subjected to interventions aimed at preserving the integrity of masonry plasters, mortars, stuccoes and coloured plasters. However, basic information such as the chemical and mineralogical composition and microstructural arrangement of original materials was still lacking. In this perspective, in situ and ex situ analyses were carried out for the first time on the masonry and decorative materials of Cefalù's Cathedral apse. Chemical analyses were carried out on original mosaic *tesserae* by means of portable X-ray fluorescence, highlighting that their manufacture involved the recycling of glass, excluding the use of natural glass and identifying the chromophores responsible for the wide colour variety; X-ray diffractometry was performed on masonry plasters and mortars allowing to recognise the use of predominantly carbonatic binders and the presence of degradation products such as calcium oxalates and sodium chloride; finally, petrographic observations carried out on stuccoes enabled the identification of various types of aggregates (carbonatic, gypsum-based, and quartz-feldspathic) embedded in a carbonatic binder, while petrographic analysis of the coloured plasters allowed the identification of three pigmentation techniques. Overall, these analyses provided very useful information on the nature of building and decorative materials as well as their mineralogical composition and degradation products, laying the foundations for future conservation work that takes into account the characteristics of each material.

1 Introduction

The diagnostic characterisation discussed in this study took place in one of the best known and most appreciated Norman cathedrals in Sicily Island (Italy). The Cathedral of Cefalù is located in a bay on the northern coast of Sicily, and there is evidence of the existence of the diocese of Cefalù as early as the ninth-century A.D. [1]. The church, consecrated to the Savior and Saints Peter and Paul, according to the "*Liber privilegiorum ecclesie Cephaleditane*" [2], was founded by Roger II in 1129, in fulfilment of a vow made after being saved from a storm at sea. The Cathedral features a *basilica* nave of seven bays with a pointed archway that rests on columns. The cathedral's flagship is its marvellous mosaics with the *Christ Pantokrator* as its focal point. The curved apse wall below is divided by ornamental bands into three registers. The upper register displays the Virgin, flanked by two archangels, while the lower registers each contain six Apostles, with inscriptions in Greek and Latin. The vaults of the presbytery are adorned with six-winged angels, accompanied by two half-figure angels. The side walls exhibit individual figures across four planes. The mosaics, predominantly Byzantine in style, are traditionally attributed to Greek artists [2] and were completed between the 1130 s and 1148, concurrently with the mosaics in the Palatine Chapel in Palermo [3]. The mosaic apparatus is made of natural (lithic) and artificial (glass) *tesserae*, embedded in mortar, whose study can provide useful information related to chronological interpretation, mosaic manufacture and production practices. Several studies can be found in the literature on mosaics of different epochs and provenance [4–10] including studies on the stunning mosaics of the Villa Romana del Casale [11, 12] and on Monreale Cathedral [13]. Studies on mortars and plasters with restoration purposes are also very common [14, 15]; however, no studies on mosaic *tesserae*, masonry plasters, mortars, stuccoes and coloured plasters of the Cathedral of Cefalù are available in the literature, making this study a forerunner in the field. Archaeometric studies of the materials of the Cathedral of Cefalù are limited to the petrographic characterisation of marly limestones in the cloister, which were subject to a very pervasive decay [16]. The characterisation under study took place as part of a conservation and restoration intervention included in the project "CHANGES—Cultural Heritage Active Innovation for Sustainable Society", which operates in the field of cultural and historical heritage protection. In particular,

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the sampling campaign and in situ and laboratory diagnostic investigations were carried out to answer specific questions posed by conservators, establishing an open and constructive dialogue between researchers and conservators themselves. The conservation intervention was considered essential since the mosaic apparatus had several issues that were quite significant. One of the main ones involved the bedding mortars of the *tesserae*; in some areas, they were so damaged that they showed obvious swelling with subsequent detachment of the *tesserae* themselves. The bedding mortars in some spots even appeared to be crumbling, producing abundant debris. The areas involved in previous conservation interventions also showed critical issues. The original bedding mortar and *tesserae* had been replaced with larger and shinier reconstruction ones, which did not match the original design. In addition, the appearance of efflorescence could also be noticed in the non-original areas. However, the range of degradation phenomena was not only limited to mosaic decorations, but also to stuccoes, mortars, masonry plasters and coloured plasters. For this reason, the sampling was carried out on a wide range of materials, selecting the areas that were most damaged. A wide-ranging analysis, such as the one carried out, was considered essential, as well as the most appropriate in order to plan suitable conservation strategies. Information concerning the material nature of the mosaic *tesserae* and their elemental composition, with a focus on chromophores, was provided by chemical analyses conducted by portable X-ray fluorescence (pXRF), while thin-section petrographic studies and X-ray diffractometry (XRD) were also carried out. These techniques have provided very useful information about the structure, texture and mineralogical composition of stuccoes and coloured plasters and of mortars and masonry plasters, respectively; the degradation products were also investigated.

The glass *tesserae* were studied with particular attention as, in addition to the identification of the chromophores, an attempt was made to understand whether the black ones were made of natural glass (obsidian). In the context of the study of mediaeval mosaics, the use of obsidian *tesserae* is a controversial and challenging topic of research, as demonstrated by the studies on the Sicilian *Dedication Wall Mosaic* in the Church of Santa Maria dell'Ammiraglio in Palermo (twelfth century) [17]. Also in the case of the mosaic apparatus located at the Cathedral of Cefalù, the presence of dark-coloured glass *tesserae* had been associated, on the basis of naked-eye observations, with the use of obsidian. This idea would have been further corroborated by the geographical proximity of the Cathedral site to perimediterranean volcanoes.

This study therefore contributes to the gaining of a good basic knowledge of the materials present in the apsidal area of the Cathedral of Cefalù, laying the foundations for careful conservation works.

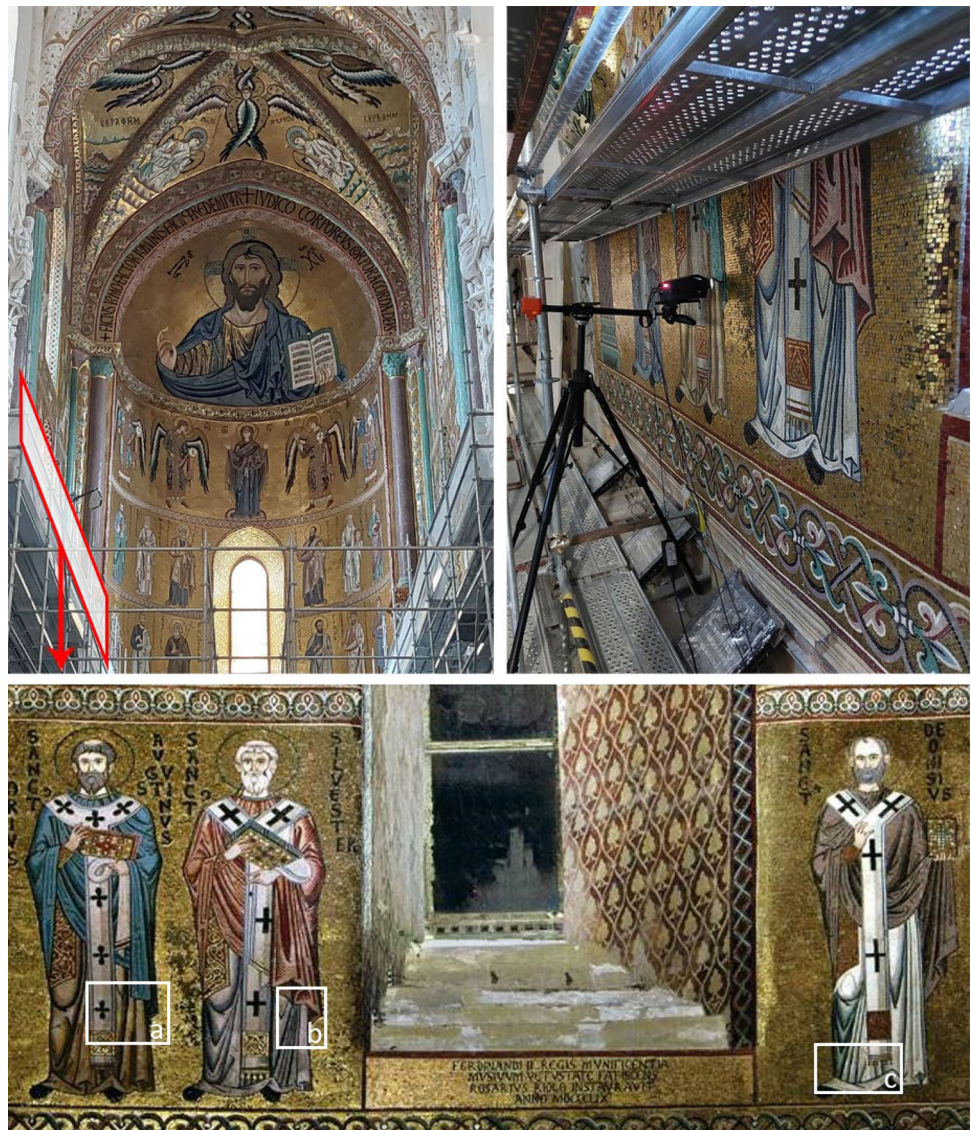
2 Materials and methods

2.1 Analysed samples

In selecting the materials for this study, a targeted approach was chosen, based on the specific question to be answered for each type of material. It follows that the analytical techniques were also chosen on the basis of the need to be addressed. Samples were collected from the apse of the Cathedral wherever possible, while on-site analysis techniques were adopted where sampling was not permitted. The analysed samples are listed below:

- A set of 28 glass mosaic *tesserae* was selected in a portion of the north wall of the Cathedral apse (Fig. 1) with the help of the conservators from Piacenti S.p.a. conservation centre. They consist of rectangular *tesserae* (ca. 7–10 mm wide and 10–15 mm long) of various colours.
- The objective of the analysis of the mosaic *tesserae* was to understand the chemical composition of the glassy matrix, avoiding any damage to the mosaic apparatus. As a reference, the Corning Archaeological Reference Glasses A, B and D [18] were also analysed. Corning A and B are two ancient recipes of soda-lime glass made, respectively, with natron and plant ash, while Corning D is a Mediaeval European glass. The chemical analysis was performed on the surface of each mosaic *tessera*, in the central area of the tiles. Moreover, it was useful to distinguish whether the glassy matrix of the 10 black *tesserae* was made of natural (volcanic) or synthetic glass. For this reason, two samples of volcanic glass (i.e. obsidian) (OL, OCC) held in the Museum of Mineralogy, Petrography and Volcanology of the Earth Sciences section of University of Catania (Italy) were also analysed to obtain a comparison with the mosaic black *tesserae*.
- A set of 6 fragments of masonry plasters were sampled from various areas of the apse: CI1 and CI2 from the vault of the apse; CI3 from the northern wall of the apse, close to the window; CI4 and CI7 from the southern wall of the apse, close to the windows; CI11 from one of the capitals located in the southern area of the apse.
- For these samples, the aim of the analysis was to determine the mineralogical composition of the constituent binders, and in particular, whether the binder was lime-based or gypsum-based.
- Two fragments of mortars (CM5 and CM6) were sampled from the southern wall of the apse, close to the windows. As for plasters, the aim was to understand the mineralogical composition of the mortars and the typology of binder, whether lime-based or gypsum-based binder.
- A set of seven fragments of stuccoes (CS1, CS2, CS3_1, CS3_2, CS4, CS5), sampled from statues of cupids located in the apsidal area, were prepared as thin sections. For these samples, the objective of the study was to assess the internal microstructure of each sample.

Fig. 1 Detail of the North wall of the Cefalù Cathedral apse involved in the diagnostic campaign with overview photograph of the apsidal area (top left) and detail of ongoing chemical analysis (top right); a, b, c are the areas investigated in situ



- A set of six fragments of coloured plasters (CT1, CT2, CT3, CT4, CT5_1, CT5_2), collected from the painted areas of the apse, were sampled and prepared as thin sections as well. In this case, the technique by which the coloured plasters were applied to the unpigmented masonry substrate was investigated, thus identifying the interface between the two.

2.2 Analytical techniques

Portable X-ray fluorescence (pXRF) analysis was used on-site to carry out chemical analyses on these mosaic *tesserae* by means of a Bruker Elio portable instrumentation with a microfocus X-ray tube (Rh target), collimated to a 1-mm spot, using a voltage of 40 kV and a current of 80 μ A applied for 180s, with no filters. The analysed spot and focussing of the beam were monitored thanks to the internal digital camera and the two laser pointers embedded in the spectrometer. The spectra were processed by PyMCA software [19] to obtain qualitative and semi-quantitative data of the main elements as well as of the traces, by using a tailored configuration file for the instrumentation, analytical settings and matrix.

Nevertheless, since pXRF measurements were taken in air, quantities of chemical elements with an atomic weight less than aluminium cannot be considered reliable. Following Coccato et al. [13], the comparison between the glass matrix of the tiles and the reference glass standards [18] was carried out by only considering the following oxides: SiO_2 , K_2O , CaO , TiO_2 , V_2O_5 , CrO , MnO , Fe_2O_3 , CoO , NiO , CuO , SrO , ZrO_2 , BaO and PbO . For comparison purposes, all the percentages are obtained by recalculating the certified values to the total of the oxides selected for this study. The correlation between the calculated wt% values and the mass fractions obtained from PyMCA proved to be linear ($R^2 > 0.95$ for all the considered oxides). This allowed to derive the calibration curves for correcting the mass fractions obtained from the portable instrumentation into percentages to the total of detected elements.

Fragments of masonry plasters and mortars were powdered in order to perform qualitative and semi-quantitative mineralogical investigations by means of X-ray diffractometry (XRD) using a Rigaku Miniflex instrument, equipped with a CuK α tube with Ni filter, operated at 40 kV and 15 mA. Analyses were set at a scanning speed of 5.0°/min, with a step size of 0.02°, in a 2 θ range of 3° to 90° for mortar and plaster and 3° to 70° for stucco. The XRD patterns were then elaborated by means of HighScore Plus software, while semi-quantitative results were obtained by means of Profex software 5.3.2 [20].

Petrographic analyses were carried out on thin section of stuccoes and coloured plasters samples using a Leica DM750P Microscope equipped with Leica ICC50 W Camera. Images were acquired at a magnification of 4 $\times$ using both plane-polarised and cross-polarised light. These analyses allowed the identification of characteristics such as the type of constituent minerals, which are essential for understanding the composition of the sample itself; the dimensions of the constituents; the texture, which refers to the spatial arrangement of constituents in the sample; the presence of a matrix and its features. The microstructure of the sample is also investigated in terms of the presence of pores, fractures, discontinuities and/or fragments of different origins included within the matrix.

Table 1 summarises the investigated samples and the analytical techniques applied to answer each of the specific questions.

3 Results and discussion

3.1 XRF of mosaic tesserae

Table 2 summarises the chemical results as a percentage of the total measured elements as oxides, from Adlington [18], as in Coccato et al. [13]. Silica dioxide (SiO₂) is the main component of a silicatic glass material, whether natural or synthetic. Moreover, constituent elements of the glassy matrix are: Na and K as flux agents, Ca and Mg as stabilisers, and Pb as network former or modifier, depending on its quantity [21–24].

Although Na₂O and MgO info is missing because of the instrumental limits of pXRF, the other oxides can still be used to discriminate different "recipes" of glass manufacture [25, 26], especially in comparison with adequate reference glass, such as Corning A, B, D [18]. On the other hand, Mn, Fe, Co, Cu are chromophore elements which, depending on their oxidation state and amount, give a wide range of colours to the glass [27–29].

In this study, the relative abundance of the oxides SiO₂, K₂O and CaO allowed to distinguish two groups of glass among the *tesserae* under investigation: *tesserae* with high SiO₂ content (between 80 and 90 wt%), lower K₂O (< 4 wt%) and lower CaO content (< 10 wt%) and, on the contrary, *tesserae* with lower SiO₂ content (< 75 wt%), higher K₂O (> 7 wt%) and higher CaO content (> 14 wt%) (Fig. 2). The analysis of the dark red glass RS reveals high Fe₂O₃ contents (ca. 10 wt%), which affects its position in the graphs of Fig. 2. With the exclusion of iron, this sample appears more similar to the first group. Finally, the green ellipse highlights the obsidians (natural volcanic glass) with negligible CaO content; the ellipse in yellow groups the blue-turquoise and brown opaque glass which belong to the group of *tesserae* having the lower quantity of SiO₂, while all the other *tesserae* analysed are grouped in red. The high silica glasses are somewhat similar to Corning A, and to a lower extent to Corning B, which correspond to plant ash and natron glasses, respectively (Egyptian, Mesopotamian, Roman, Byzantine and Islamic), while Corning D, a standard of a Medieval European potash-lime silicate glass, shows similarities with the samples in the yellow ellipse (Fig. 2) [18]. It therefore appears that the mosaic *tesserae* of the Cathedral were manufactured following different recipes; the recycling of glass through mixing different batches, thus giving intermediate compositions, cannot be excluded [30, 31]. Finally, Table 2 shows that the SiO₂ content detected in black mosaic *tesserae* is slightly lower with respect to natural obsidians (~ 83 against ~ 89 wt%); the substantial difference, however, lays in the content of K₂O (~ 6.5 wt% in the natural obsidian and ~ 1.6 wt% in the mosaic *tesserae*) and CaO, which is extremely low in the obsidian but present in the mosaic *tesserae*: we can therefore exclude that natural glass was used for making these latter, but they were instead made of synthetic glass.

Looking further into the results of the chemical characterisation, it is evident that the *tesserae* with the highest K₂O and CaO, i.e. the blue-turquoise and brown opaque glasses, are also those that contain a higher amount of Pb (up to ca. 5 wt% PbO), as can be seen from the graph in Fig. 3a. Lead is historically known for lowering the melting point of glass, depending on the composition of the glass and the amount of lead [24, 32], but also as an opacifier of the glass itself; in fact, the addition of lead oxides to molten glass during the production process allows the modification of the optical refractivity of the glass, through the precipitation of crystalline phases, giving an opaque or semi-transparent appearance [33]. As far as chromophore elements are concerned, Fig. 3b shows a linear correlation between iron and manganese in the black *tesserae* (grey ellipse), which does not reflect the abundance of these elements within the obsidians (green ellipse). A negative linear correlation seems to exist for brown *tesserae* M2 and M3, as well as light green. *Tesserae* AS, T2, T3, V2, BV, RC, P and D show an enrichment in manganese, with the highest values observed in the purple and transparent glass of the gilded glass. Depending on the oxidation state, manganese is known to give glass various shades of purple and dark violet [34], but when in combination with iron it alternatively leads the colour to darker shades [35], or to transparency thanks to the optical counteracting of green by purple [36]. Iron itself determines the dark green/black colour of the glass [37]. The black *tesserae* of this study (series "N") are all enriched in iron and cobalt, and show a greenish tint when illuminated with white light. Cobalt is also detected as CoO > 1% in the following coloured glass: light blue (A2), red (RC, RS), turquoise (T1–T3), green (V1–V4). The highest cobalt content is observed in the black glass, and in the dark green *tesserae* [38].

Table 1 List of samples under investigation and applied analytical techniques applied according to the question to be solved

Sample	Typology	X-ray fluorescence	X-ray diffractometry	Optical microscopy on thin sections
A1	Light blue <i>tessera</i>	X		
A2	Light blue <i>tessera</i>	X		
B	Blu <i>tessera</i>	X		
BV	White <i>tessera</i>	X		
D	Golden <i>tessera</i>	X		
M1	Brown <i>tessera</i>	X		
M2	Brown <i>tessera</i>	X		
M3	Brown <i>tessera</i>	X		
N1-N10	Black <i>tesserae</i>	X		
P	Purple <i>tessera</i>	X		
RC	Light red <i>tessera</i>	X		
RS	Dark red <i>tessera</i>	X		
T1	Turquoise <i>tessera</i>	X		
T2	Turquoise <i>tessera</i>	X		
T3	Turquoise <i>tessera</i>	X		
V1	Light green <i>tessera</i>	X		
V2	Green <i>tessera</i>	X		
V3	Green <i>tessera</i>	X		
V4	Dark green <i>tessera</i>	X		
OL-OCC	Obsidians	X		
CI1	Masonry plaster		X	
CI2	Masonry plaster		X	
CI3	Masonry plaster		X	
CI4	Masonry plaster		X	
CI7	Masonry plaster		X	
CII1	Masonry plaster		X	
CM5	Mortar		X	
CM6	Mortar		X	
CS1	Stucco			X
CS2	Stucco			X
CS3_1	Stucco			X
CS3_2	Stucco			X
CS4	Stucco			X
CS5	Stucco			X
CT1	Coloured plaster			X
CT2	Coloured plaster			X
CT3	Coloured plaster			X
CT4	Coloured plaster			X
CT5_1	Coloured plaster			X
CT5_2	Coloured plaster			X

The dark red *tessera* (framed by the dark red ellipse in Fig. 3b) shows the highest iron oxide content (10.5 wt%) among all the other *tesserae* and especially compared to the light red *tessera*, indicating that the iron content determines the dark red colour to the mixture. All reference Corning glasses contain little Fe_2O_3 and MnO , with a different ratio compared to the black artificial glass, and to the obsidians, whose MnO content is negligible. Finally, a higher copper content is found in the turquoise, green and blue *tesserae* (ca. 1.5–5.0 wt% CuO , blue ellipse in Fig. 3c); in fact, when the glass contains copper ions, especially when lead is also present, it can take on various shades of blue and green depending on the oxidation state of the copper itself [28, 39]. A higher copper content is also detectable in the dark red (ca. 2 wt% CuO , dark red ellipse in Fig. 3c), compared to the rest of the analysed *tesserae* ($\text{Cu} < 0.5$ wt%). Metallic copper was historically used also for obtaining red coloured glass [39]. For the black *tesserae*, a linear correlation is also found between iron and copper (grey ellipse in Fig. 3c). The obsidians contain much less copper than the black glass *tesserae*, again confirming the synthetic nature of these latter.

Table 2 pXRF chemical characterisation of the analysed mosaic *tesserae*

Mosaic tessera	SiO ₂	K ₂ O	CaO	TiO ₂	V ₂ O ₅	CrO	MnO	Fe ₂ O ₃	CoO	NiO	CuO	BaO	PbO
A1	90.08	1.89	4.83	0.19	0.01	0.00	0.72	1.94	0.03	0.02	0.03	0.16	0.04
A2	68.95	8.05	13.89	0.04	b.q.l	0.04	0.20	0.21	2.03	0.03	2.03	0.04	5.10
B	88.23	1.94	4.61	0.39	0.01	0.01	1.36	3.05	0.07	0.01	0.07	0.15	0.05
BV	88.49	2.13	6.24	0.13	0.01	b.q.l	1.48	1.22	0.10	0.01	0.10	0.14	0.05
D	84.00	2.88	7.26	0.43	0.01	0.01	2.45	2.63	0.08	0.02	0.08	0.15	0.04
M1	69.29	7.96	20.18	0.10	0.01	b.q.l	0.59	1.53	0.02	0.01	0.02	0.16	0.14
M2	71.61	8.61	16.95	0.05	0.01	b.q.l	0.37	1.05	0.01	0.02	0.01	0.16	1.14
M3	88.87	2.45	6.79	0.12	0.03	0.01	0.29	1.19	0.03	0.02	0.03	0.15	0.04
N1	84.24	1.30	3.67	0.42	0.02	0.02	0.87	2.52	3.70	0.02	3.70	0.15	0.06
N2	85.61	1.24	3.07	0.36	0.01	0.01	0.81	2.30	3.37	0.02	3.37	0.15	0.05
N3	83.89	1.33	4.00	0.41	0.02	0.01	0.91	2.54	3.66	0.02	3.66	0.14	0.05
N4	83.97	1.32	3.79	0.43	0.01	0.01	0.91	2.57	3.74	0.02	3.74	0.16	0.06
N5	83.14	1.45	4.12	0.46	0.02	0.01	0.98	2.74	3.84	0.01	3.84	0.17	0.06
N6	81.59	1.48	4.44	0.45	0.01	0.01	0.98	2.83	3.99	0.02	3.99	0.14	0.06
N7	80.30	1.59	4.77	0.50	0.01	0.01	1.07	3.04	4.49	0.02	4.49	0.14	0.05
N8	80.43	1.77	4.30	0.71	0.03	0.01	1.19	3.63	3.69	0.03	4.69	0.14	0.06
N9	81.90	1.35	4.45	0.42	0.01	0.01	0.93	2.71	3.96	0.02	3.96	0.15	0.06
N10	82.28	1.45	4.55	0.44	0.02	0.01	1.03	2.88	3.10	0.02	4.10	0.14	0.05
P	85.81	2.11	6.73	0.35	0.01	0.01	2.30	2.38	0.07	0.02	0.07	0.15	0.05
RC	82.75	3.46	6.34	1.06	0.02	b.q.l	1.29	1.39	1.77	0.04	1.77	0.52	0.15
RS	72.11	3.17	9.63	0.37	0.01	0.01	1.19	10.46	1.04	0.01	2.04	0.15	0.08
T1	65.30	9.33	15.53	0.07	b.q.l	b.q.l	0.39	0.36	1.35	0.04	4.35	0.13	3.59
T2	68.26	7.83	14.70	0.06	b.q.l	0.05	0.29	0.29	1.92	0.04	1.92	0.13	5.43
T3	82.75	3.46	6.34	1.06	0.02	b.q.l	1.29	1.39	1.77	0.04	1.77	0.52	0.15
V1	61.81	8.31	18.51	0.13	b.q.l	b.q.l	1.23	0.94	2.01	0.03	5.01	0.13	1.90
V2	90.17	0.96	3.58	0.14	0.11	b.q.l	0.22	1.31	1.86	0.02	1.86	0.15	0.05
V3	82.65	2.04	6.00	0.23	0.01	0.01	0.67	1.82	3.33	0.02	3.33	0.15	0.06
V4	83.85	1.08	4.58	0.39	0.02	0.01	0.57	2.63	3.65	0.02	3.65	0.14	0.05
OL	89.26	6.80	b.q.l	0.16	0.00	0.01	0.18	3.33	0.04	0.02	0.01	b.q.l	0.15
OCC	88.70	7.00	b.q.l	0.20	0.00	0.01	0.19	3.65	0.03	0.02	0.01	b.q.l	0.15
Corning A	83.71	3.54	6.23	1.01	0.01	b.q.l	1.28	1.37	0.21	0.04	1.71	0.01	0.60
Corning B	81.28	1.38	11.49	0.21	0.05	0.01	0.40	0.55	0.07	0.13	3.40	0.03	0.14
Corning D	66.31	13.58	17.67	0.35	0.02	b.q.l	0.57	0.52	0.02	0.05	0.32	0.01	0.29

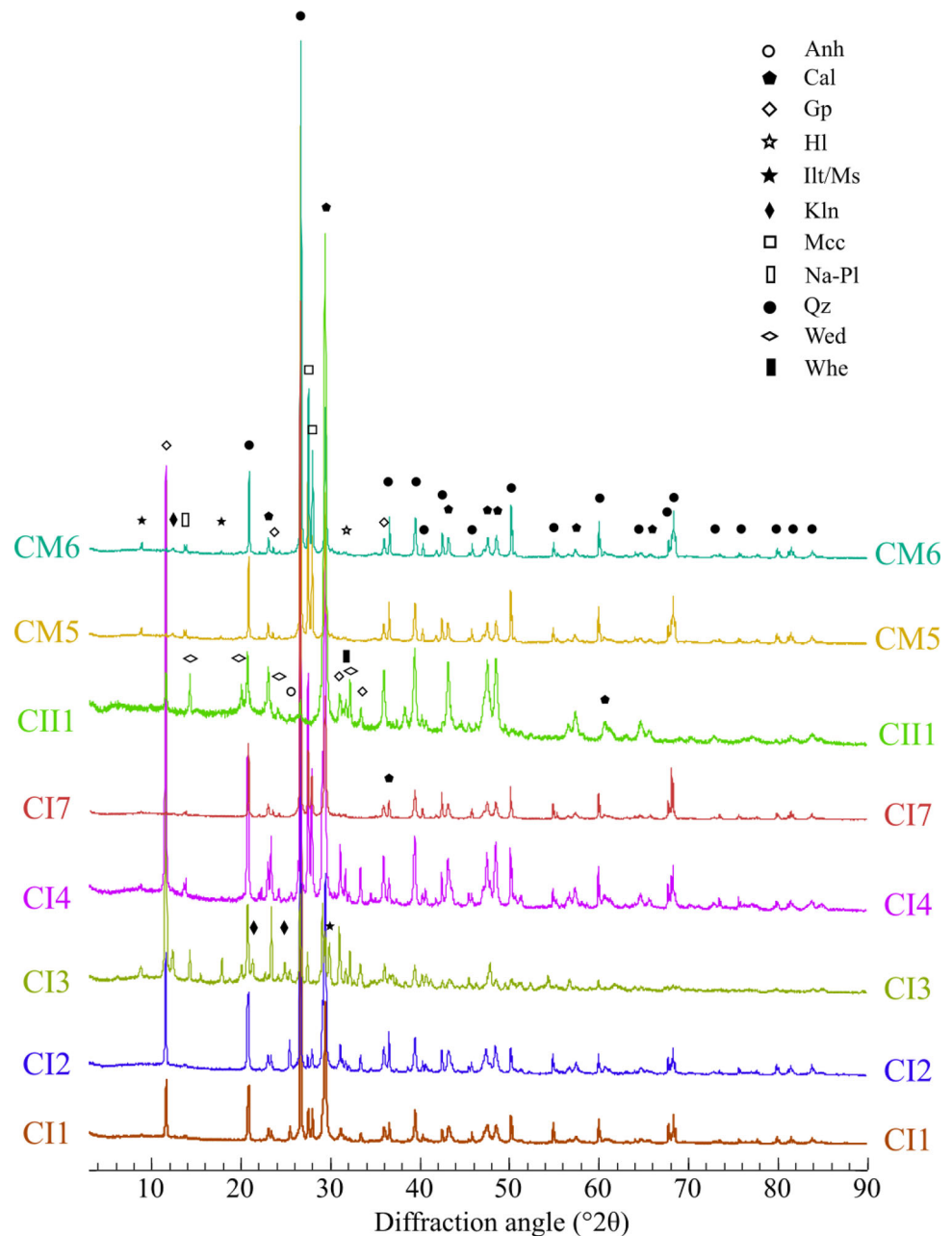
Elements are listed as recalculated percentages of oxides to the total of detected ones, as explained in the methods section

B.q.l. below quantification limit

3.2 XRD of masonry plasters and mortars

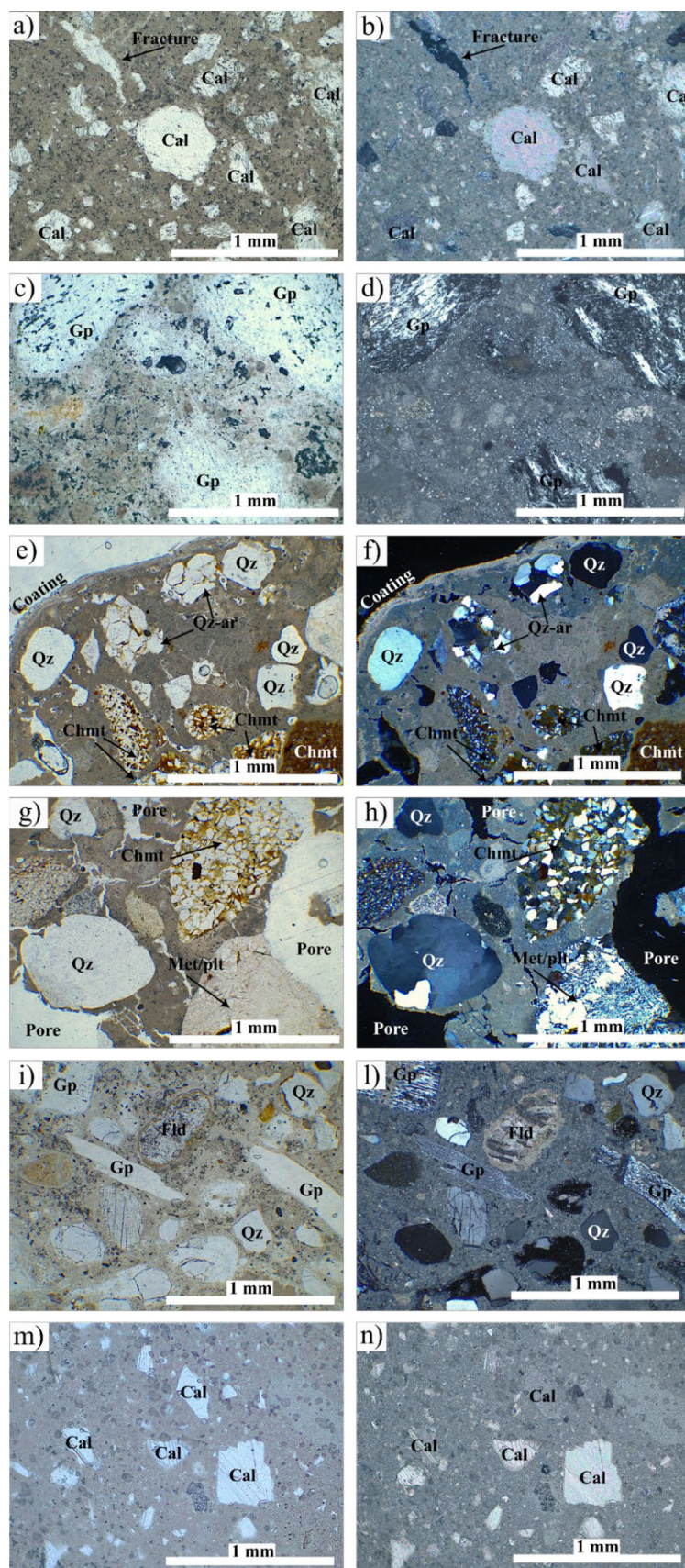
Diffraction analyses carried out on the powders of the sampled materials allowed to define the relative quantity of mineralogical phases present within masonry plasters and mortars. Table 3 summarises the obtained results. Globally, all samples have a high calcite content. The presence of calcite indicates that the used binder was a carbonatic one consisting of lime, but the abundance of calcite may also be due to the use of aggregates of carbonate origin (limestone or marble). Sample CI3 (Fig. 4), however, differs from the others since it has a calcite content of less than 10 wt%. The gypsum content of the samples is highly variable. It varies from a minimum content of 1.1 wt% in sample CI5 (Fig. 4) to a maximum of 30.2 wt% in sample CI3 (Fig. 4). The presence of gypsum could be related to the presence of a gypsum-based binder, the use of which therefore cannot be completely excluded, or to its addition to the mixture, or to ongoing sulphation processes of the carbonate phases. This phenomenon is particularly harmful to materials of carbonatic nature. Sulphuric acid, which forms through the reaction of sulphur dioxide (SO₂) with water, reacts with calcium carbonate present in plasters or mortars, producing gypsum [40, 41]. The formation of gypsum causes an increase in volume that can cause surface degradation of materials, compromising their integrity and aesthetic appearance [42, 43]. The presence of anhydrite can be also related to gypsum, as this phase represents the anhydrous form of gypsum itself. In addition, the presence of quartz and microcline is related to the nature of the inclusions, while the abundance of kaolinite and illite/muscovite phases in sample

Fig. 4 XRD patterns of masonry plasters (CI1, CI2, CI3, CI4, CI7, CII1) and mortars (CM5, CM6). Less intense peaks are not indexed



sometimes filled by secondary crystalline phases (Fig. 5a–b). CS2 has a more heterogeneous matrix with reddish-brown and orange-brown regions; within the matrix, millimetric to sub-millimetric aggregates with a subrounded to angular shape are observed. These minerals consist mainly of gypsum (Fig. 5c–d). This sample also exhibits abundant porosity due to micro-fractures partially filled by secondary crystalline phases. CS3_1 is characterised by sub-millimetric-sized, fairly graded, subrounded aggregates consisting mainly of quartz, feldspars and fragments of metamorphic/plutonic rocks, calcarenites and quartz-arenites (Fig. 5e–f). Among the aggregates, the presence of millimetric-sized chamotte is detected. Porosity is predominantly constituted by holes and shrinkage cracks. A thin layer consisting only of coating, probably of organic nature, can be recognised on the surface. Similarly, CS3_2 presents a bimodal distribution of millimetric to sub-millimetric aggregates, rounded in shape and composed of quartz, feldspars and fragments of chamotte, metamorphic/plutonic rocks, calcarenites and quartz-arenites (Fig. 5g–h). This sample is poorly compact due to the presence of dissolution pores interconnected by shrinkage cracks. CS4 has a heterogeneous matrix with brownish-yellow and dark-brown portions with poorly graded sub-millimetric to millimetric aggregates, predominantly subrounded in shape, consisting of quartz, gypsum and feldspars (Fig. 5i–l). This sample does not show a significant porosity. CS5 shows a very compact and homogeneous matrix with sub-millimetric, fairly graded, subrounded to angular aggregates composed of spathic calcite (Fig. 5m–n). Binder-to-aggregate ratio in thin sections of the samples is higher for CS1, CS2 and CS5 and lower for CS3_1, CS3_2 and CS4.

Fig. 5 Photomicrographs of stuccoes thin sections at plane-polarised light (left column) and cross-polarised light (right column); **a–b**: CS1; **c–d**: CS2; **e–f**: CS3_1; **g–h**: CS3_2; **i–l**: CS4; **m–n**: CS5. Cal = calcite; Fld = feldspar; Gp = gypsum; Qz = quartz; Chmt = chamotte; Met/plt = metamorphic/plutonic fragments; qz-ar = quartz-arenite

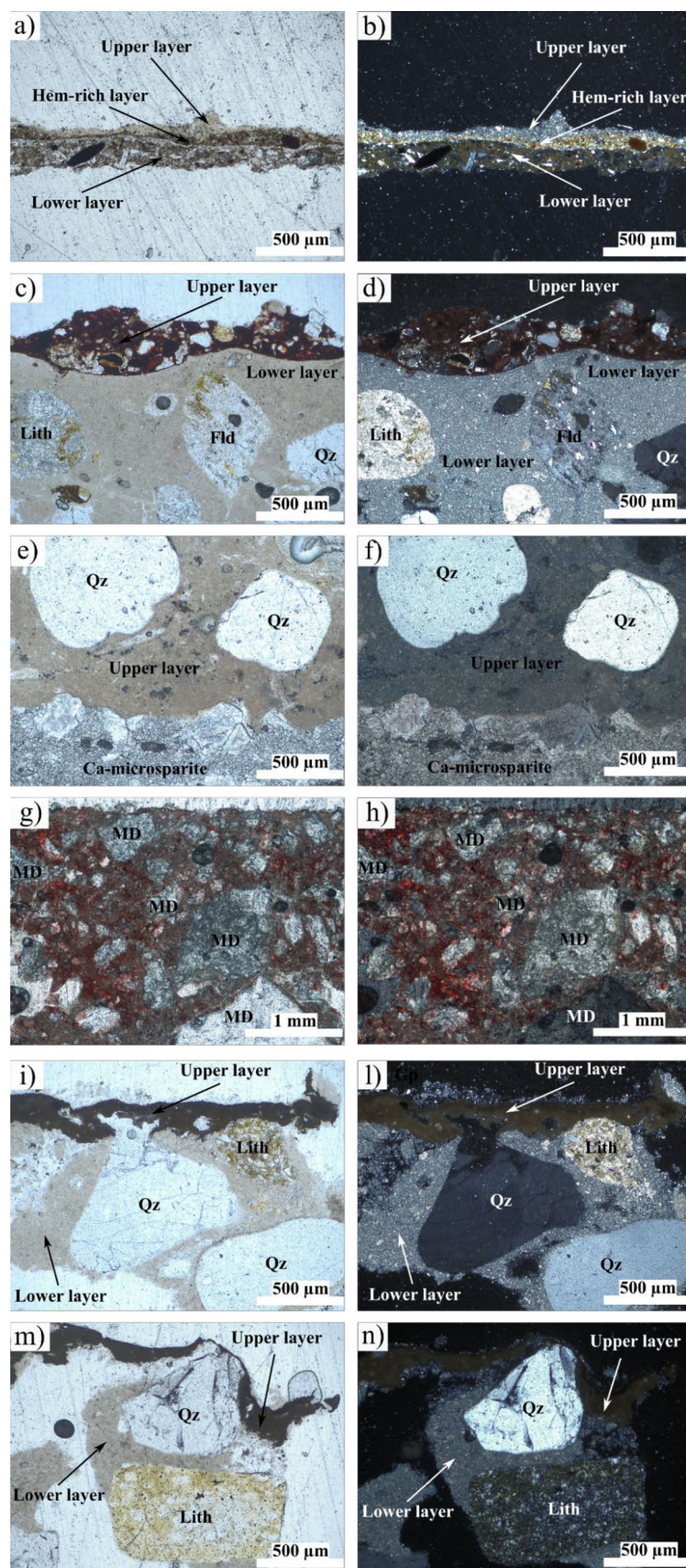


The thin sections of coloured plasters are displayed in Fig. 6. The petrographic observation on CT1 revealed the presence of three layers (Fig. 6a–b). The deepest layer, corresponding to the masonry mortar itself, consists of a brownish-grey microcrystalline matrix with a few sub-millimetric inclusions mainly constituted by feldspars; the middle layer is a plaster characterised by a matrix without inclusions in which hematite is recognisable, suggesting the pigmentation of the plaster by using red ochre [51, 52]. The upper layer is a plaster consisting of a yellowish-brown gypsum matrix where no inclusions are observed. CT2 consists of two clearly distinguishable layers with net contact (Fig. 6c–d). The lower layer, corresponding to the unpigmented masonry substrate, is characterised by a homogenous, micritic, brownish-yellow matrix rich in nearly millimetric-sized, moderately graded, subrounded inclusions consisting mainly of quartz, feldspars and lithic fragments. The upper coloured plaster consists of a homogenous, dark brownish matrix, poorly birefringent and rich in inclusions predominantly formed of quartz and lithic granules. CT3 (Fig. 6e–f) shows a lower unpigmented masonry layer formed by a carbonate microsparite topped by an upper coloured mortar layer formed by a yellowish, microcrystalline, porous mortar with nearly millimetric to millimetric-sized inclusions consisting mainly of quartz. CT4 is characterised by a highly heterogeneous matrix where poorly graded, sub-millimetric to millimetric-sized inclusions of marble dust are observed; a bright red pigmented matrix is widespread around the marble fragments (Fig. 6g–h); no layering can be recognised in this sample. The inclusions show a subrounded to angular in shape. In the samples CT5_1 and CT5_2, two different layers having a clear contact can be distinguished; the upper coloured plaster has an amorphous matrix of dark colour, while the lower unpigmented masonry layer has a homogenous and micritic, yellowish-grey matrix where sub-millimetric, moderately graded, subrounded inclusions are recognisable, consisting of quartz, feldspars and lithic fragments (Fig. 6i–l and m–n). Overall, in most of the samples, the aggregate grain size gradually decreases progressively towards the surface. This feature reflects a common and well-established practice that responds to technical and aesthetic requirements. From the petrographic observation of the thin sections of coloured plasters, it is possible to identify three techniques of pigmentation. The most common method is to mix the pigment with a plaster mixture containing smaller granules than those of the unpigmented masonry layer on which the coloured plasters are spread (see samples CT1, CT2, CT5_1 and CT5_2). The reduced size of the inclusions facilitates the spreading of the coloured plaster itself, and the transition from the pigmented (upper) layer to the unpigmented masonry (lower) layer is very clear. The second method observed in CT3 is the pigmentation of a mortar, since the aggregates are significantly larger than in the previous technique. This practice, very common, has also been recognised in the materials of the *Domus Aurea* (Rome) [53] and in some mosaic bedding mortars [54, 55]. Here too, the transition from the upper pigmented layer to the lower masonry layer is very clear. Finally, in CT4, there is no distinction between an upper and lower layer, since the integral pigmentation of the masonry layer is evinced, whereby the pigment is diffused between the granules of the masonry itself.

4 Conclusions

The present study provided interesting information not only in the context of archaeometric characterisation of the materials used in the decorations of Cathedral of Cefalù, but also for the purpose of a proper planning of conservation interventions. Considering the variety of materials analysed, the application of the question–answer method gave the opportunity to work specifically on the questions posed with regard to the different materials. Chemical analyses conducted by portable X-ray fluorescence (pXRF) and the comparison with reference glasses (both artificial and natural) allowed to recognise that the mosaic *tesserae* were manufactured by the recycling of glass, thus giving intermediate compositions with respect to those of the reference glasses. Moreover, chemical analyses confirmed the artificial origin of the black-coloured *tesserae*, allowing us to rule out the possibility that they were natural obsidian. In addition, elemental analyses allowed to identify the chromophores responsible for the wide range of colours detected in the mosaic decorations. Petrographic observation of coloured plasters in thin section provided information about the texture and pigmentation techniques; moreover, the simultaneous minero-petrographic characterisation of mortars, masonry plasters and stuccoes were useful in defining the type of binder (predominantly carbonatic) and aggregates, providing important data about degradation products, associated with the presence of calcium oxalates and sodium chloride. The identification of these mineralogical phases, in fact, provides valuable information about the conservation conditions and degradation processes that the materials have undergone. In-depth understanding of the properties of materials, through the use of both in situ and ex situ analytical techniques, is a key tool to ensure the preservation of this priceless heritage for future generations.

Fig. 6 Photomicrographs of coloured plasters thin sections at plane-polarised light (left column) and cross-polarised light (right column); **a–b**: CT1; **c–d**: CT2; **e–f**: CT3; **g–h**: CT4; **i–l**: CT5_1; **m–n**: CS5_2. Ca-microsparite = calcitic microsparite; Fld = feldspar; Lith = lithic fragment; Qz = quartz; MD = marble dust



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Data Availability Statement Data will be made available on reasonable request.

Declarations

Conflict of 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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