

## Study of the pigments in medieval polychrome architectural elements of “Veneto-Byzantine” style

Stefano Roascio <sup>a</sup>, Alessandro Zucchiatti <sup>b,\*</sup>, Paolo Prati <sup>b</sup>, Aurora Cagnana <sup>c</sup>

<sup>a</sup>Università di Genova, Facoltà di Lettere e Filosofia, Via Balbi 4, 16100, Genoa, Italy

<sup>b</sup>INFN e Dipartimento di Fisica dell'Università, Via Dodecaneso 33, 16146, Genoa, Italy

<sup>c</sup>Museo Archeologico Nazionale, P.zza Duomo 13, 33043, Cividale del Friuli (Udine), Italy

### Abstract

An analysis of pigment traces obtained from an ensemble of marble and limestone finely sculpted architectural elements, kept in the National Archaeological Museum of Cividale del Friuli (Italy), has been performed using scanning electron microscopy (SEM), particle induced X-ray emission (PIXE) and, for the white paint, Raman spectroscopy (RS). The experimental results on six different colours, combined with the historic, stylistic and documentary evidences provided by a recent study, strengthen the hypothesis of the dating and the provenance of all the sculptures in a prestigious building of Cividale in Veneto-Byzantine style, the palace of the Patriarch of Aquileia. The analyses also allow a first insight into the conservation history of the ensemble of architectural decorations. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

*Keywords:* SEM; PIXE; Raman; Medieval pigments; Veneto-Byzantine

### 1. Research aim

The National Archaeological Museum of Cividale del Friuli, in Italy, has an impressive collection of architectural decorative or structural elements sculpted in “Veneto-Byzantine” style. Amongst the decorative elements are a group of 12 *pateras* (an ornamental round bas-relief as in Fig. 1 left, typical of the middle ages) and three ribbed panels in relief (as in Fig. 1 centre). Amongst the structural elements are five pilasters (as in Fig. 1 right), five corbels and several fragments from broken frames. All the pieces feature similar phytomorphous decorations and animal fights and appear to be stylistically, dimensionally and functionally related. They can be dated, on stylistic grounds to the second half of the XII century, a period of splendour for the city of Cividale under the patronage of the patriarch of Aquileia [1], the second most important catholic authority, after the Pope, in the Italian peninsula. These sculptures have been the object of previous historic and artistic investigations [2] that assessed the style of the pieces, and their dating; suggestions were made on the possible provenance from the Cividale Cathedral, but were often con-

fused with respect to the origin of the materials and their function, not to mention that very little attention at all was paid to the original polychromy of the ensemble. Only very recently [3,4], a comprehensive study of the group of architectural elements, including the instrumental investigations on the pigments presented in this paper, has been undertaken with the aim of discussing the possibility of a common origin of the pieces with regard to the workshop in which they were produced, of the building to which they belonged and, finally, of their specific function.

### 2. Historical and stylistic considerations

In the middle ages, the architectural use of *pateras* and panels was widespread in Venice and the Veneto region of which Cividale del Friuli was a part. Even today, hundreds of these pieces are visible on the façades of the Venetian palaces, often accompanied by frames and friezes. Their shapes and motifs [5] are very similar to those of the pieces exhibited at the museum of Cividale. The unifying iconographic motifs of the ensemble of sculptures are the scenes of animal fights and of the so-called “life tree” (see Fig. 1 centre). They are probably of ancient Mesopotamic origin, have been known in Byzantium through the market of small

\* Corresponding author.

E-mail address: zucc@ge.infn.it (A. Zucchiatti).



Fig. 1. Three examples of architectural elements from the museum of Cividale: a patera (left), a panel (centre) and a pilaster (right). Reproduced for photographic plates of the 1950s. Courtesy of Soprintendenza BAAAS of Friuli Venezia Giulia (authorisation no. 222/2001).

art objects, incorporated in the Byzantine artistic tradition and spread over the area of Byzantine cultural influence, including notably Venice and its region (Veneto), also by the intermediation of the western Islamic art. Birds, wolfs, racemes are repeated in the *pateras*, in the panels and in the pilasters, although in a different scale determined by the size of the architectural element. The superior quality of the figures sculpted on the *pateras* and panels with respect to that found on the pilasters, does not necessarily imply production in different workshops or by different hands since it can be simply ascribed to the different texture of the stones. From petrographic analyses previously reported [3], the *pateras* are made of marble, probably sliced from stubs of old Roman columns as was the common practice at the time, and are therefore smoothly manufactured. The pilasters are made of a local limestone, called *Pietra di Aurisina*, a less expensive stone, available in various sizes, but much more porous and brittle than marble with the consequence that the artefacts made of it had poorer surface quality. The stylistic arguments and the choice of materials favour the hypothesis that the sculptures are indeed medieval and have been produced in the same workshop using scraped and local materials.

As regards dating, scholars have taken as a time reference a major documented event [6], i.e. the disastrous fire

that in 1186 destroyed the cathedral complex and assumed the ensemble of sculpted elements to be part of the architectural decorations made during the reconstruction. It has been recently inferred [3,4] that, since the use of *pateras* and friezes was a common practice in buildings but very rare in churches, the sculpted artefacts should have belonged probably to the patriarchal palace which was annexed to the cathedral. The palace [7] which had served as the prestigious seat of the Patriarch of Aquileia, afterwards became the *Palazzo dei Provveditori Veneti* that hosts today the National Archaeological Museum. A XVI century testimony, given by the notary Marcantonio Nicoletti on the occasion of the demolition of the palace in 1553, reports the existence of a small church built inside the *curia*, dedicated to San Paolino of Aquileia: "... a nice little church of barbarian structure but rich, and sumptuous, with the altar made of small columns of various colours..." ("*...una chiesiola di struttura barbara, ma ricca, e sontuosa, con l'altare a colonnelle di varii colori...*") [8]. In the XVIII century, Gaetano Sturolo, a priest of Cividale, enclosed a drawing that reproduced the medieval aspect of the patriarchal palace in a volume on the city history (Fig. 2). Sturolo presumably followed some original text or drawing that he could personally consult but which is today lost. In his drawing, the façade shows *pateras* and phytomorphic

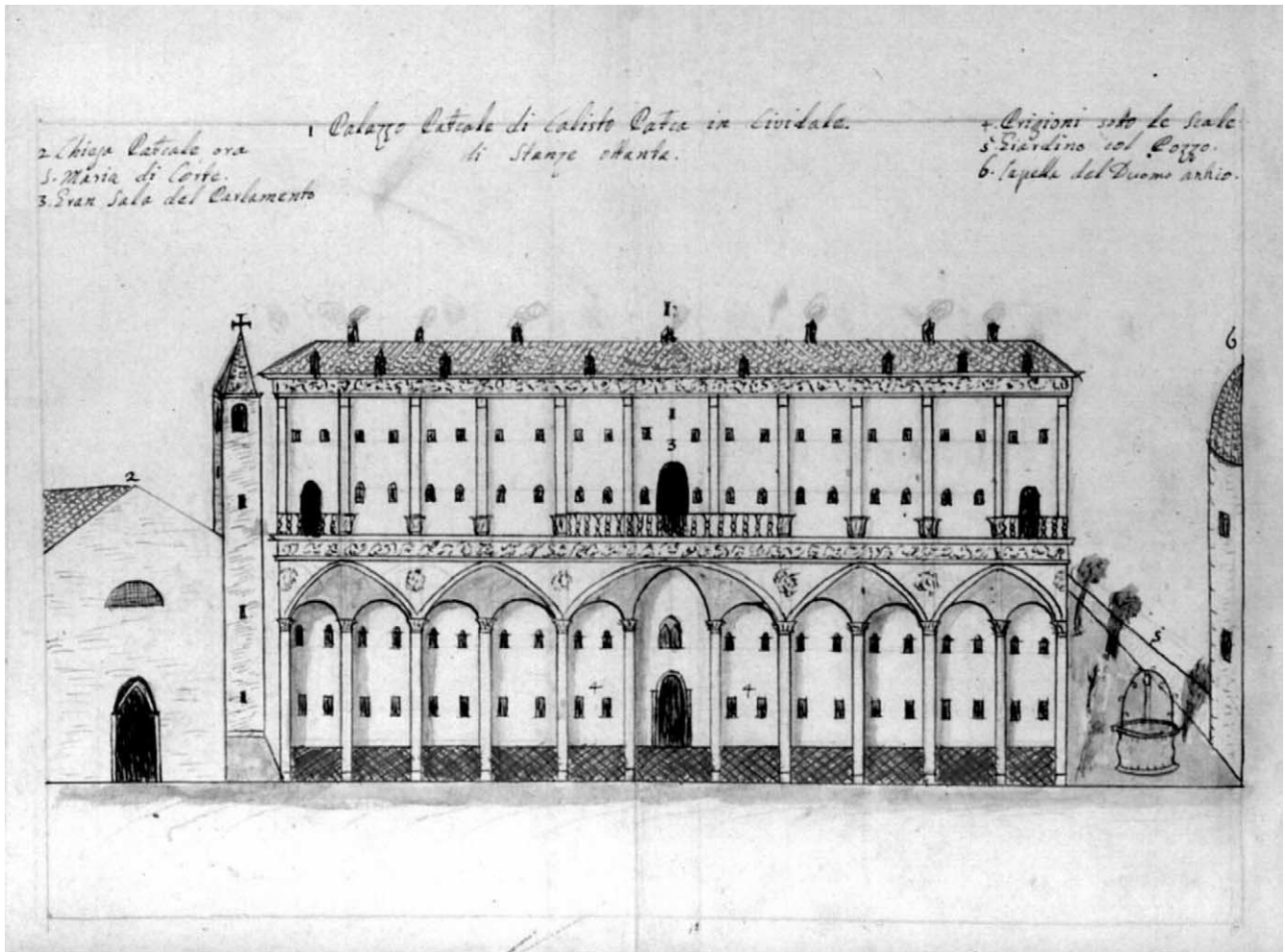


Fig. 2. The drawing of Gaetano Sturolo that depicts the patriarchal palace of Cividale before the XVI century demolition. Courtesy of Soprintendenza BAAAS of Friuli Venezia Giulia (authorisation no. 222/2001).

friezes that recall the ones we have studied. In addition, during a stratigraphic excavation performed in the 1980s over the foundations of the *Palazzo dei Provveditori Veneti*, a portion of a *patera* and a fragment of a frieze, very similar in style, size and marble quality, to the ones we have studied, have been recovered.

In the light of these facts, it is reasonable to assume that the group of sculptures of the Cividale museum was part of the patriarchal palace: *pateras* and friezes being displayed on the façade and the pilasters being part of the annexed San Paolino church.

The most remarkable characteristic of the sculptures, confirmed by the finding of definite traces of pigments in all pieces, to which previous scholars [2] did not pay attention, is that they were conceived to be completely painted in brilliant colours and having a vivid appearance, quite different from the dreary aspect of today. The history of the conservation of these pieces is for the most part unknown: when and why the original colours have been lost is not documented. For a part of the sculptures, the date of acquisition by the museum is known and it is between 1818 and 1899. It is possible that the pieces were acquired in the

condition that they were, i.e. almost completely scraped but it cannot be excluded that they were scraped at the moment of acquisition to follow the neo-classical style of the time. At least one episode concerning such a habit is documented. A polychrome marble head of Ulysses, which was excavated in early 1900s is now completely white [9], in the museum of Sperlunga.

### 3. Experimental methods and results

It has been possible to scrape, in the pilasters only, a few scales in the remaining traces of the former colours to attempt the analysis of pigments. We have taken a total of six samples whose colour appeared: white, red, yellow, green, vivid blue and dark blue. The samples have been sorted under an optical microscope, to choose from each colour a suitable fragment, which was glued on an adhesive carbon foil, and mounted over aluminium discs used for scanning electron microscopy (SEM). Three analytical tools that have been used: SEM [10,11] coupled to energy dispersive spectroscopy (EDS), Raman spectroscopy (RS)

Table 1

The analyses performed on paint samples from remaining traces of the former colours

Colour	SEM imaging	SEM/EDS	RS	PIXE
White	× *	×	×	×
Yellow	×	×		×
Green	×	×		×
Red	× *	×		×
Blue	×	×		×
Dark blue	×	×		×

[12] only for one white sample, and particle induced X-ray emission (PIXE) [11,13–15], to perform a series of measurements summarised in Table 1. All the analyses have been performed using the equipment of the Centre de Recherche et Restauration des Musées de France (C2RMF) at the Louvre museum.

SEM imaging and SEM/EDS have been used to describe the microscopic structure of the samples and to identify in a semi-quantitative way the nature of the matrix and, if possible, of the embedded pigment grains. The electron-gun working conditions have been set at 20 kV, 80  $\mu$ A and we have operated in back-scattered electron mode (BSE) normally under vacuum. This was enough, in most cases, to avoid discharging even without coating the samples with a conductive carbon layer as usual, with the aim of preserving the integrity of samples throughout all our analyses. In critical cases (marked with \* in Table 1), the chamber pressure was increased to 0.5 mbar with a tolerable loss in image quality. X-ray spectra have been collected either in spot mode or scan mode to characterise pigment grains and describe the matrix.

RS has been used to apportion calcium carbonate and calcium sulphate in the white sample. A laser line at 531.82 nm (1 mW power) has been used to excite the characteristic Raman lines of the compounds. Either an enlargement of 10X (corresponding to a spot of 20  $\mu$ m) or 100X (2  $\mu$ m diameter) has been used.

PIXE was performed with the AGLAE accelerator. A proton micro-beam [15] of 20–30  $\mu$ m diameter and 3 MeV energy, extracted in air was used to scan the surface of the samples over an area of 0.5  $\times$  0.5 mm<sup>2</sup>, with the exception of the dark blue sample that was irradiated in spot mode. The PIXE spectra were de-convoluted by the GUPIX [16,17] package, in its thick target option following a well-proven procedure [18]. It has been assumed that all elements were in oxide form, as is normally true for minerals and therefore for mineral pigments, except calcium which was assumed to be in carbonate form. The oxide concentrations were extracted from an iterative procedure that took into account the energy loss of the incoming protons and the attenuation of the outgoing elemental characteristic X-rays in the matrix and normalised the sum of concentrations in any step to 100%.

### 3.1. White paint

The white paint consisted of several superposed layers of the basic pigment CaCO<sub>3</sub> (Fig. 3a). Well-developed calcite crystals are seen in the SEM image of Fig. 3b. The EDS spectrum (not shown), obtained from the scanning of a 200  $\times$  150  $\mu$ m<sup>2</sup> area, was dominated by Ca K <sub>$\alpha$</sub>  and K <sub>$\beta$</sub>  peaks with minor peaks of Mg, Al, Si, P, S, and K having 60–100 times lower intensity. Since the coloured samples appeared to be all based on a calcite base, the white paint was analysed by RS as well. As seen in Fig. 4a, the Raman spectrum obtained with a spectrometer lens magnification of 10  $\times$  (spot of 20  $\mu$ m diameter) shows only the calcite peaks at 281.1, 712.0 and 1087.6 cm<sup>-1</sup>. When the enlargement is increased to 100  $\times$  (Fig. 4b) and the surface is searched for other compounds, the line at 1008.0 cm<sup>-1</sup> of gypsum (calcium sulphate CaSO<sub>4</sub>) is seen in some places. No other compound, like calcium oxalate, is seen. Since in PIXE spectra Ca should come mostly from the calcite base, this element is considered in the GUPIX data deconvolution to be in the form of CaCO<sub>3</sub>. The PIXE analysis of the white paint (Table 2) confirms that it consists, for the major part of calcite, of amounts of MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and SO<sub>3</sub> all around 1%. Sulphur could well come from the gypsum identified by RS, either admixed with calcite at the origin or due to chemical alteration of calcite by the atmospheric sulphur. The origin of magnesium, aluminium and silicon, has not been investigated: one possibility is that they come from the stone itself.

### 3.2. Blue paint

It was evident to the eye, that there were two different shades of blue, one vivid and the other dark; both have been sampled. SEM images in the same scale (Fig. 5) show a clear texture difference. The SEM/EDS spectra of the large areas in Fig. 5 revealed a markedly different composition: the vivid blue (Fig. 5a) is based on calcite and is rich in Na, Al, Si, S and K; the dark one (Fig. 5b) shows, besides minor quantities of the above elements, a large contribution of sulphur, barium and iron (Fig. 6). With a spot measurement, we could deplete the calcite signal to appreciate better the composition of a mineral grain in the vivid blue, as seen in Fig. 6. This was rich in Na, Al, Si and S, showing the first evidence of lapislazuli.

Lapislazuli is a natural stone formed by the admixture [19–21] of minerals of the *sodalite* group, which gives the stone a characteristic vivid blue colour. The main one is *lazurite*: Na<sub>6</sub>Ca<sub>2</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>[(SO<sub>4</sub>),S,Cl,(OH)]<sub>2</sub>; other minerals are *sodalite* itself: Na<sub>8</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>Cl<sub>2</sub> and *Haiiyne*: (Na,Ca)<sub>4–8</sub>Al<sub>6</sub>Si<sub>6</sub>(O,S)<sub>24</sub>(SO<sub>4</sub>,Cl)<sub>1–2</sub>. The sodalite group minerals can be accompanied by secondary minerals like *diopside*: CaMg(Si<sub>2</sub>O<sub>6</sub>), *wollastonite*: CaSiO<sub>3</sub> and *orthoclase* (potassic feldspar): KAlSi<sub>3</sub>O<sub>8</sub>. The lapislazuli stone has peculiar inclusions of calcite, CaCO<sub>3</sub> and pyrite, FeS<sub>2</sub> that distinguish, *inter alia*, this natural pigment from the

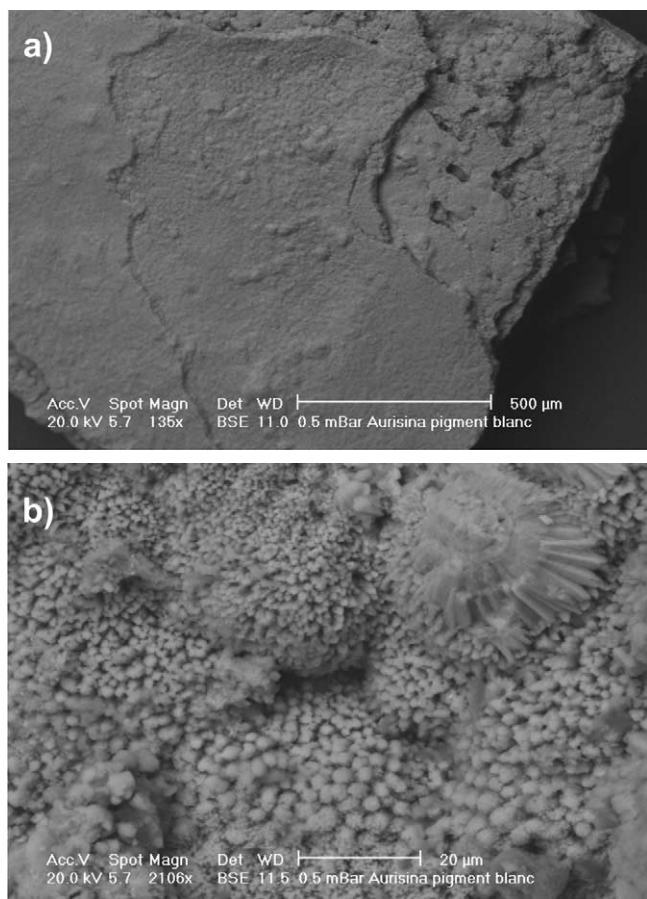


Fig. 3. (a) The SEM image of a  $1 \times 1.5 \text{ mm}^2$  area of our white paint shows that it consists of several superposed layers. (b) Well-developed calcite crystals are evident in the enlargement of a  $60 \times 90 \text{ }\mu\text{m}^2$  area in the same sample.

artificially produced *ultramarine blue*. The PIXE analysis of blue paints is reported in Table 2. If we look at the vivid blue we observe first that Na, Al, Si and S are the most abundant elements, besides Ca, and exceed 5% of the total oxide mass. Furthermore, only the elements that could be contributed by the minerals and are expected to be present in the lapislazuli pigment, as listed above, exceed the 0.2% level, in particular Fe and K, which are absent in the white sample, and are also absent in the artificial *ultramarine blue*. This is the first indication of the presence of lapislazuli. Since we observe only traces of Cu, we can exclude the presence of azurite,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , another blue pigment known and widely used in the middle ages. A further evidence of the presence of lapislazuli comes from the elemental ratios. If we exclude Ca, as it is not possible to separate the amount contributed by the pigment from that contributed by the calcite basis, and concentrate on the most abundant elements in the sample profile, i.e. Na, Al, Si, S we can compare the elemental ratios obtained by PIXE with those expected from the chemical formulae of the minerals. This is shown in Table 3. The Al/Si ratio does not change in the sodalite group minerals, since in their chemical formula, six atoms of aluminium and six of silicon are always

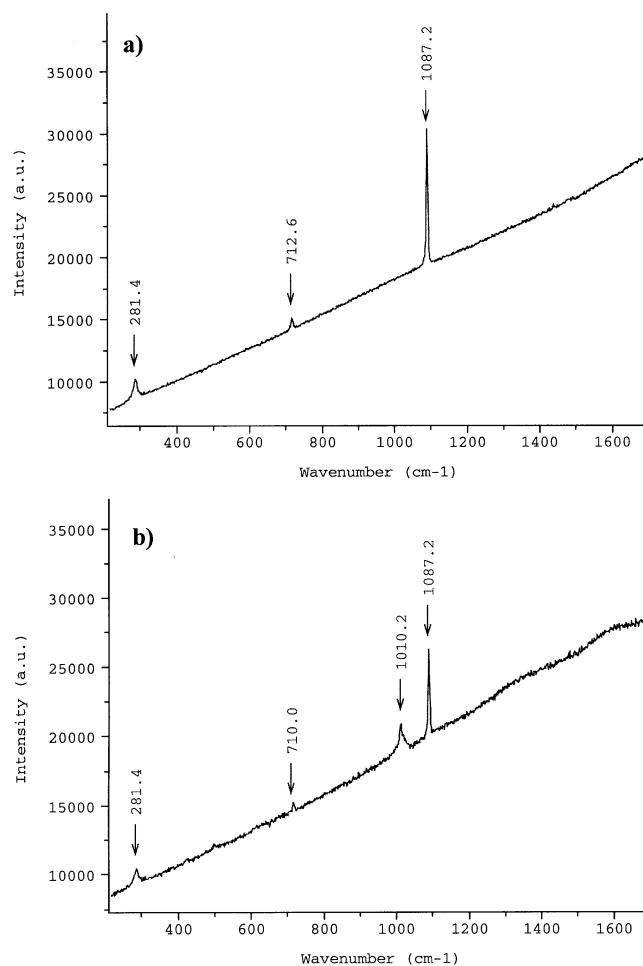


Fig. 4. (a) The white paint Raman spectrum over a  $20 \text{ }\mu\text{m}$  diameter spot (spectrometer lens magnification  $10 \times$ ) shows only the calcite peaks. (b) Increasing the enlargement to  $100 \times$  and searching the surface reveal at times the presence of calcium sulphate.

present. The experimental Al/Si ratio is correct within the measurement errors. The ratios of Na to Al and Si are only 25% higher than in lazurite but the amount of Na, contrary to Al and Si, changes in the different minerals as seen in Table 3. The ratios to S are all about a half of what they should be in lazurite. An extra source of S is evidently present. A small amount should be associated to the detected Fe (only 0.21% of  $\text{Fe}_2\text{O}_3$  from the GUPIX analysis) in the form of pyrite. The major part should not be related to the pigment but may be assumed to come from the gypsum identified by RS in the white paint since, in none of the minerals of the sodalite group, the ratio to sulphur changes in the same way for Al, Na and Si.

The PIXE analysis of the dark blue paint confirms the SEM/EDS observations. The high amounts of  $\text{SO}_3$  and BaO are in a weight ratio (0.56) close to that in barium sulphate (0.52), perfectly compatible with the hypothesis of a  $\text{BaSO}_4$  based paint admixed with a  $\text{CaCO}_3$  matrix contaminated by gypsum. The amounts of Na, Al, and Si are definitely above those found in the white paint and lower than those in lapislazuli. In the dark blue paint, Fe is at the 3% level, the

Table 2

The results of PIXE analysis for the six paint colours. All concern the irradiation of a  $0.5 \times 0.5 \text{ mm}^2$  area with the exception of the dark blue, which has been irradiated in spot mode

Oxide	White	Lapislazuli	Dark blue	Yellow	Green	Red
Na <sub>2</sub> O		5.70	2.73	1.60	0.29	0.38
MgO	1.47	1.10	2.02	0.84	1.15	1.56
Al <sub>2</sub> O <sub>3</sub>	0.28	7.27	2.80	0.43	6.50	2.10
SiO <sub>2</sub>	1.17	8.77	6.61	1.47	7.15	5.86
P <sub>2</sub> O <sub>5</sub>				0.38	0.08	0.40
SO <sub>3</sub>	1.00	8.16	16.08	3.33	1.23	3.69
Cl	0.13	0.18	0.36	0.23	0.12	0.16
K <sub>2</sub> O		0.39	0.45	0.01	0.10	0.35
CaCO <sub>3</sub>	95.33	68.08	35.61	87.53	82.70	82.82
TiO <sub>2</sub>		0.02			0.03	0.10
Cr <sub>2</sub> O <sub>3</sub>			0.06	0.03		
MnO		0.01	0.11		0.01	0.04
Fe <sub>2</sub> O <sub>3</sub>		0.21	3.00	0.47	0.58	2.33
CoO			0.02			
NiO			0.01	0.01		
CuO		0.07	0.50	0.46		
ZnO	0.01	0.01	0.31		0.01	0.01
SrO	0.02	0.02	0.23	0.02	0.03	0.04
SnO <sub>2</sub>	0.18					
BaO			28.84	0.10		0.01
PbO	0.01	0.01	0.27	3.10	0.01	0.16
Total	99.60	99.99	100.00	100.00	99.98	99.99

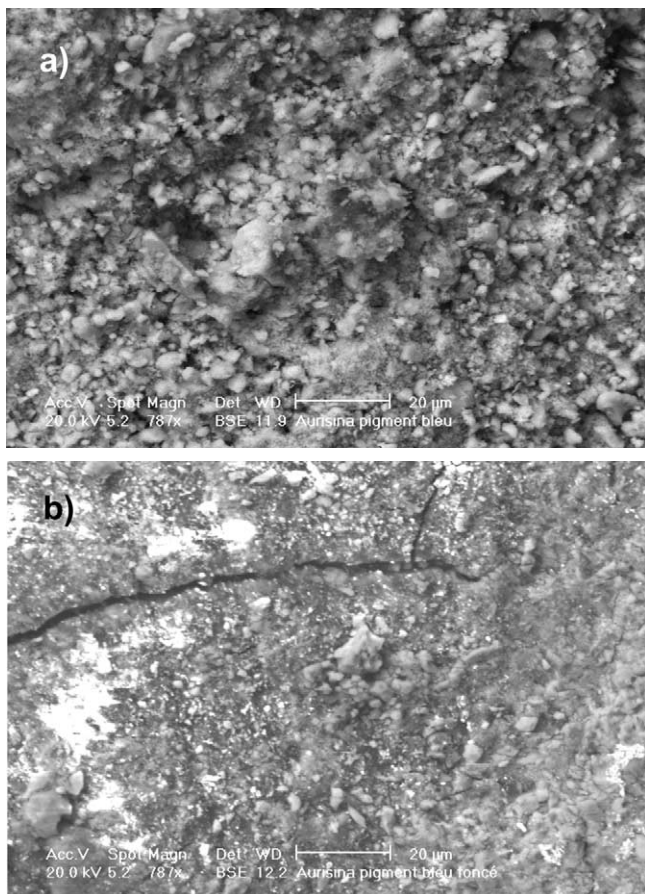


Fig. 5. (a) The SEM image of a  $100 \times 150 \mu\text{m}^2$  area of our vivid blue paint sample. (b) The SEM image of a  $100 \times 150 \mu\text{m}^2$  area of our dark blue paint sample.

highest value in all samples. Fast white ( $\text{BaSO}_4$ ) is an inorganic pigment that was available only from the second half of the XVIII century. Almost of the same period is the so-called “Paris blue”, an artificial pigment produced since the beginning of the XVIII century. It has a chemical formula  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  and could account for the high amount of iron measured in the sample.

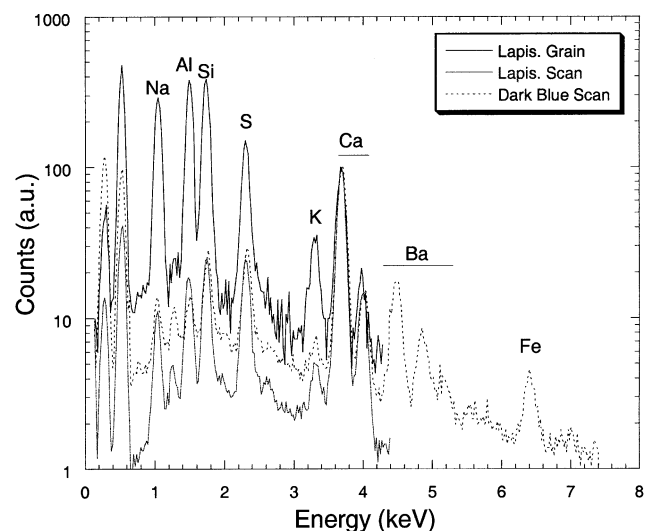


Fig. 6. Some SEM/EDS spectra of the blue paints. In black (full line) is the spectrum from a spot in our sample containing a mineral grain of lapislazuli. In grey (full line) is the spectrum coming from the scan of a  $100 \times 150 \mu\text{m}^2$  area of the same sample. In black (dotted curve) is the spectrum coming from the scan of a  $100 \times 150 \mu\text{m}^2$  area of our dark blue paint, rich in Ba and Fe.

Table 3  
The weight ratios of the most abundant elements detected by PIXE and the same ratios expected for lazurite, the principal constituent of lapislazuli

	Pixe			Lazurite			Sodalite			Hauyne		
	Al	Si	S	Al	Si	S	Al	Si	S	Al	Si	S
Na	1.09	1.02	1.29	0.86	0.82	2.15	1.13	1.09	–	0.57–1.13	0.54–1.09	0.12–5.7
Al		0.91	1.18		0.96	2.53		0.96	–		0.96	0.19–5.1
Si			1.26			2.62			–			0.33–2.6

### 3.3. Yellow paint

The PIXE analysis of a  $0.5 \times 0.5 \text{ mm}^2$  area (Fig. 7a) shows a spectrum rich in calcite and lead with additional iron and copper and only 0.1% in weight of barium-oxide (Table 2). The PIXE data are compatible, in the first instance, with a paint made of litharge (3.10%) in a calcite basis. No yellow ancient or modern pigment is based on copper (0.46%) or iron (0.47%) and the presence of these elements could be related to the will of modifying the shade of the yellow paint through the addition of minor quantities of other pigments. On the contrary the absence of arsenic and antimony excludes the presence of two other yellow pigments known in early medieval times: orpiment ( $\text{As}_2\text{S}_3$ ) and Naples yellow ( $\text{Pb}_3(\text{SbO}_4)_2$ ). The absence of tin excludes the presence of lead–tin yellow ( $\text{Pb}_2\text{SnO}_4$ ) known in late medieval time.

The SEM/EDS analysis of the yellow sample shows essentially the presence of calcium and lead in agreement with PIXE, when a large area is scanned. However, a few spots containing in addition to  $\text{BaSO}_4$  and Cl, as shown in the spectrum of Fig. 7b, have been found. As for the dark blue paint, this suggests the use of modern pigments also on the yellow painted pilaster, e.g. a fast white mixed with mineral yellow ( $\text{PbCl}_2 \cdot 7\text{PbO}$ ). However, the low BaO concentration should prove that the extent of retouches is minimum and the presence of sulphur and chlorine in any of the samples does not allow to identify and quantify a modern pigment like mineral yellow and distinguish it from litharge ( $\text{PbO}$ ). The data are also compatible with the presence of minium ( $\text{Pb}_3\text{O}_4$ ) known from Roman times: in this case, the original colour of the piece would have been orange-red that turned to yellow with time: a well-known degradation process.

### 3.4. Green paint

On a well-crystallised calcite basis, a few pigment grains have been identified by SEM. They show the presence of Na, Mg, Al, Si, Fe, and K. The PIXE analysis (Table 2) confirms in a quantitative way the presence of these elements, in particular, Mg, Al and Si besides Ca and S, which have now been established as typical of the calcite and gypsum base. The pigment elemental content is compatible with a green earth colour. The absence of Cu excludes the presence of other green pigments known in early medieval times like verdigris ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) and malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ).

### 3.5. Red paint

The red paint has a peculiar microscopic aspect (Fig. 8a) with large craters due perhaps to the evaporation of water droplets or to the production of  $\text{CO}_2$  gas from dissolved calcite. Grains of pigment (Fig. 8b), very rich in  $\text{Fe}_2\text{O}_3$ , are easily detected in SEM/EDS (Fig. 9). The PIXE analysis confirms that Fe is quite abundant in the sample, as would be expected for red ochre. The absence of mercury and a little amount of lead show that we do not have cinnabar ( $\text{HgS}$ ) or minium ( $\text{Pb}_3\text{O}_4$ ) in the sample.

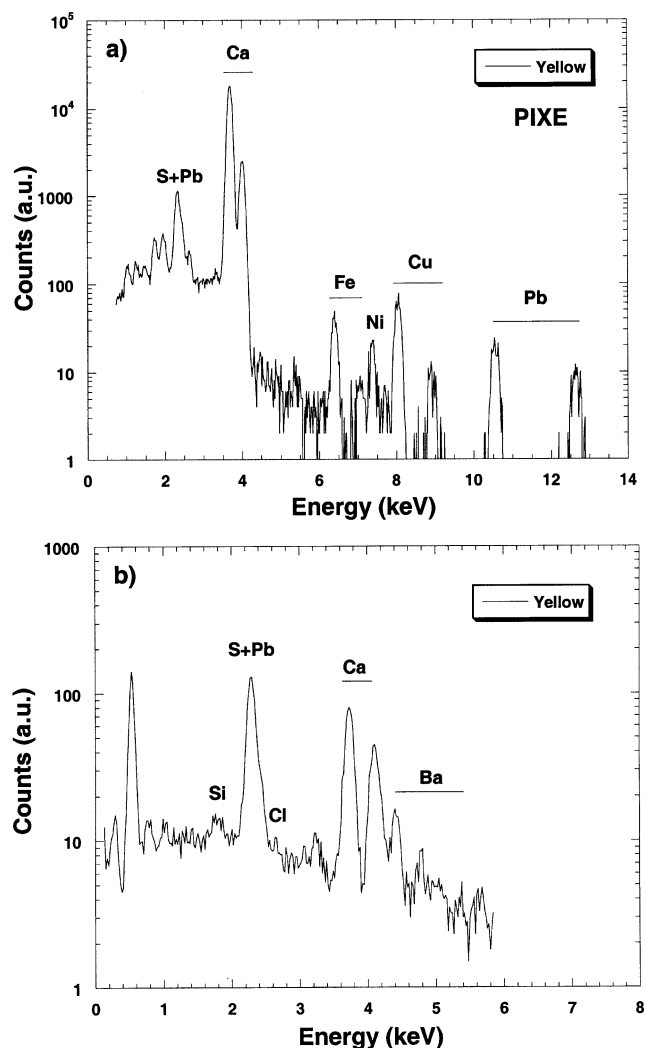


Fig. 7. (a) The PIXE spectrum collected from a  $0.5 \times 0.5 \text{ mm}^2$  area in the same sample. Here, the barium  $L_{\alpha}$ ,  $L_{\beta}$ ,  $L_{\gamma}$  peaks are not visible. (b) The SEM/EDS spectrum of a barium-rich spot in our yellow paint sample.

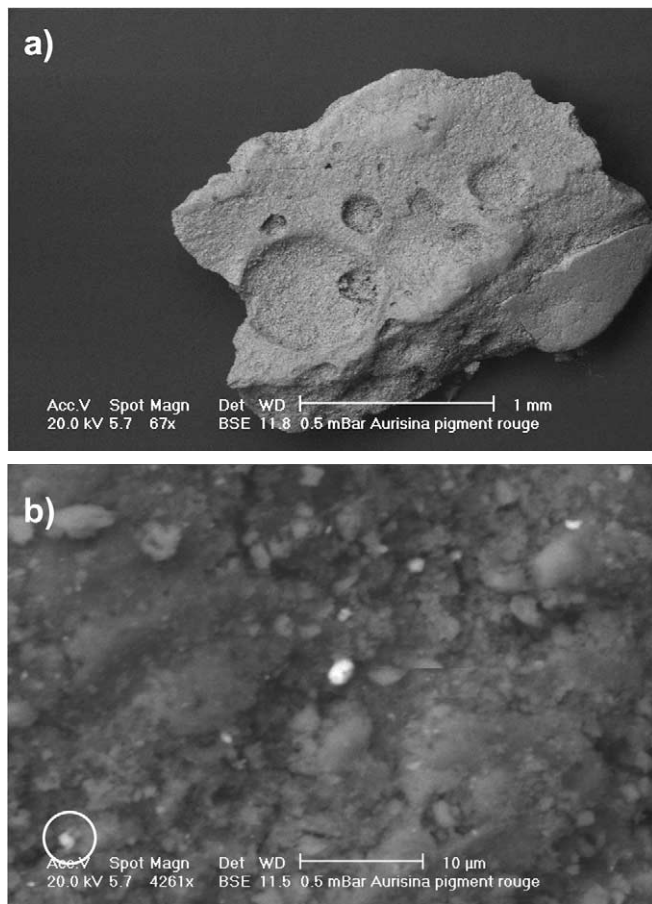


Fig. 8. (a) The SEM image of our red paint fragment showing several regular craters on the surface. (b) Encircled is a grain of pigment in the same sample whose EDS spectrum shows the presence of high amounts of Fe.

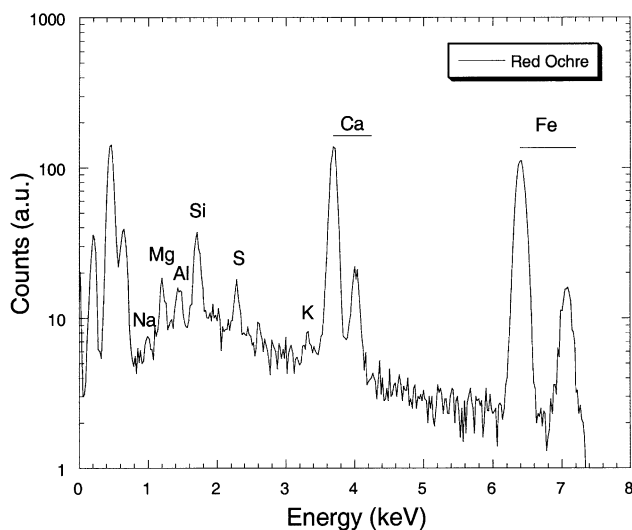


Fig. 9. The SEM/EDS spectrum of the pigment grain encircled in the SEM image of Fig. 6 right.

#### 4. Discussion

All paints collected and analysed contain pigments certainly known and widely used at the time of the documented rebuilding of the Cividale Cathedral and patriarchal palace, i.e. in the second half of the XII century. The red ochre, the green earth, calcite and litharge, are known from antiquity and it is not surprising to find them in our context. Very important is the finding of lapislazuli. This blue pigment, almost as expensive as pure gold, originated from where Afghanistan is today and was reserved exclusively for rich and prestigious decorations. Most of its use was in miniatures, paintings and frescoes [22]. As far as we know, this is the first observation of its use on decorative architecture. The most natural consequence of our finding is that such a rich material, of which Venice had the trade monopoly, should have been used only for the most prestigious palace of Cividale, the palace of the patriarch of Aquileia—a substantial support to the historical and stylistic considerations made above.

The presence of blue in the palette of the Cividale artists provides indirect support to the dating of the pieces. It has been demonstrated that in the western world blue began to be preferred to red not only in art but also in many aspects of daily life (dresses, coats of arms, objects,) and had replaced almost completely the red in the XVII century [23]. In the same pilaster there is evidence of opposite faces painted in red and blue and this is typical of the medieval style where no isolated colour is used but a colour contrast is normally desired. The contrast of red and blue is the most typical and documented one [24].

We have, however, found modern materials, like fast white and perhaps Paris blue and mineral yellow that were not available before 1750. Since the pieces were acquired by the museum only starting from 1818, it cannot be excluded that, at some stage between 1750 and 1820, somebody had attempted to bring the pieces to their original polychrome aspect by making extensive paint retouches with the available materials and with no attention to the integrity of the remains of the original paints. Also the retouched pieces have been evidently scraped on the acquisition by the museum.

#### 5. Conclusions

The analysis of pigments has increased in a substantial way the knowledge of the pieces and helped considerably in finding a solution of the various questions raised about the ensemble of sculpted architectural elements of the Cividale museum. The dating of the elements finds further support from the characterisation of the pigments known and used in middle ages. In particular, the presence of blue is consistent with the chromatic preferences of the XII century artists. The finding of lapislazuli promotes quite strongly and naturally the idea that the *pateras*, friezes and pilasters come



from the most prestigious palace of Cividale: the palace of the Patriarch of Aquileia. The finding of modern materials witnesses a very complex conservation history, which must have passed through several drastic operations on the pieces before their actual state.

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