

Unveiling the use of *creta* in Roman plasters: analysis of clay wall paintings from *Brixia* (Italy)

ROBERTO BUGINI¹, CRISTINA CORTI², LUISA FOLLI¹, LAURA RAMPAZZI^{2*}

¹CNR-Istituto per la Conservazione e la Valorizzazione dei Beni Culturali, via Roberto Cozzi 53, 20125 Milano, Italy

²Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, via Valleggio 11, 22100 Como, Italy

*Corresponding author

Laura Rampazzi, email address: laura.rampazzi@uninsubria.it; phone number: +390312386475; fax number: +390312386449

Abstract

The paper describes the analysis of a particular kind of plaster from the walls of the Roman Sanctuary (first half of the 1st century BCE) in the centre of Brixia (now Brescia, Italy), which is an outstanding example of Roman Republican architecture. The walls were plastered and painted with different patterns, imitating marble panels and curtains. Optical microscopy on thin sections, X-ray diffraction, and infrared spectroscopy were performed on several samples of the plaster in order to reveal the execution technique. The palette consisted of glauconite, celadonite, Egyptian blue, and red and yellow ochres. In some cases, an organic compound, possibly a lipidic compound, was present in the external paint layer, as a surface treatment.

*The plaster contains two superimposed coats: the render coat with lime binder and sandy aggregate; the finish coat with a clay fraction (illite, chlorite, kaolinite), together with calcite from slaked lime and grains of quartz, silicate and carbonate rocks. Although Vitruvius' *De Architectura* reported the use of *creta* (clay) as daub smeared on reed vaults, the Sanctuary of Brixia represents the first documented use in Roman buildings in a painted plaster laying on a stone masonry wall.*

Keywords: clay plaster, Roman painting, Optical Microscopy, XRD, FT-IR

Introduction

Many publications have traced the history and execution technique of Roman wall paintings, which were generally true frescoes, implying that pigments were applied to wet lime plaster and thus fixed to the wall. Unconventional plasters using alternative binders in painted plaster walls have been illustrated in ancient treatises, although few papers have been published on this topic (Laurie 1910; Granger 1934; Mora et al. 1984).

This paper presents the results of an analytical investigation of Roman wall paintings, from the 1st century BCE Sanctuary (archaeological area of *Capitolium*) of ancient Brixia (Brescia, Italy) located in the west of the *Regio X Venetia* (Northern-Italy) (Figure 1a). The town used to be one of the most important Roman settlements in northern Italy, along the route of the *Via Gallica* (from Milan to Verona) on the edge of the fertile Po Valley and Padana plain. In the last decades of the 1st century CE the Sanctuary was buried during the construction of the *Capitolium*, a hexastyle temple closing the northern side of the *Forum*, a long and narrow square measuring 140 x 40 metres and flanked by colonnades. These buildings were the result of a huge urban transformation, following the victory of Vespasian in the struggle for power (69 CE). The building stone was a cream carbonate rock classified as a dolomitic limestone (called

“Botticino”) after a petrographic comparison with samples coming from quarries located North-East of Brescia (Botticino Mattina) and pertaining to a lower Jurassic formation called “Corna”. The *Capitolium* and the *Forum* were later abandoned, reused by the Goths and Longobards, then rearranged into new buildings from the Renaissance to the Neo-classicism. Brescia remained under the rule of the Venetian Republic from 1428 to 1796, becoming an important site of weapon manufacturing thanks to the iron mines (siderite) located in the nearby Val Trompia. The Roman remains of the Capitolium area were excavated and restored between 1939-43 (Rossi 2002; Rossi 2014).

The four-cellas Sanctuary, located in the centre of *Brixia* (Figure 1b), is the most outstanding and the best-preserved example of Roman Republican architecture. Three rectangular cellas were discovered between 1823 and 1826: masonries (*opus reticulatum*) made of pyramidal elements of a Jurassic limestone (called Medolo) and painted plasters together with stone mosaic pavements. The 1990-94 excavations unearthed the westernmost cella. This was divided in three naves by two rows of brick and stucco columns, three walls (which are still standing about 3 m from the ground) were plastered and painted as a colonnade supporting an entablature and holding an imitation marble panel in the middle and curtains and veils in the lower part (Figure 1c).

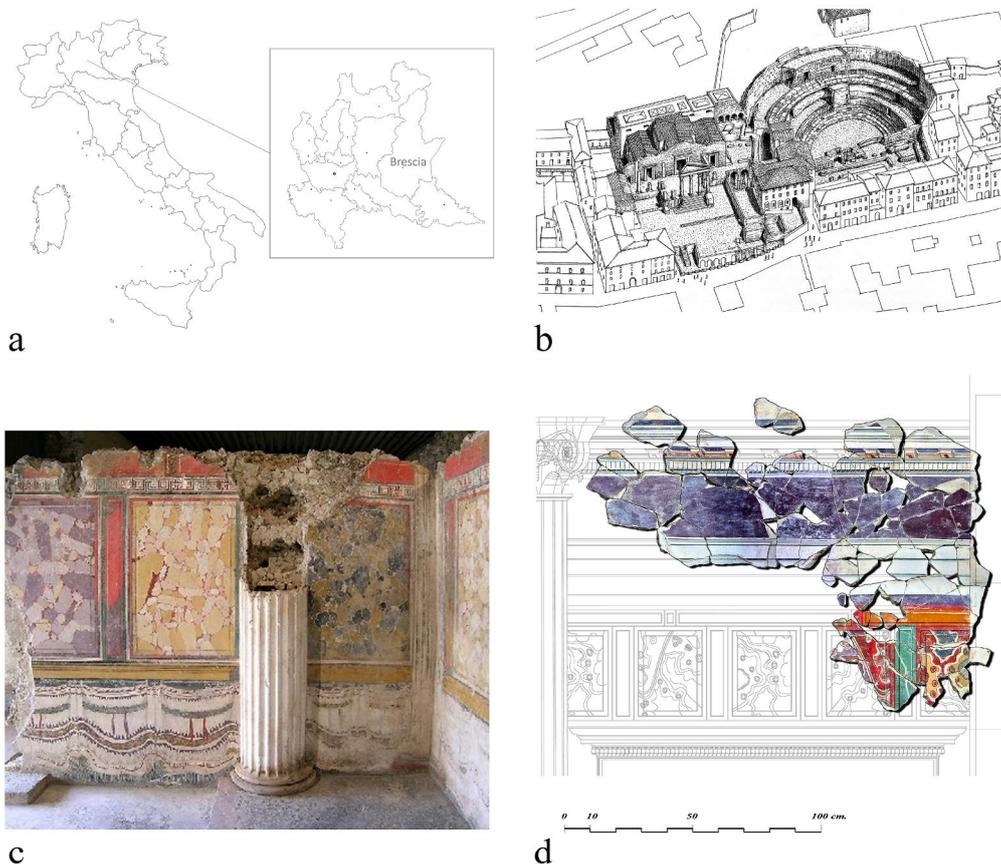


Figure 1 Location of the investigated site: Brescia, Lombardy, Northern-Italy (a); present-day appearance of the Capitolium: the republican Sanctuary is located on the left, under the colonnade (b); the western cella of the Sanctuary, showing the paintings of the southern wall (c); reconstructed fragments of the southern wall (sample group A) (d) (Bianchi 2014).

During the conservation work, an analytical survey was carried out in order to reveal the painting technique and the composition of the plasters, and to verify the state of conservation of the wall paintings (Bugini and Folli 1997; Bugini et al. 2000; Bugini and Folli 2014).

The preliminary mineralogical analyses identified a particular kind of plaster coat with a typical clay texture and a distinct greenish colour. To the best of our knowledge, clay mortars have rarely been documented in the literature, and

the wall paintings of the Capitolium Sanctuary are a unique example of Roman architecture. Gettens (Gettens 1938a; 1938b) describes the clay wall support of the wall paintings from Bamiyan (Afghanistan) and from Kizil (Chinese Turkestan). Paramasivan provides another example of the use of clay in the Indian wall paintings in the Bagh caves (7th century CE), made of “earth stucco” and pigments (Paramasivan 1939). In the central Andes, mural paintings (1800 BCE to 1600 CE) were found to be traditionally executed on clay plaster (Bonavia and Lyon 1985). In the same area, Ortega studied the wall paintings of *Templo Mayor* (Mexico City), dating back to the Atzec Culture (1300-1500 CE), revealing clay substrates that contained pigment particles (Ortega et al. 2001), and Barba determined that, during the Mesoamerican Classic period, the substrates of lime plasters in Teotihuacan (Central Mexico) were prepared with beaten earth (Barba et al. 2009). 15th century Nepalese mural decorations were investigated highlighting ground and preparation layers made of clay as a binder (Mazzeo et al. 2004). The painted walls of the Egyptian tomb of Amenhotep III (1400-1360 BCE) were also made of clay (Uda 2004). There appears to be only one article regarding the Italian heritage, which describes the investigation of traditional Etruscan paintings in the 5th century *Tomb of the Monkey* (Chiusi, Italy), where pigments were applied on fine clay layers (Diaz-Herraiz et al. 2013).

An examination of Roman authors, however, suggested the use of clay in wall paintings. In fact, Vitruvius’ *De Architectura* uses various terms (*argilla*, *creta*, *lutum*) to describe a clayey component of plasters. Vitruvius mentions that the Romans commonly used clay (*argilla*) to fill in the cracks in thermal baths: “*Earumque camararum superiora coagmenta ex argilla cum capillo subacta liniuntur*” (Book 5, Chapter 10.3: “*The joints on the outer face of the vaults should be coated with clay mixed with hair*” - Schofield 2009).

The term *creta* is reported with reference to brick making and vault plastering: “*Cameris dispositis et et intextis imum caelum eaurum trullisetur, deinde harena derigatur, postea autem creta aut marmore poliatur*” (Book 7, Chapter 3.3: “*Once the vaults have been put in place and woven with reeds, the soffit should be rough-plastered, then spread with sand-mortar, after which it should be finished off with chalk or powdered marble*” - Schofield 2009). The term *chalk* used by English translators, like the term *craie* (used in France) or *kreide* (used in Germany), does not match the Latin term *creta*. This term (used also in Italian) is a plastic earthy material made of clay minerals used in brick making. *Chalk* or *craie* or *kreide* is a typically white, soft and porous calcium carbonate generally pure, made of Coccoliths, Foraminifera and other organisms. The same term also identifies a Cretaceous geologic formation, including clay-rich levels towards the base, widely outcrops in northern France (Bassin de Paris), southern England, Flanders and western Germany.

Vitruvius describes the use of *lutum* for the plaster coatings of on timber partitions with reeds: “*Sin autem in craticiis tectoria erunt facienda, quibus necesse est in arrectariis et transversariis rimas fieri, ideo quod, luto cum liniuntur, necessario recipiunt humorem, cum autem arescent, estenuati in tectoriis faciunt rimas (...)*” (Book 7, Chapter 3.11: “*But if revetments are to be applied to half-timbered walls, cracks will certainly appear along the uprights and cross-bars because they are coated with clay-mortar and cause cracks in the revetments when they dry and shrink.*” - Schofield 2009).

Examples of clay plasters have been detected in archaeological sites in Lombardy, such as Brescia (Mariani 1996), Calvatone (Mariani 1997) and Milan (Miranda 1995; Pagani 1995; Pagani 2004), in Switzerland (Lausanne - Berti and Castella 1992) and in France (Paris - Eristov 1995 or Rouen - Carel 1995), but they regard the daubing of ceiling interwoven with reeds or the earthen architecture (*adobe*, *pisé*, *torchis*).

Thus, the particular findings in the Sanctuary led us to exploit further analyses in order to focus on the clay fraction. The identification of constituent materials was the basic objective. Samples from walls were examined by well-

established analytical techniques, capable of providing rich chemical and mineralogical information on the samples: X-ray diffraction (XRD), optical microscopy on thin sections (OM) and Fourier transform infrared spectroscopy (FTIR).

Materials and methods

Several plaster fragments were collected from the rubble filling the western cella of the Sanctuary and were classified into three groups (Table 1):

- group A, containing samples from the upper part of the southern wall (near the impost of the vault), covered by a painted plaster reproducing an entablature (Bianchi 2014) (Figure 1d);
- group B, containing samples from the southern wall, with a reproduction of a ship (Mariani 2002) (Figure 2a);
- group C, containing samples from the southern wall, with a monochrome painted surface (Munsell not. 5GY 6/1) (Mariani 2002).

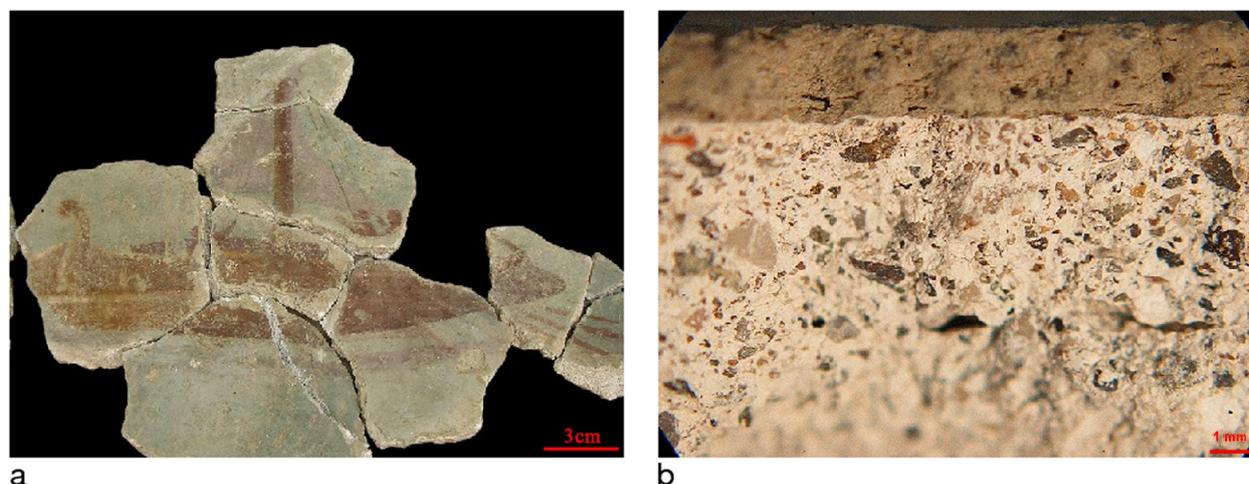


Figure 2 Photographs of samples of Group B: reconstructed fragments of the ship painting (a); polished cross section of sample 5243 showing the thin finish coat (top) and the thick render coat (down) (bar=1 mm) (b).

Sample	Group	Stratigraphic Unit	Description
4936	A	574+592	Monochrome painting
4937	A	1437	Monochrome painting
3644	B	312	Painting depicting a ship
4748-4749	B	1440	Painting depicting a ship
5125-5126	B	380	Painting depicting a ship
5240/5243	C	-	Monochrome painting
5244-5245	C	-	Monochrome painting

Table 1 Description of the plaster samples

Optical microscopy

Preliminary morphological observations were carried out on micro-fragments using a Leitz Wild M420 stereomicroscope. Thin cross sections (30µm thick) of the samples were observed in reflected light using a Leitz Ortholux microscope with Ultrapack illuminator and in transmitted polarized light by a Nikon Eclipse E400Pol

microscope with Nikon Pol objectives. All microscopes were equipped with a digital-image capture system. Samples were impregnated by a resin without interference on the optical properties of the plaster components, the cut was carried out using a diamond saw.

X-ray diffraction

Fragments were detached, using a cutter, from the finish coat of each sample (weight 0.05 g – 0.11 g), gently pulverised in a mortar and then diluted in water (30 ml). The coarse grains (dolomite, calcite and quartz; size 1200 - 100 micrometres) were removed using wet sieving (sieve of 71 micrometres) and each dried sample was placed on glass slides for the first XRD analysis. The analysis was repeated after two hours of exposition to ethylene glycol at about 60°C and cooling, and after two hours in a muffle furnace at about 550°C and cooling. After the treatment, hydrochloric acid was added to the sample to remove the chlorite. PANalytical X'Pert PRO MPD instrument was used with the following conditions: generator settings 40mA and 40kV; radiation Cu-Ka $\lambda=1.5406 \text{ \AA}$; scan range 3-35° 2 θ ; step size 0.017 2 θ ; scan step time 10.3376 s; continuous scan type; software PANalytical X'Pert HighScore.

Fourier transform infrared spectroscopy

The samples scraped off the paint layer were analyzed as KBr (Sigma-Aldrich FTIR Grade) pellets by a FTIR spectrophotometer BioRad Excalibur Series FTS 3000, DTGS detector, in the transmission mode (400 to 4000cm⁻¹, 4cm⁻¹ resolution, 16 scans). Regarding the extraction protocol, around 50mg of fine powders from the paint layer and from the bulk of the samples were put in a glass test tube, completely dipped into organic solvents (around 0.5mL) and sonicated for 15 minutes. The extractions were conducted using hexane (Sigma-Aldrich 95% anhydrous), toluene (Sigma-Aldrich 99.8% anhydrous) and ethyl acetate (Sigma-Aldrich 99% anhydrous), in order to extract nonpolar and polar components respectively (Derrick et al. 1999). The test tubes were centrifuged for 3 minutes. The soluble fraction was placed on a NaCl plate and analysed in the transmission mode after gentle evaporation of the solvent. Solvent blanks were prepared to check for contaminations.

Results and Discussion

Optical observations of the plasters of the Republican Sanctuary in Brescia showed two superimposed coats: the render coat lying on the stone masonry and the finish coat supporting a painted layer.

The former is made of a mortar containing calcite from slaked lime and fine grained clasts from an alluvial sand, together with an addition of crushed brick (Table 2). The composition resembles the render coat coming from the middle part of the walls of the Sanctuary (Bugini and Folli 2014) and in several archaeological sites of Lombardy (Bugini and Folli 2013).

The composition of the finish coat enlightened by optical observation and XRD analysis is described in Table 2. The layer has a regular thickness (about 2.0 mm) but, in many cases, abrasions caused by friction among the rubble produced an uneven thickness.

As concerns group A, sample 4936 shows grains of dolomite, quartz and gneiss in a ground containing illite, chlorite, kaolinite and calcite; thin fissures run parallel to the coat surface (Figure 3a). Sample 4937 contains a ground made of illite, chlorite, kaolinite and calcite with elliptical pores running parallel to the coat surface (Figure 3b) and it is covered by a painted layer (0.15 mm thick) containing rounded grains of glauconite and celadonite (green earth, size 0.02 mm) and blue angular crystalline fragments (Egyptian blue, size 0.01 mm).

Grains of metamorphic rocks (quartz and silicates) as well as quartz crystals (Figure 3c) in a ground made of illite, chlorite, kaolinite and calcite were determined in the samples from the fragments reproducing the ship (group B), with

thin fissures and elliptical pores running parallel to the coat surface; the painted layer (0.1-0.2 mm thick) contains green earth and Egyptian blue, as suggested by both optical observations and XRD results.

Samples from group C are mainly composed of grains of quartz and dolomite, in a ground made of illite, chlorite, kaolinite and calcite with some elongated pores running parallel to the coat surface (Figure 3d); the pigments in the painted layer (about 0.15 mm thick) were recognized as green earth—and Egyptian blue. XRD analysis showed the presence of iron oxide.

Render coat				
Sample	Binder	Aggregate - Grain composition		Grain size (mm)
4936 (A)	microcrystalline calcite	Limestone, dolomite, flint, gneiss, (brick)		0.1-2.5
4937 (A)	microcrystalline calcite	Limestone, dolomite, flint, gneiss, (brick)		4.0
Group B	microcrystalline calcite	Limestone, dolomite, flint, gneiss, (brick)		0.2 – 1.0
Group C	microcrystalline calcite	Limestone, dolomite, gneiss, (brick)		4.0
Finish coat				
Sample	Coat thickness (mm)	Mineralogical composition (XRD analysis)	Grain composition (optical microscopy observation)	Grain size (mm)
4936 (A)	1.0 – 1.2	Ill, Ch, Qz, Calc,	Qz, Gn, Dol	0.4-0.8
4937 (A)	0.8-4.0	Ill, Ch, Qz, Calc,	Qz, Gn, Lim, Dol	0.4-1.0
3644 (B)	1.0-1.2	Ill, Ch, Qz, Calc,	Gn, Lim	0.3-1.2
4748 (B)	1.8-2.0	Ill, Ch, Qz, Calc,	Gneiss	0.1-0.8
4749 (B)	0.1-0.2	Ill, Ch, Qz, Calc,	Dolomite	0.4
5125 (B)	0.2-1.2	Ill, Ch, Qz, Calc,	Qz, Gn, Dol	0.3-0.8
5126 (B)	2.2-2.8	Ill, Ch, Qz, Calc,	Qz, Gn	0.4-1.4
5240 (C)	1.4-1.6	Ill, Ch, Qz, Calc,	Qz, Gn, Dol	0.2-1.2
5242 (C)	0.1-0.4	Ill, Ch, Qz, Calc,	Quartz	0.2
5243 (C)	0.2-0.8	Ill, Ch, Qz, Calc,	Gneiss	0.2
5244 (C)	2.0-2.4	Ill, Ch, Qz, Calc,	Gn, Dol, Lim	0.4-1.0
5245 (C)	2.0-2.4	Ill, Ch, Qz, Calc	Qz, Gn, Dol, Lim	0.2-1.2

Table 2 Mineralogical analysis of the render coat and of the finish coat of the samples

[Legend: Ill=illite; Ch=chlorite and kaolinite, Calc=calcite; Qz=quartz, Gn=gneiss, Lim=limestone, Dol=dolomite

The grain size refers to aggregate grains independently from their mineralogical composition.

XRD analysis refers to the finer fraction obtained by sieving the plaster coat.

Optical microscopy observation refers to the coarser fraction obtained by sieving the plaster coat]

In general terms, the finish coat appears as a decussate texture ground containing rock grains together with voids of various shape and size. Rock grains (quartz, gneiss, dolomite or limestone) are considered as a natural non-plastic constituent; the grain morphology generally shows equant shape, sub-angular corners (quartz and gneiss) or sub-rounded corners (carbonate rocks) with a size ranging from 0.1 to 1.4 mm. XRD analysis, carried out on samples treated as previously described, detected illite, chlorite, and kaolinite, acting as a binder, together with calcite. Calcite is referred to the carbonation of a slaked lime intentionally mixed with clay minerals. As the coarse grains of limestone and dolomite, present as non-plastic constituents, were removed from the samples before the XRD analyses, the presence of calcite is most likely due to the addition of slaked lime.

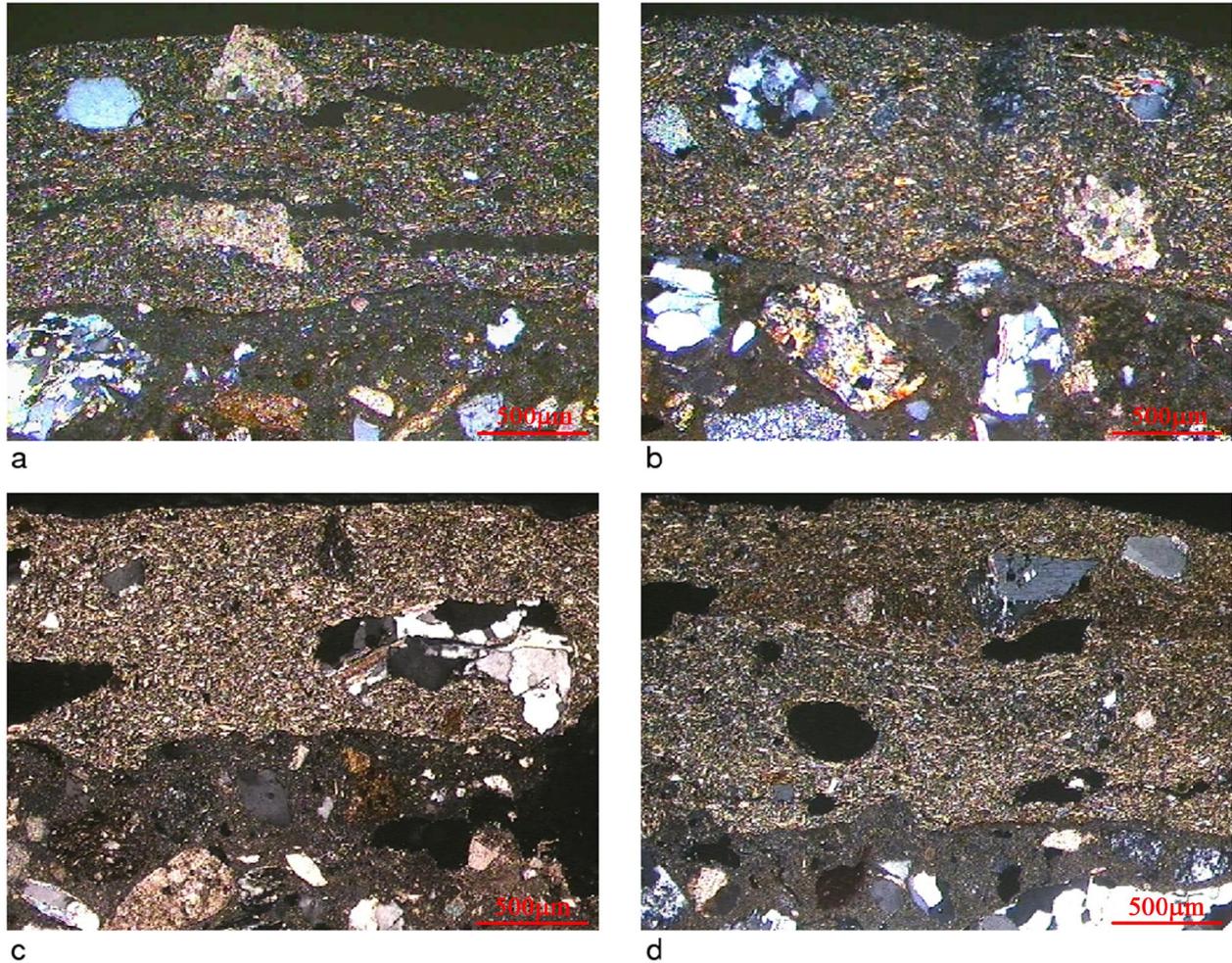


Figure 3 Thin cross sections of finish coats of samples 4936 (a), 4937 (b), 3644 (c), and 5240 (d), showing the decussate texture of clay binder containing non plastic constituents (quartz, metamorphic or carbonate rocks) together with elliptical pores and sinuous fissures (cross polarized light) (bar=500µm).

There is no evidence of exploitation of this kind of deposits in the surroundings of Brescia in the Roman period: a Roman brick furnace was unearthed near Lonato (about 25 km east), but the raw materials were not analyzed (Roffia 2008). In modern times different sites near Brescia have been exploited for brick manufacturing: lacustrine deposits (massive to laminate carbonate silts and clay - Upper to Middle Pleistocene) located south of Iseo (Borgonato, Timoline), whose composition is reported as "mainly illitic", but a precise identification of clay minerals is not available (Carta Geologica 2011); grey-brownish lacustrine deposits (Cerezata, Ome) associated to the morainic amphitheatre of lake Iseo (Riss); fluvioglacial and fluvial deposits in the Prealpine area (Gavardo - Mindel); recent deposits in the plain (Milzanello) (Carta Geologica 1970).

The composition of the finish coat is different from that observed in plasters from the middle part of the walls of the Sanctuary (Bugini and Folli 2014), which are painted plasters, depicting marble panels or woven curtains, featuring calcite (lime) as binder and crushed dolomite as aggregate. The use of crushed carbonate rock as plaster aggregate, instead of the usual "marble powder", has been detected in other plasters coming from different archaeological sites of Lombardy (Bugini and Folli 2013). The painted layers contain pigments (green earth, Egyptian blue, iron oxides), which have been frequently detected in Roman wall paintings of Lombardy (Bugini et al. 2015).

FTIR spectra completed the results of mineralogical analyses, proving very effective in identifying iron oxide pigments and the organic component of the plaster. In some cases, the analysis confirmed the mineralogical data. In all the

samples the presence of calcium carbonate, in the mineralogical form of calcite, was suggested by an asymmetric CO stretching band around 1435 cm^{-1} and by the absorbance at 874 (out-of-plane bending vibration) and 713 cm^{-1} (in-plane bending vibration) (Derrick et al. 1999).

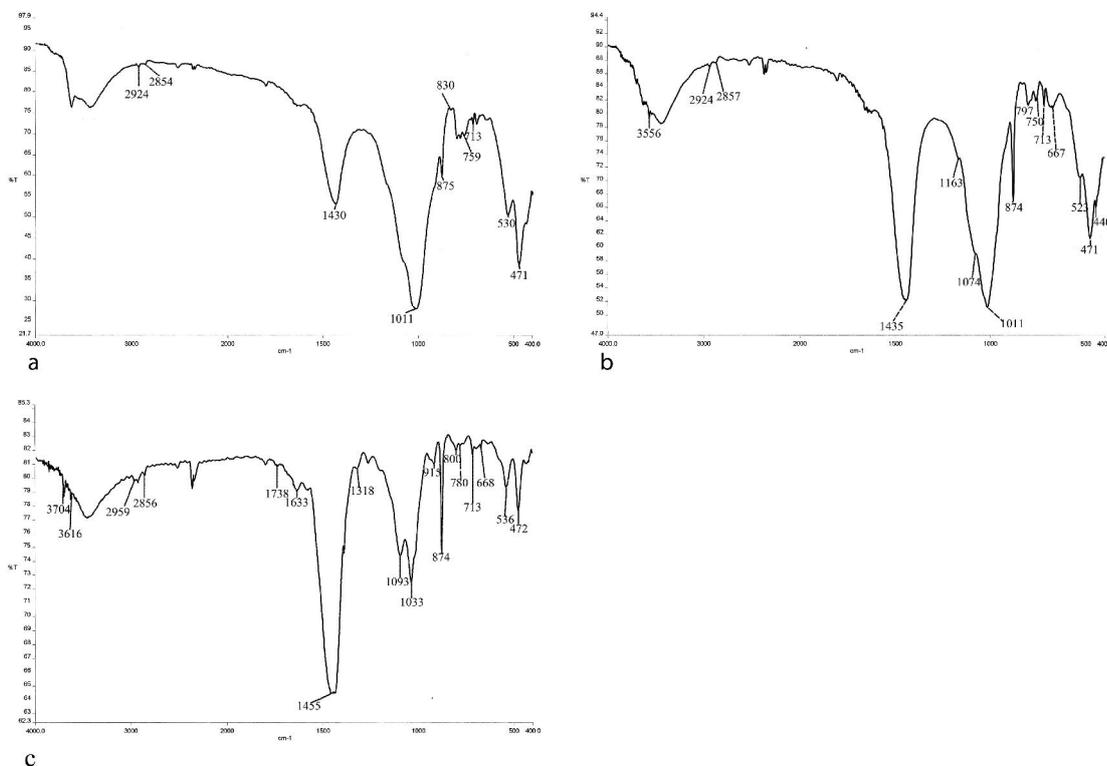


Figure 4 Infrared Spectroscopy transmission spectra of sample 4749 (a, b) and sample 5243 painted layer (c). The finish coat of sample 4749 (a) shows the signals of calcite: 1430 , 875 , 713 cm^{-1} ; clay minerals: 3623 , 1011 , 830 , 759 , 530 , 471 cm^{-1} ; and organic compounds: 2924 , 2854 cm^{-1} . The painted layer (b) presents the signals of calcite: 1435 , 874 , 713 cm^{-1} ; green earth: 3556 , 1074 , 1011 , 797 , 471 , 440 cm^{-1} ; Egyptian blue: 1163 , 750 , 667 , 523 cm^{-1} ; and organic compounds: 2924 , 2857 cm^{-1} ; the painted layer of sample 5243 (c) shows the signals of calcite: 1455 , 874 , 713 cm^{-1} ; red ochre: 3704 , 3616 , 1093 , 1033 , 915 , 800 , 536 , 472 cm^{-1} ; whewellite: 1633 , 1318 , 780 , 668 cm^{-1} ; and organic compounds: 2959 , 2856 , 1738 cm^{-1} (Petrov and Soptrajanov 1975, Mirti et al. 1995, Derrick 1999, Ospitali et al. 2008).

Sometimes, as in sample 4749 (Figure 4a), the OH stretching band at 3623 cm^{-1} coupled with $830\text{--}759\text{ cm}^{-1}$ doublet, SiO stretching band at 1011 cm^{-1} and SiO deformation bands at 530 and 471 cm^{-1} may be attributed to clay minerals, such as illite (Wilson, 1994), although FTIR analysis cannot be diagnostic without the support of mineralogical investigations. The green pigment observed on the clay finish coat of the same sample was confirmed as Egyptian blue (Figure 4b) (Mirti et al. 1995). The peaks at 1163 (antisymmetrical SiOSi stretching modes) and $750\text{--}667\text{ cm}^{-1}$ (symmetrical SiOSi stretching modes) were in fact diagnostic (Mirti et al. 1995). The SiO bending signal at 523 cm^{-1} is also typical. The OH stretching and deformation bands at 3556 and 797 cm^{-1} respectively (Figure 4b), as well as the SiO stretching bands at $1074\text{--}1011$ and $471\text{--}440\text{ cm}^{-1}$ suggests the presence also of green earth (Wilson 1994, Ospitali et al. 2008). The pigment is generally composed of $(\text{K,Na})(\text{Fe}^{3+}, \text{Al,Mg})_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$ (glauconite) and $\text{K}[(\text{Al,Fe}^{3+}), (\text{Fe}^{2+}\text{Mg})](\text{Al}, \text{Si}_3, \text{Si}_4)\text{O}_{10}(\text{OH})_2$ (celadonite), which are chemically very similar, although their origin differs. The red pigment in sample 5243 (Figure 4c) was identified as red ochre. According to literature, an ochre is a natural earth containing silica and clay, and owing its color to iron oxide (Gettens and Stout 1966). The dominance of anhydrous iron oxide (Fe_2O_3) and hydrous ferric oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) reveals a dominant red and yellow color respectively. The identification of red ochre through FTIR occurred due to the presence of very specific bands peculiar of hematite at

536-472 cm^{-1} and of the accessory minerals, whose bands at 3704-3616 cm^{-1} (kaolinite's outer and inner hydroxyl ions stretching) 1093-1033 cm^{-1} (SiO stretching bands of quartz and kaolinite), and 915-800 cm^{-1} (OH deformation of kaolinite) were clearly evident (Wilson 1995, Bikiaris et al. 1999). When present, the yellow pigment was identified by FTIR as yellow ochre for the signals of hydrous ferric oxide at 3150, 895 and 792 cm^{-1} (Wilson 1995, Bikiaris et al. 1999).

Organic matter was found as traces in some samples, with peaks in the regions around 2800-2900 cm^{-1} , which could be ascribed to CH signals. As usual when dealing with archaeological samples, the amount of organic substances was too low for a reliable identification, due to natural and anthropic decay. A survey on organic solvent-soluble portions was designed. All the samples were extracted with various organic solvents, as described in the Materials and Methods, and the residues were analysed. A residue of about 1 weight percent was recovered only in case of hexane extraction. Spectra showed peaks typical of organic compounds. Generally, a CH bond was suggested by stretching and bending absorbance signals at 2925 and 2854 cm^{-1} , respectively. The stretching absorbance of the CO bond was observed as a weak peak around 1738 cm^{-1} . A comparison with reference standards of aged organic binders and the spectra found in the literature (Derrick et al. 1999), suggested that the samples obtained after extraction might contain a lipidic compound, possibly an oil.

A pair of samples containing organic compounds also presented the particular peaks of calcium oxalate. For example, sample 5243 (Figure 4c) showed signals at 1633 and 1318 (CO stretching vibration), 780 and 668 cm^{-1} (OCO bending vibrations), which could be ascribed to whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), which is the calcium oxalate monohydrate mineralogical phase (Petrov and Soptrajanov 1975).

Conclusions

The results highlighted the uncommon use of clay (*creta*) to make plaster on stone masonry. Clay was obviously used by the Romans in earthen architecture (*lateres*) or to make baked bricks (*testae*) as reported in Italian and European sites.

The Republican Sanctuary, unearthed in 1990-92 under the colonnaded Capitulum of *Brixia*, shows a particular kind of plaster made of two superimposed coats: a render coat with lime binder and sandy aggregate, a finish coat made of a clay fraction (illite, chlorite, kaolinite) together with an addition of calcite from slaked lime; grains of quartz, silicate and carbonate rocks pertain to the clay fraction. A different kind of plaster, still *in situ* in the middle part of the walls of the Sanctuary, shows on the contrary a finish coat made of lime as binder and carbonate rock fragments as aggregate.

The finish coat containing clay minerals seems to match a recipe reported by Vitruvius in regard to making of plaster for ceiling, but the Latin Author takes account of the use of clay mainly for daubing on reeds (*De Architectura*, Book 7, Chapter 3-Schofield 2009).

Thus, the finding sheds a light on a particular building technique set up during the Roman period, but never documented in a scientific report before now. This unique case is also of main concern for conservators, for planning the best repair mortars, that is to say as similar and compatible as possible to the original composition. In light of the survey results, the use of clay should be considered.

Regarding the painting materials, the palette consisted of glauconite, celadonite, Egyptian blue, red and yellow ochres. In some cases, an organic compound, possibly a lipidic compound, was present in the external paint layer. Calcium oxalate was detected in two samples. It might have originated from the occurrence of a micro-organism colonisation on the surfaces, or from the degradative oxidation product of organic materials used as a medium, or from past

conservation of the surface (Cariati et al. 2000; Rampazzi et al. 2004). Residues of organic compounds on the Sanctuary wall paintings would seem to indicate that past conservation treatments were the cause, in fact since the Roman age, natural organic treatments have been applied to stone surfaces for protection and maintenance (Rossi Manaresi 1993; Weil 1967). The compounds might be present as additives as well (Rampazzi et al. 2015 and references therein), for example with aims of improving the durability and the resistance, reducing the drying shrinkage, or increasing the plasticity and workability. Pliny the Elder in his *Naturalis Historia* and Vitruvius in his *De Architectura* mention that the Romans commonly used various additives in order to enhance the resistance of mortars, although the determination of additives in historical mortars has rarely been documented (Rampazzi et al. 2015 and references therein). In the case of the Republican Sanctuary, conservators [private communication] involved in the recent works, referred to the authors about a “shiny” appearance of the wall painting, which seems to suggest the use of organic compounds for surface treatment, rather than an original ingredient of the plasters.

Acknowledgements

The authors thank F. Rossi (Soprintendenza Archeologica della Lombardia) for kindly supplying the samples and Roberto Mauri for the elaboration of the infrared spectra.

References

- Barba, L., Blancas, J., Manzanilla, L. R., and Ortiz, A., 2009, Provenance of the limestone used in Teotihuacan (Mexico): a methodological approach, *Archaeometry*, **51**, 525-545.
- Berti, S., and Castella, M.C., 1992, Architecture de terre et de bois à Lausanne-Vidy VD, *Archaeologie der Schweiz*, **15**, 172-179.
- Bianchi, B., 2014, La decorazione pittorica del Santuario Repubblicano di Brescia, in *Un luogo per gli dei* (eds. Rossi F.), 223-260, All’Insegna del Giglio, Firenze, Italy.
- Bikiaris D., Daniilia S., Sotiropoulou S., Katsimbiri O., Pavlidou E., Moutsatsou A.P., Chryssoulakis Y., 1999, Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies: application on wall paintings at Meteora and Mount Athos, Greece, *Spectrochimica Acta Part A*, **56**, 3-18.
- Bonavia, D., and Lyon, P.J., 1985, Mural painting in ancient Peru, Indiana University Press, Bloomington.
- Bugini, R., and Folli, L., 1997, Materials and making techniques of Roman Republican wall paintings (Capitolium, Brescia, Italy), in *Roman Wall Painting: Materials, Techniques, Analyses and Conservation, Proceedings of the International Workshop* (eds. Bearat A, Fuchs M, Maggetti M, Paunier D), 121-130, Fribourg, Germany.
- Bugini, R., and Folli, L., 2013, Critères pour la comparaison des enduits peints romains de la Lombardie, *Archéosciences*, **37**, 41-50.
- Bugini, R., and Folli, L., 2014, Materiali da costruzione e metodologie di messa in opera nel Santuario repubblicano di Brescia, in *Un luogo per gli dei* (eds. Rossi F), 273-281, All’Insegna del Giglio, Firenze, Italy.
- Bugini, R., Folli, L., and Vaudan D., 2000, Les pigments vert et rouge d’une peinture murale d’époque romane républicaine, in *Art et Chimie. La Couleur* (eds. Goupy J, Mohen JP), 119-120, Paris.
- Bugini, R., Folli, L., Mariani, E., and Pagani, C., 2015, Pigment composition and applying methods in Roman wall paintings of Lombardy (2nd century BCE – 4th century CE), in *AIPMA Proceedings*, Athens 2014, in press.
- Carel, P., 1995, Peintures provenant de la fouille du parking “Delacroix-Beaux Arts” à Rouen, in *AFPMA Proceedings 1990-93*, 265-267.

- Cariati, F., Rampazzi, L., Toniolo, L., and Pozzi, A., 2000, Calcium oxalate films on stone surfaces: experimental assessment of the chemical formation, *Studies in Conservation*, **45**, 180-188.
- Carta Geologica d'Italia alla scala 1:50.000 (2011), Note illustrative al foglio 099 Iseo, Regione Lombardia, Milano.
- Carta Geologica d'Italia alla scala 1:100.000, 1970, Note illustrative al foglio 47 Brescia, Servizio Geologico d'Italia, Roma.
- Derrick, M.R., Stulik, D., and Landry, J.M., 1999, *Infrared Spectroscopy in Conservation Science*, The Getty Conservation Institute, Los Angeles.
- Diaz-Herraiz, M., Jurado, V., Cuezva, S., Laiz, L., Pallecchi, P., Tiano, P., Sanchez-Moral, S., and Saiz-Jimenez, C., 2013, The Actinobacterial Colonization of Etruscan Paintings, *Scientific Reports*, **3**, 1-6.
- Eristov, H., 1995, Quelques observations techniques dans les décors de Lutece, in *AFPMA Proceedings 1990-93*, 203-204.
- Gettens, R.J., 1938a, The materials in the wall paintings of Bamiyan, Afghanistan, *Technical studies in the field of the fine arts*, **6**, 186-193.
- Gettens, R.J., 1938b, The materials in the wall paintings from Kizil in Chinese Turkestan, *Technical studies in the field of the fine arts*, **6**, 281-294.
- Gettens R.J., Stout G.L., 1966, *Painting Materials, A Short Encyclopaedia*, Dover, New York.
- Laurie, A. P., 1910, *Greek and Roman methods of painting*, Cambridge University Press.
- Mariani, E., 1996, Gli affreschi del saggio sotto il Santuario tardo-repubblicano, in *Carta Archeologica Lombardia - Brescia: la città* (eds. F. Rossi), Modena, 131-134.
- Mariani, E., 1997, Calvatone romana - Un pozzo e il suo contesto, *Quaderni di Acme*, **29**, 185-203.
- Mariani, E., 2002., Intonaci con raffigurazione di una nave dal Santuario tardo-repubblicano: problemi tecnici e iconografici, in *Nuove ricerche sul Capitolium di Brescia - Scavi, studi e ricerche*, (eds. F.), 77-84, Edizioni Et, Milano.
- Mazzeo, R., Baraldi, P., Luján, R., and Fagnano, C., 2004, Characterization of mural painting pigments from the Thubchen Lhakhang temple in Lo Manthang, Nepal, *Journal of Raman Spectroscopy*, **35**, 678-685.
- Miranda, S., 1995, Intonaci dipinti e tipologie costruttive: la nuova documentazione dello scavo dell'Università Cattolica di Milano, in *AFPMA Proceedings 1990-93*, 277-281.
- Mirti, P., Appolonia, L., Casoli, A., Ferrari, R.P., and Laurenti, E., 1995, Spectrochemical and structural studies on a Roman sample of Egyptian blue, *Spectrochimica Acta*, **51A**, 437-446.
- Mora, P., Mora L., and Philippot P., 1984, *Conservation of Wall Paintings*, Butterworths, London.
- Munsell Book of Color, 1976, Munsell Color, Baltimore.
- Ortega, M., Ascencio, J.A., San-Germán, C.M., Fernández, M.E., and López, L., 2001, Analysis of prehispanic pigments from "Templo Mayor" of Mexico city, *Journal of Materials Science*, **36**, 751-756.
- Ospitali F., Bersani D., Di Lonardo G., Lottici P.P., 2008, 'Green earths': vibrational and elemental characterization of glauconites, celadonites and historical pigments, *Journal of Raman Spectroscopy*, **39**, 1066-1073.
- Pagani, C., 1995, Pittura parietale romana a Milano: alcuni esempi di scavi stratigrafici dell'ultimo decennio, in *AFPMA Proceedings 1990-93*, 269-276.
- Pagani, C., 2004, La decorazione parietale della *domus* di via Correnti 24, in *L'Anfiteatro di Milano e il suo quartiere* (eds. A. Ceresa Mori A), 58-63, Milano.
- Paramasivan, S., 1939, The wall paintings in the Bagh Caves - An investigation into their methods, *Proceedings of the Indian Academy of Science*, **X**, 85-95.

- Petrov, I., Soptrajanov, B., 1975, Infrared spectrum of whewellite, *Spectrochimica Acta*, **31A**, 309-316.
- Rampazzi, L., Andreotti, A., Bonaduce, I., Colombini, M.P., Colombo, C., and Toniolo, L., 2004, Analytical investigation of calcium oxalate films on marble monuments, *Talanta*, **63**, 967-977.
- Rampazzi L., Colombini M.P., Conti C., Corti C., Lluveras-Tenorio A., Sansonetti A., Zanaboni M., 2015, The historical mortars from the Arsenal of Amalfi (Italy): a look into the organic additives, *Archaeometry* DOI: 10.1111/arc.12155.
- Roffia, E., Portulano, B. and Rossi, F., 2008, *Le fornaci romane di Lonato*, Edizioni ET, Milano.
- Rossi, F., 2002, *Nuove ricerche sul Capitolium di Brescia*, Edizioni ET, Milano.
- Rossi, F., 2014, *Un luogo per gli dei*, All'Insegna del Giglio, Firenze.
- Rossi Manaresi, R., 1993, Stone protection from the antiquity to the beginning of the industrial revolution, *Science and Technology for Cultural Heritage*, **2**, 149-160.
- Schofield, R., 2009, *Vitruvius - On Architecture*, Penguin Books, London.
- Uda, M., 2004, In situ characterization of ancient plaster and pigments on tomb walls in Egypt using energy dispersive X-ray diffraction and fluorescence, *Nuclear Instruments and Methods in Physics Research B*, **226**, 75–82.
- Weil, P.D., 1967, Contributions toward a history of sculpture techniques: I. Orfeo Boselli on the restoration of antique sculpture, *Studies in Conservation*, **12**, 81-101.
- Wilson, M.J., 1994, *Clay mineralogy: spectroscopic and chemical determinative methods*, Chapman&Hall, London