

# Copper-zinc hydroxychlorides: origin and occurrence as paint pigments in Arcos de la Frontera's Chapel of Mercy (Spain)

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**Abstract:** This paper deals with the characterization of a green paint layer covering ornamental stone elements in the Presbytery of Arcos de la Frontera's Chapel of Mercy (Cádiz, Spain), a 16<sup>th</sup>-century building. Optical microscopy, X-ray diffraction, Fourier-transformed infrared spectroscopy and scanning electron microscopy were used to determine that the layer derived from a treatment of the stone (calcarene) consisting of applying mixtures of gypsum and zinc-copper basic chlorides as paint pigments. Among the different salts, zinc-stabilized paratacamite, clinoatacamite and atacamite could be present. Very scattered dark-maroon speckles appear on the green layer (mainly composed of cuprite). Both these salts and other greenish, synthetic copper-containing compounds may be products deriving from artificial corrosion of brass or other copper alloys.

**Key-words:** copper-zinc hydroxychlorides, polymorphous compounds, verdigris paint pigments, brass corrosion products, Chapel of Mercy.

## 1. Introduction

The purpose of this research was to study the green layer coating the stone elements (fleurons and corbets) used as construction materials in the Chapel of Mercy, a monument built in the first half of the 16<sup>th</sup> century in Arcos de la Frontera (Cádiz, Spain). The building belonged to the Hospital of Mercy and is in a late-gothic architectonic style with a Castilian influence. The Presbytery contains a ribbed vault with various transepts that include several fleurons with different ornaments bearing a greenish paint layer on their surface. This green layer also appears in the corbets supporting the large ramrods that allow the prolongation of the false cleavages onto the wall.

Visual inspection revealed that the verdigris layer seems to be a very thin, non-continuous layer with scattered small, dark-maroon speckles. Green colouring for painting has historically been obtained by using copper-containing pigments, more precisely, the sequence of basic copper chlorides. In addition, zinc-copper trihydroxychlorides, such as botallackite, atacamite, zincian paratacamite and clinoatacamite, have all been reported as ancient pigments in a wide variety of archaeological objects, polychrome sculptures and architectural monuments (Dunkerton & Roy, 1996; Martin *et al.*, 1995). However, what remains debatable is whether these occurrences represent original pigments, or instead derive from copper chloride transformation.

Copper chloride (CuCl) is a very important compound in the corrosion processes of brass and other copper alloys; as

a corrosion product it may lie dormant until contact with moisture and oxygen precipitates a reaction (Scott, 2000). The mineral form was identified and named nantokite after the mines near Nantoko in Chile (Palache *et al.*, 1951).

Of all the basic copper chlorides, the polymorphs of  $\text{Cu}_4(\text{OH})_6\text{Cl}_2$  (Tables 1 and 2) have had a tumultuous history, clarified by Braithwaite *et al.* (2004). Botallackite (monoclinic) is the most unstable of the four compounds; it is quite rare and was first found in the Cornwall mines, England, together with other polymorphs (Frondel, 1950). Atacamite (orthorhombic) is the most common polymorph and was named after the northern desert of Atacama in Chile, where it was originally identified. The colour of the mineral varies from emerald green to blackish green (Palache *et al.*, 1951). Synthetic atacamite is comparatively rare, and this form has been observed in only a few paintings; it is sometimes assigned a slightly different composition from the natural mineral. Clinoatacamite is the monoclinic polymorph and was described by Jambor *et al.* (1996) from the Anarak province in Iran (*cf.* 'anarakite' of Adib & Ottmann, 1972). One out of the four Cu atoms can be substituted by Zn and the crystal symmetry changes to rhombohedral when about one third of Cu in this site (*i.e.* for a bulk Cu/Zn atomic ratio of 11) is substituted by Zn, thus giving paratacamite (first described by Smith, 1906, as the rhombohedral polymorph of atacamite from several mines in Chile). If Zn becomes dominant in this site (*i.e.* for a bulk Cu/Zn atomic ratio between 7 and 3), the mineral name herbertsmithite applies, with the end-member composition  $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$

Table 1. Most relevant characteristics of main copper and zinc-copper hydrochlorides (ICDD, 202) used as pigments in painting and other cultural heritage media.

Metals	Formula	Compound name	Lattice	Colour
Copper	CuCl(OH)	Belloite	Monoclinic	Olive green
	Cu(OH,Cl) <sub>2</sub> ·3H <sub>2</sub> O	Anthonyite	Monoclinic	Pale blue
	Cu(OH,Cl) <sub>2</sub> ·2H <sub>2</sub> O	Calumetite	Orthorhombic	Azure blue
	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	Paratacamite	Rhombohedral	Pale green
	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	Atacamite	Orthorhombic	Vitreous green
	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	Botallackite	Monoclinic	Bluish green
	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	Clinoatacamite	Monoclinic	Pale green
	Cu <sub>4</sub> Cl(OH) <sub>7</sub> ·2H <sub>2</sub> O	Claringbullite	Hexagonal	Light blue
	Cu <sub>5</sub> Cl <sub>2</sub> (OH) <sub>8</sub> ·2H <sub>2</sub> O	Bobkingite	Monoclinic	Pale blue
	Cu <sub>7</sub> Cl <sub>4</sub> (OH) <sub>10</sub> ·H <sub>2</sub> O	Atacamite, syn	Orthorhombic	Vitreous green
Copper and zinc	(Cu,Zn) <sub>2</sub> Cl(OH) <sub>3</sub>	Paratacamite, zincian	Rhombohedral	Light green
	Cu <sub>3</sub> ZnCl <sub>2</sub> (OH) <sub>6</sub>	Hebertsmithite	Rhombohedral	Dark green

Table 2. Lattice, Cu/Zn atomic ratio and formula of the copper-zinc trihydroxychlorides.

Mineral	Botallackite	Atacamite	Clinoatacamite	Zincian paratacamite	Hebertsmithite
Lattice	Monoclinic	Orthorhombic	Monoclinic	Rhombohedral	Rhombohedral
Cu/Zn	∞	∞	> 11	11–7	7–3
Formula	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	(Cu,Zn) <sub>2</sub> Cl(OH) <sub>3</sub>	(Cu,Zn) <sub>2</sub> Cl(OH) <sub>3</sub>	Cu <sub>3</sub> (Zn,Cu)Cl <sub>2</sub> (OH) <sub>6</sub>

(Braithwaite *et al.*, 2004). The data on ‘anarakite’ (Adib & Ottemann, 1972) were most likely collected on both clinoatacamite (optics? XRD) and zincian paratacamite (chemistry, IR; Jambor *et al.*, 1996; Braithwaite *et al.*, 2004).

The use of zinc-copper trihydroxychlorides as pigments in paintings on canvas and in frescoes (Naumova & Pisareva, 1994) can be substituted by other copper hydroxychloride pigments such as calumetite, Cu(OH,Cl)<sub>2</sub>·2H<sub>2</sub>O, anthonyite, Cu(OH,Cl)<sub>2</sub>·3H<sub>2</sub>O, and other minerals. Anthonyite is quite rare and its identification is fairly recent (Selwyn *et al.*, 1996). This compound is a naturally occurring mineral that has not yet been reported as a pigment. On the other hand, although calumetite is unusual, it does appear in an archaeological context. This mineral was first identified together with anthonyite (Bimson, 1980). It is also subject to dehydration, as are the remaining hydrated basic copper chlorides mentioned here.

Other basic copper chlorides have yet to be identified on specific paintings. The first one, claringbullite, Cu<sub>8</sub>(OH)<sub>14</sub>Cl<sub>2</sub>·2H<sub>2</sub>O, which has been found in mines with cuprite, is very rare and probably unstable when compared with connellite (Pollard *et al.*, 1983). Belloite, CuCl(OH), is a secondary mineral associated with paratacamite and rather unstable in humid environments; in an aqueous solution it transforms into botallackite and atacamite (Schlüter *et al.*, 2000). Finally, bobkingite, Cu<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>·2H<sub>2</sub>O, is similar to atacamite and occurs on crusts of malachite and azurite that overlie massive cuprite in oxidized waste material consisting of quarried diorite with copper inclusions (Hawthorne *et al.*, 2002).

## 2. Methods

A sample about 3 cm<sup>2</sup> and 4 mm thick was extracted from one of the corbets inside the presbytery. It consisted of a

stone base of calcarenite on which a non-uniform greenish layer had been applied. In addition, very scattered maroon speckles also appeared. The main goal of the building restorer in obtaining the sample was to cause the least possible damage to the architectural element that was being restored to its original state.

The greenish layer's surface and section was observed by means of light microscopy (Nikon Stereoscopic SMZ-2T) with an outside light source. The sample was impregnated with synthetic resin at low pressure, then cut using a diamond blade and finally ground. The surface texture was examined using scanning electron microscopy and a chemical analysis was done as well. A Jeol JSM 6460-LV microscope was used, equipped with an energy-dispersive X-ray (EDX) microprobe, a beryllium ATW2 window and specific software (Oxford INCA) for semiquantitative chemical analyses. SEM images in both secondary electron mode (SE) and in back-scattered electron mode (BSE) were acquired using several gold-coated pieces of sample. The estimated detection limit for major elements after ZAF correction (Scott & Love, 1983) was 0.01 wt. %. International standards (Govindaraju, 1989) were used throughout.

The mineralogical composition was studied in different zones of the raw material (stone, green layer and maroon speckles) by X-ray diffraction (XRD) using a Bruker-AXS D8 Advance diffractometer equipped with a copper filament, CuK $\alpha$  radiation, tube conditions of 40 kV and 30 mA, fixed slot and sparkle detector. The diffractograms were obtained using the powder technique. XRD patterns in the range 10 to 70° 2 $\theta$  were acquired applying a 0.05° step scan with a 1 s step time. Subsequently, a sample of green layer was analysed once again, performing a scan in the 10 to 70° 2 $\theta$  range using a 0.02° step scan with a 5 s step time for better resolution.

Finally, Fourier-transform infrared spectroscopy (FTIR) allowed a complete identification of the mineralogical com-

position by means of a Bomem MB-120 spectrophotometer with  $4\text{ cm}^{-1}$  resolution and spectra recorded between  $4000$  and  $400\text{ cm}^{-1}$ .

### 3. Results

#### 3.1. Light microscopy analysis

The first layer observed was white, ranging from  $80\text{ }\mu\text{m}$  to  $1240\text{ }\mu\text{m}$ , and the second one was non-uniform and green, varying between  $30\text{ }\mu\text{m}$  and  $130\text{ }\mu\text{m}$ . It was not possible to observe the existence of sublayers within the analysed layers (Fig. 1).

Figure 2 presents a view in detail of the scattered maroon speckling (thickness ranging from  $130\text{ }\mu\text{m}$  to  $300\text{ }\mu\text{m}$ ) on the outer surface of the green layer. This coating is formed by crystalline-looking platy globules interspersed with glistening crystals from the green layer.

Finally, the sample surface was illuminated tangentially, revealing various roughened areas. A series of lined-up strokes were observed, indicating that a paintbrush was used to apply the greenish layer on the stone.

#### 3.2. Scanning electron microscopy

*White and green layers.* When observing the sample surface (white and green layers), large areas composed of lens-shaped and platy-shaped crystals (Fig. 3a, b) can be seen. Its chemical composition shows an abundance of calcium and sulphur (Fig. 3c), which indicate the presence of gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . These analyses have also shown the existence of silicon and oxygen, probably quartz. Crystals in sheets can be observed in secondary electron mode (Fig. 4a), showing a light contrast in back-scattered electron mode. Moreover, the above-mentioned semiquantitative elementary microanalysis has detected copper and chlorine as the most abundant elements (Fig. 4b), while oxygen, silicon and calcium are minor elements. According to these results, the greenish coloration indicates the presence of copper chlorides.

*Maroon speckling.* The analysed zone on the sample's surface also contained scattered maroon speckling, with the presence of superimposed flakes (Fig. 5a). EDX analysis of this area (Fig. 5c) showed copper and oxygen as the most abundant elements, which most likely indicates the existence of copper oxide and nearly 10% zinc. Moreover, chlorine, calcium, sulphur and silicon were also detected.

Table 3 shows the chemical composition of the two above-mentioned layers – the greenish paint and the dark speckling. Both the analysed coats show the following qualitative composition: copper, zinc, calcium, chlorine, sulphur, silicon and oxygen. Several variations in the semiquantitative chemical composition can be noted, since the chlorine content is lower in the maroon speckles than in the green layer. In contrast, carbon and zinc show higher concentrations in the maroon speckles. None of the other elements varied significantly between the two areas.

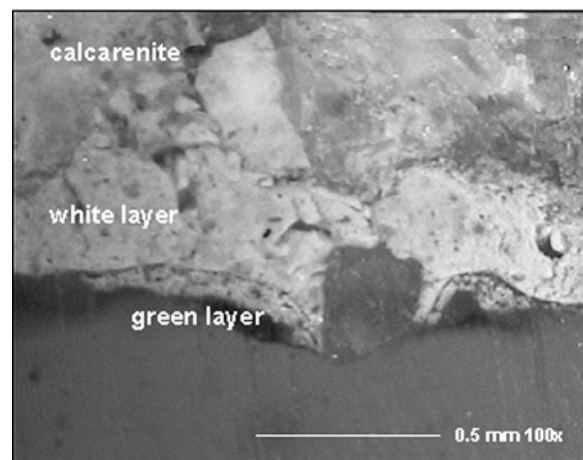


Fig. 1. Photograph displaying the sectioned structure of the sample, including the white and green layers.

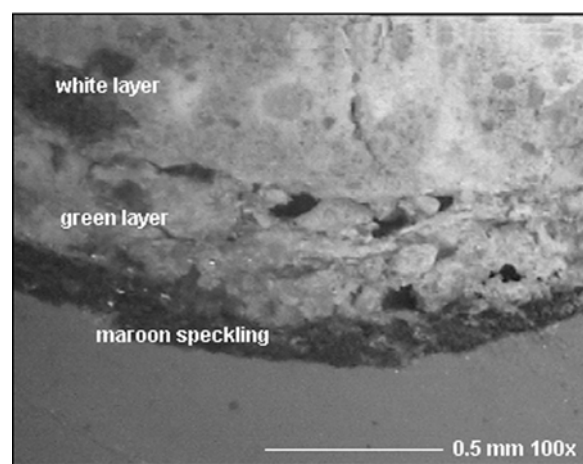


Fig. 2. Photograph displaying the sectioned structure of the sample, including the maroon speckling.

#### 3.3. XRD analyses

The mineralogical composition of the four areas (calcarenite, white layer, green paint and maroon speckling) of the sample have been studied using XRD analysis (see Fig. 6 for a comparison of the results). To that effect, every layer has been scraped using a scalpel to separate out a small piece of it. As expected, the results showed calcite and quartz as the main minerals in calcarenite. Gypsum is also present, with its most probable origin being its infiltration through the calcarenite porous system when the gypsum-bearing priming coat was applied. The presence of calcite and gypsum in the white layer corroborates the above results. Most probably a priming coat composed of gypsum, or lime and gypsum, was applied prior to the green layer.

Further XRD analysis obtained directly from the greenish layer showed a more complex composition. An initial diffractogram acquired using a  $0.05^\circ$  step scan and a 1 s time step has shown gypsum, calcite, quartz and several compounds belonging to the zinc-copper hydroxychloride series. Because of the very similar XRD patterns of such hydroxychloride compounds, a second, higher-resolution dif-

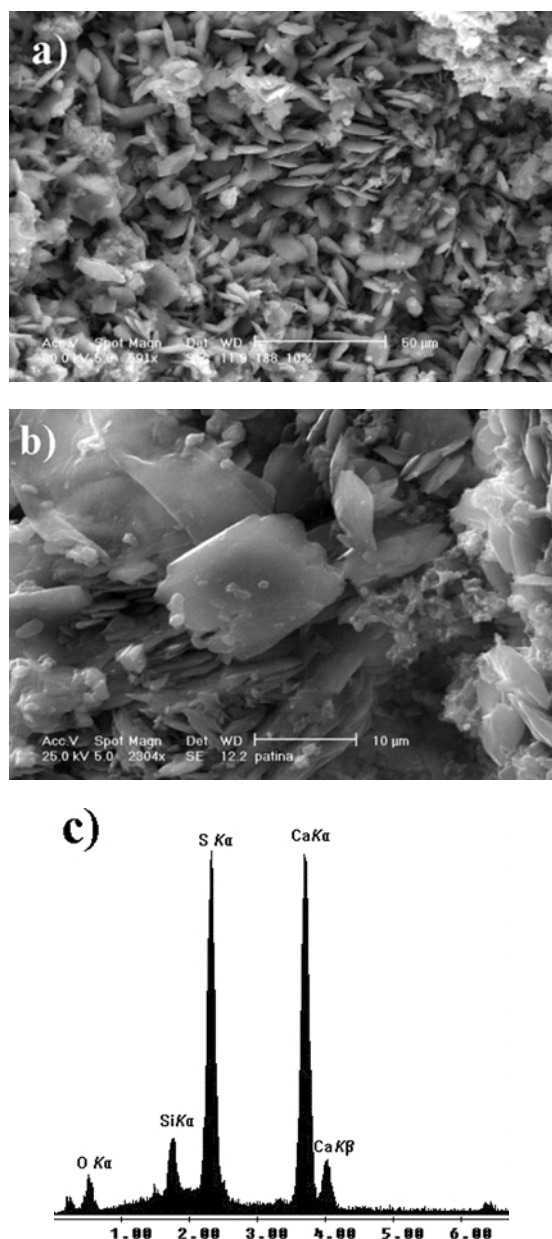


Fig. 3. Scanning electron micrographs and EDX analysis of the greenish layer: a) lens-shaped crystals, b) platy-shaped crystals, and c) EDX spectrum of these crystals.

fractrogram (with a  $0.02^\circ$  step scan and a 5 s time step) was run. It suggests the possible presence of the following phases (Fig. 7): atacamite,  $\text{Cu}_2\text{Cl}_4(\text{OH})_{10}\cdot\text{H}_2\text{O}$  (23-0948); clinoatacamite,  $\text{Cu}_2\text{Cl}(\text{OH})_3$  (86-1391); zincian paratacamite ( $\text{Zn,Cu}_2\text{Cl}(\text{OH})_3$ ); synthetic P24 of Dutrizac (Braithwaite *et al.*, 2004; Jambor *et al.*, 1996) and the above-mentioned doubtful “anarakite”.

As regards the maroon speckling, XRD data show the following mineralogical composition: copper oxide or cuprite ( $\text{Cu}_2\text{O}$ ) as its principal mineral and as minor compounds: quartz, calcite, gypsum, atacamite, clinoatacamite, zincian paratacamite. Although halite and other minerals such as hydrate copper acetate –  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot\text{H}_2\text{O}$  – (28-0392) and even ashoverite,  $\text{Zn}(\text{OH})_2$  (41-1359), have not been identi-

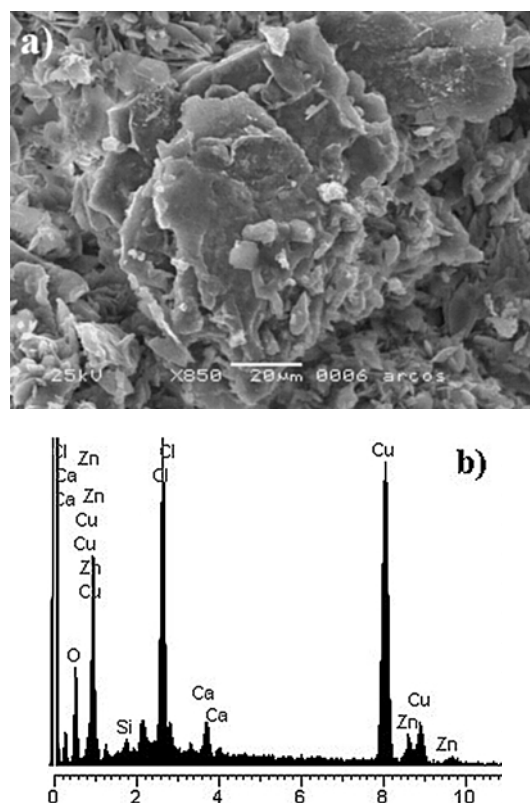


Fig. 4. The green layer: a) secondary-electron (SE) mode image reveals crystals in sheets, and b) relevant EDX spectrum.

fied with certainty, the presence of all these compounds cannot be ruled out.

### 3.4. FTIR analysis

Several absorption bands were related to different compounds in agreement with reference data in the literature (Jones & Jackson, 1993; Kühn, 1993). The infrared spectrum of the analysed sample was clearly useful to identify dihydrate calcium sulphate, which shows absorption bands at 1140, 1090, 671, 602 and  $469\text{ cm}^{-1}$ , characteristic of the sulphate group (vibration modes of sulphur-oxygen bonds). In particular, bands over  $3000\text{ cm}^{-1}$  ( $3547$  and  $3408\text{ cm}^{-1}$ ) are related to water incorporated in the gypsum structure (O-H stretch vibrations), apart from other wavenumbers of absorption maxima ( $1686$  and  $1620\text{ cm}^{-1}$ ), likely due to vibrations resulting from the water bonds. With calcium carbonate, the positions of the main bands are assigned to different deformations:  $2513$  and  $1790\text{ cm}^{-1}$  absorption maxima (combination bands) and other significant ones ( $1433$ ,  $1090$ ,  $876$  and  $712\text{ cm}^{-1}$ ) correspond to vibration modes of carbon-oxygen bonds belonging to the carbonate group. Finally, several easily distinguishable bands were also observed ( $1090$ ,  $799$ ,  $777$ ,  $695$  and  $462\text{ cm}^{-1}$ ). These less-intensive absorption bands are due to silicon-oxygen bond stretch vibrations related to quartz.

FTIR results seem to indicate that the sample contained no copper-zinc trihydroxychloride compounds. In fact,  $3100$  and  $3600\text{ cm}^{-1}$  absorption bands (OH stretching vibra-

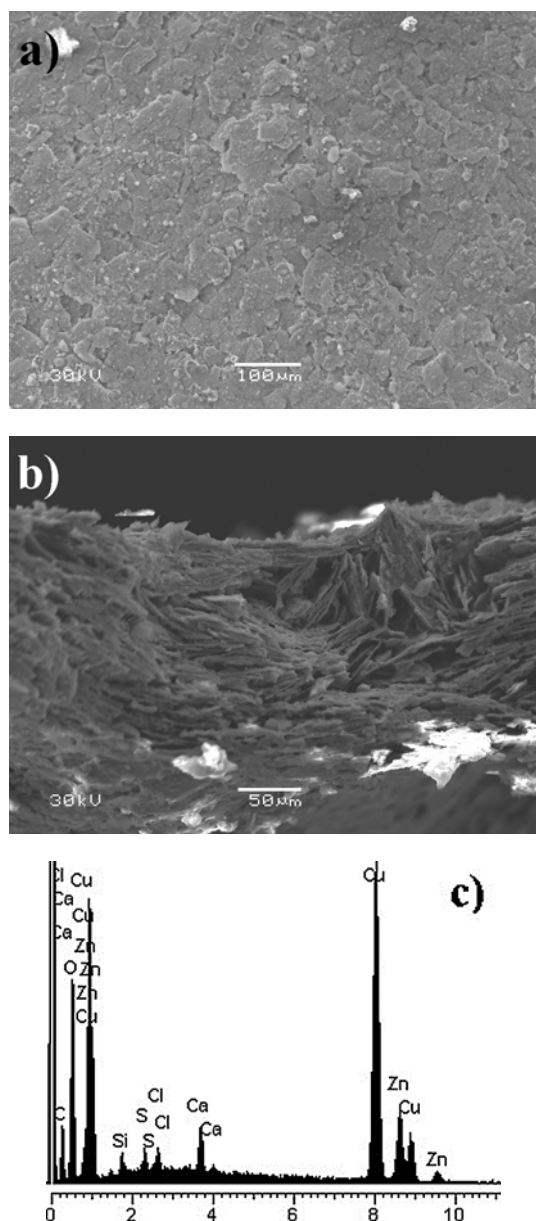


Fig. 5. Maroon speckling: a) SE-mode image of the surface displays a superimposed flake structure; b) SE-mode image of a transverse section; and c) relevant EDX spectrum.

tions) do not appear in the resulting spectrum or are overlapped. We have found no absorption maxima in the 700–1000  $\text{cm}^{-1}$  range (characteristic of  $\text{CuO-H}$  and  $\text{ZnO-H}$  deformations) nor in the region from 400 to 600  $\text{cm}^{-1}$  (due to metal-oxygen stretching vibrations according to Braithwaite *et al.*, 2004). Low proportions of zinc-copper trihydroxychlorides

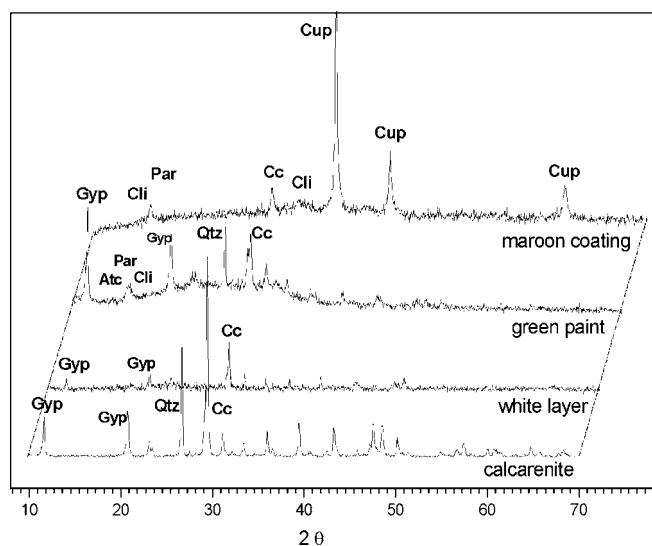


Fig. 6. Comparison of X-ray diffraction patterns of three different zones of the raw material (calcarenite, white and green layer, and maroon speckling) acquired applying a  $0.05^\circ$  step scan with a 1 s step time. Legend after Kretz (1983): Atc = atacamite; Cc = calcite; Cli = clinoatacamite; Cup = cuprite; Gyp = gypsum; Par = paratacamite; Qtz = quartz.

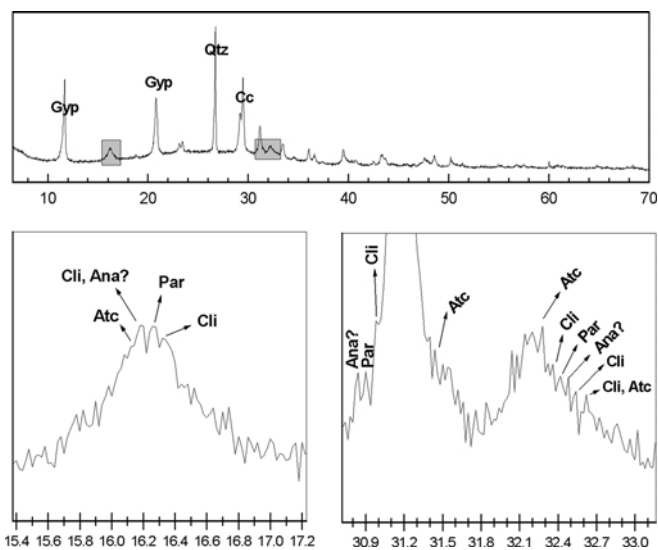


Fig. 7. General XRD diffractogram of the green layer (a); detail of the 16 to  $16.5^\circ$   $2\theta$  explored area (b); and detail of the range  $30.5$  to  $33^\circ$   $2\theta$  (c). Legend as in Fig. 6; Ana = anarakite; after Kretz (1983).

rides relative to gypsum, calcite and quartz contents may explain these results. A significant presence of an organic binder cannot be established because we cannot identify any peaks corresponding to aliphatic and/or aromatic C-H absorption bands.

Table 3. EDX analyses of the greenish crystalline phase and maroon speckling.

% Element	O	C	Si	S	Cl	Cu	Zn	Mg	Ca	K	Al
Green crystal	21.37	0.00	0.92	0.00	16.37	53.11	4.62	1.38	1.79	0.44	0.00
Maroon speckles	29.06	20.57	0.79	0.66	0.61	37.02	9.61	0.00	1.42	0.00	0.25

## 4. Discussion

Both the white and the green layers are composed of gypsum. Although this compound is frequently found in wall paintings as a deterioration product (Baglioni *et al.*, 1998), calcite can only turn into gypsum in urban and/or industrial environments with a sufficient content in sulphur dioxide (Gauri & Holdren, 1981; Wittemburg & Dannecker, 1994). Since this sample does not come from a polluted environment (the interior of a chapel), total or partial alteration of calcarenite into gypsum cannot be established. We believe that, instead, the gypsum was used as a binder either alone or mixed with lime.

The mineralogical composition of the greenish pigments is given in Table 4, allowing a comparison of the green layer's chemical composition (using microanalysis) with clearly differentiated main members in the copper-zinc trihydroxychloride sequence, such as atacamite and herbertsmithite.

Based on this table, we can state that the proportions of oxygen and chlorine found in the analysed area are about the same as any members belonging to the copper-zinc trihydroxychloride series. On the other hand, the greenish layer's Cu/Zn atomic ratio (11.5) would fall into the clinoatacamite range, making this phase a likely candidate (but it could result as well from a mixture of *e.g.* atacamite and zincian paratacamite).

As the light microscopy, SEM-EDX and XRD results show, the analysed greenish layer was made by mixing gypsum and probably lime with zinc-copper compounds as pigments. Considering all detected minerals in both the green-coloured layer and the maroon speckling, there are three possible origins:

- They are alteration products of a copper pigment, either a natural copper mineral – such as malachite and/or azurite – or verdigris.
- They are original pigments derived from a natural mineral.
- The origin of the copper trihydroxychlorides is artificial and can be attributed to the corrosion of brass or another copper alloy in the presence of corrosive chloride salts in acid conditions.

The first option implies a complete transformation of several natural copper minerals or verdigris into copper hydroxychlorides and cuprite (Howard, 2003; Saunders & Kirby, 2004). The presence of a minimal amount of chloride ions – halite – has only been established in the scattered maroon speckling. Since a source of chlorides has not been determined, however, this option seems unlikely. Regarding the origin of cuprite, it is generally thought that copper oxide results from the transformation of copper chlorides,

caused by a preservation treatment with an alkali (Baglioni *et al.*, 1998); however, in this case the sample had not been treated with any kind of preservative.

The second option refers to the possibility of green pigments deriving from a natural mineral. Copper hydroxychlorides are not very unusual minerals; in fact, there are several deposits in Spain. On the other hand, the cuprite present is apparently not an alteration product, although it can be considered as a feasible impurity, a part of the chlorides. This option would explain the sample structure: the liquid state, corresponding to the applied paint layer consisting of gypsum, zinc-copper hydroxychlorides and cuprite, would have caused cuprite settling (gypsum, quartz, calcite, hydroxychlorides and cuprite densities are 2.3, 2.6, 2.6, 3.7 and 6.1 g/cm<sup>3</sup>, respectively).

The last option means that the copper trihydroxychloride origin is attributed to the artificial corrosion of brass or another copper alloy in the presence of corrosive chloride salts in acid conditions. As a metal, copper is oxidized by hydronium ions (H<sub>3</sub>O<sup>+</sup>) the usual oxidant, which is reduced to hydrogen, H<sub>2</sub>. This process tends to result in the precipitation of the basic cupric chlorides. The traditional way of making copper trihydroxychlorides, that is, the immersion of a sheet of metal into an acid solution of halite or another chloride salt, produces first a thin coating of cuprite over the copper, followed by a layer of basic copper chloride polymorphs. Cuprite can be formed as a thin coat adjacent to the metal surface if cuprous chloride and copper are mixed together and regularly moistened with corrosive liquids such as old wine, vinegar, urine, different oils or lemon juice (Scott, 2000). According to Theophilus (1961), a mixture of copper acetates and copper trihydroxychlorides can occur by sprinkling common salt over brass or other copper alloys brushed with a corrosive liquid and placing them over old wine or vinegar.

This third origin is theoretically possible, although in practice it has never been reported. The presence in our sample of cuprite and minimal amounts of sodium chloride or copper acetate indicate a possible artificial origin of the greenish pigments. In this case, the sample structure can also be explained after consideration of the cuprite as an impurity.

## 5. Conclusions

Textural, mineralogical and chemical analyses of the green paint pigments in the Chapel of Mercy has led to the following interpretations:

- The studied coat is mainly composed of a double white and green layer. The thickness of the greenish layer varies from 30 µm to 130 µm. Empirical data show that this lay-

Table 4. Comparison of EDX analysis of the greenish crystal with several copper-zinc trihydroxychlorides.

wt% element	O	Cl	Cu	Zn	Cu/Zn
Greenish phase	21.37	16.37	53.11	4.62	11.5
Atacamite	22.47	16.60	59.51	0.00	∞
Clinoatacamite	22.5	16.6	59.51–54.08	0.00–4.91	> 11
Paratacamite	22.4	16.5	54.08–51.96	4.91–7.64	11–7
Herbertsmithite	22.4	16.5	51.96–44.90	7.64–14.90	7–3

er is composed of gypsum, calcite, quartz and copper-zinc basic chlorides, compounds responsible for its green colouring. The greenish layer probably consists of gypsum and lime-based paint, pigmented with zinc-copper trihydroxychloride, and applied with a paintbrush.

- The existence of scattered maroon speckling with high amounts of cuprite and small quantities of copper acetate and halite could be used to hypothesize the artificial origin of the above-mentioned zinc-copper chlorides. The original pigment could be derived from a natural mineral.
- Although the Cu/Zn ratio of the greenish layer matches that of a pure clinoatacamite specimen, the latter phase could actually co-exist in the sample with zinc-stabilized paratacamite and atacamite, but the low proportion of the copper-zinc chloride(s) in the mixture does not allow XRD or FTIR spectroscopy to be definitive in this respect.

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