Microsc. Microanal. 21, 518–525, 2015
doi:10.1017/S1431927615000094

Microscopy AND Microanalysis

On the Use of the Unusual Green Pigment Brochantite ($Cu_4(SO_4)(OH)_6$) in the 16th-Century Portuguese-Flemish Paintings Attributed to The Master Frei Carlos Workshop

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Abstract: This paper reports an unusual green pigment, brochantite ($Cu_4(SO_4)(OH)_6$), on 16th-century Portuguese-Flemish paintings, attributed to the Master Frei Carlos workshop. This green mineral is usually identified as an impurity or alteration product in the green pigments verdigris ($Cu(CH_3COO)_2$ $n$$Cu(OH)_2$) or malachite ($CuCO_3$ $Cu(OH)_2$). However, after thorough investigation with a broad range of analytical techniques, it became clear that, in this case, brochantite was applied as a pigment. The abundance, pigment granulometry, and pigment morphology suggest intentional use by this Portuguese-Flemish Master as a natural pigment rather than its accidental use as an alteration product. This seems to be a distinguishable feature to other painters (Flemish and Portuguese) working in Portugal at the beginning of the 16th century.

The multi-analytical study of these easel paintings was first performed by physical imaging techniques and material characterization was carried out by optical microscopy, micro-Fourier-transform infrared-spectroscopy, micro-Raman spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectrometry, and micro-X-ray diffraction analysis (XRD).

Key words: microanalysis, easel paintings, green pigment, brochantite

Introduction

Green Pigments in Paintings

In treatises and research works covering medieval and renaissance painting techniques (Cennini, 1933; Doerner, 1934; Gettens & Stout, 1947), generally three green mineral pigments are mentioned: green earths (a general term for Cu and Fe containing silicate materials, like chrysocolla), malachite ($CuCO_3$ $Cu(OH)_2$) and verdigris ($Cu(CH_3COO)_2$ $n$$Cu(OH)_2$). Malachite is a green mineral that is typically associated with the blue mineral pigment azurite ($2CuCO_3$ $Cu(OH)_2$), while verdigris is a general term for a group of copper acetates that differ in chemical composition and hue. Some verdigris samples have a more blueish hue, while others are more green. They were synthesised according to different recipes, e.g., by exposing strips of metallic copper to acetic acid fumes. From the conservation point of view these acetates are a serious threat to the artwork as their functional groups can react and cause serious damage, such as holes in medieval parchments. In some cases, verdigris reacts in an oil or resinous paint medium, thus forming a copper soap or copper resinate, a paint that over time often turns dark brown due to oxidation.

It is well known that copper and copper salts may react to form a series of copper corrosion or alteration products. These products include, amongst others, sulphates (e.g., antlerite ($Cu_3(SO_4)(OH)_4$), chalcanthite ($CuSO_4$ $5H_2O$), brochantite ($Cu_4(SO_4)(OH)_6$) or posnjakite ($Cu_4(SO_4)(OH)_6$ H_2O)), chlorides (e.g., atacamite ($Cu_2Cl(OH)_3$), clinoatacamite ($Cu_2Cl(OH)_3$), botallackite ($Cu_2Cl(OH)_3$), calumetite ($Cu(OH,Cl)_2$ $2H_2O$)) or phosphates (e.g., libethenite (Cu_2PO_4OH), or pseudomalachite ($Cu_5(PO_4)_2(OH)_4$)) (Bouchard & Smith, 2003). As these minerals are often reaction products or degradation products, they are frequently found on artworks associated with copper materials or pigments.

Copper sulphate minerals in works of art are usually associated with corrosion products in bronzes (Frost, 2003; FitzGerald et al., 2006; Arafat et al., 2013). In the literature a few examples of the presence of brochantite in green pigment in mural paintings, usually interpreted as a natural mineral associated to malachite in copper ores (Bersani et al., 2003) or as the result of malachite degradation are

Received June 5, 2014; accepted January 12, 2015
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mentioned (Pérez-Alonso et al., 2006; Castro et al., 2008). Although this pigment was not frequently identified, its use was also reported in illuminations from the 14th century in Europe (Gilbert et al., 2003) and 16th-century Italian oil paintings on copper (Pitarch et al., 2011).

In easel paintings, the use of green copper-sulphate pigments is usually associated with verdigris green glazes (van den Berg et al., 2000) or malachite (Bersani et al., 2008) as impurities or degradation products. Intentional use of brochantite as a pigment have been reported in a few 15th-century Italian easel paintings (Martin & Eveno, 1992; Martin et al., 1995; Bersani et al., 2008) and more recently in 16th-century Netherlandish paintings (Campbell, forthcoming).

In this paper, we describe a multi-analytical approach to prove the intentional use of brochantite, ($Cu_4(SO_4)(OH)_6$), as a green pigment by Frei Carlos, one of the Portuguese-Flemish Masters that settled in Portugal during the Reign of King Manuel I (1495–1521). It is extremely important to combine this data with the material, technical and historical study of the works attributed to this workshop in order to relate it to his Flemish (Coremans et al., 1952; Coremans, 1954) and Portuguese influence.

Historical Context—16th-Century Portuguese-Flemish Painting and The Master Frei Carlos Workshop

In the early 16th century in Portugal painting techniques and styles were changing, mainly due to the influence of intense trading with Flanders, which introduced the new artistic movement that was developing there. Artistic objects were imported from Bruges and Antwerp, while Portuguese and Flemish masters were travelling between the two countries, bringing the Flemish style and technique to Portugal.

"Portuguese-Flemish Painting" is a common expression used in Portuguese Art History to describe the work of Flemish masters who settled in Portugal during the reign of King Manuel (1495–1521) contributing decisively to the process of renewal of Portuguese painting in the first third of the 16th century (Santos, 1971).

The most important Flemish masters that worked in Portugal during this period include King Manuel's favorite painter Francisco Henriques (active between 1506–1518) (Caetano, 1997, 1998), a master known as Mestre da Lourinhã (active between 1520–1540) (Batoreo, 2004) and Frei Carlos, a monk in the Covent of Espinheiro in Évora (active between 1517–1544) (Carvalho, 1993, 1998; Carvalho, 2006).

Master Frei Carlos left a large number of works mainly coming from the Espinheiro's Convent where he made the Profession of Faith (in 1517). The first step to understand Frei Carlos' work was the study by Couto (Couto, 1943) about the Espinheiro workshop in Evora. In this study, visual examination was combined with radiography and raking light photography of the paintings attributed to Frei Carlos. Couto concluded that the technical and stylistic differences did not show changes in the way of painting of a single master, but instead were the result of collaboration of several official painters. The most recent critical review was done by Seabra Carvalho (Carvalho, 1993, 1998; Carvalho, 1998, 2011, 2013), expanding the available historical and technical documentation combined with laboratory infrared (IR) photographs.

Methods and Materials

This study encompasses the analytical and technical research of fifteen paintings attributed to Frei Carlos' workshop (Table 1), with a special focus on the study of green areas. This study was also extended to seven paintings attributed to Francisco Henriques, two paintings attributed to Master of Lourinhã, and the twelve paintings from the Funchal Cathedral altarpiece (Madeira, Portugal) that have been attributed to the same group of Masters by different art historians (Table 2).

The selection of representative areas for micro-sampling was supported by physical imaging techniques, namely standard light photography, UV fluorescence photography, and IR reflectography. Microfragments were collected and mounted in epoxy resin for the study of the stratigraphy of the paint layers.

Optical microscopy and the corresponding photographic documentation were performed with a dark field microscope DM2500 (100× and 200× magnifications) equipped with a DFC 290HD camera, both from Leica (Leica Microsystems, Wetzlar, Germany).

Micro-Fourier transform infrared spectroscopy (μ-FTIR) was performed with a Nexus 670 FTIR spectrometer coupled to a Nicolet Continuum microscope by Thermo Nicolet (Thermo Fisher Scientific, Waltham, MA, USA), in the range 600–4,000 cm^{-1}, with an IR source, KBr beam splitter, and a DMCT detector for MIR measurements. Individual layers of samples were obtained by physical dissection and thin sections were obtained by squeezing each sample between two diamond cells. For each sample 256 scans were recorded with a resolution of 4 cm^{-1}. The FTIR experiments were performed in order to permit the assignment of characteristic absorption bands of functional groups associated, allowing us to identify green copper-sulphate pigments.

Cross-sections of green areas of the paintings were analyzed with a Horiba Xplora confocal micro Raman spectrometer (Horiba Ltd., Kyoto, Japan) equipped with an Olympus BX41 microscope and CCD detector. In the study of the green pigments a He–Ne laser operating at 632.8 nm was used. Non-destructive analyses were ensured by combining density filters (maximum 10%) and a 100× objective, resulting in a power at the sample of ~1 mW.

Scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDX) was carried out using a Hitachi S-3700 N SEM (Hitachi High Technologies, Berlin, Germany), coupled with a Bruker XFlash 5010 SDD Detector (Bruker Nano Analytics, Berlin, Germany). The samples were analysed throught low vaccum, at 40 Pa and the current used was 20 kV. Microsamples mounted in epoxy resin were polished in order to distinguish between the different layers and to easily identify the composition of particles with backscattered electron imaging and also to obtain good quality

Table 1. Location of Brochantite in Paintings Attributed to the Frei Carlos Workshop.

Painting's Title/No. Inventory	Date	Location of Brochantite in Painting
Nativity/ME1525	16th century (c. 1520–1525)[a]	Landscape (vegetation)
Good Shepherd/1pint	16th century (c. 1520–1525)[a]	Landscape (vegetation): floor tiles
Appearance of Christ to the Virgin/2pint	Dated 1529[a]	Floor tiles
Lamentation/74pint	16th century (c. 1530)[a]	Landscape (rocky area)
Mystic marriage of Saint Catherine/54pint	16th century (c. 1517–1538)[b]	Book
Three Saints/174pint	16th century (c. 1517–1538)[b]	Landscape (vegetation) Sta Inês: inner of the mantle
Verónica/51pint	First half of 16th century	Angels'wings
St. Brás/ME1523	16th century (c. 1530–1535)[b]	Inner of the mantle
Anunciation/677pint	Dated 1523[a]	Angel Gabriel: inner of the mantle
St. Sebastian e St. Vicent/100pint	First half of 16th century	Landscape: vegetation and rocky area
Assumption of the Virgin/82pint	16th century (c. 1520–1530)[c]	Landscape: vegetation and rocky area
Ascension of Christ/83pint	16th century (c. 1520–1530)[b]	Landscape: vegetation and rocky area
Profession of Sta Paula/85pint	First half of 16th century	Landscape (vegetation)
Calvary Triptych/2173pint	16th century (c. 1520–1530)[b]	Landscape: vegetation and rocky area
Virgin with a child and an angel/58pint	16th century (c. 1520–1530)[b]	Landscape (vegetation): floor tiles

[a]Caetano (2011).
[b]Archival Inventory database matriz net: www.matriznet.imc-ip.pt
[c]Carvalho (2011).

Table 2. List of Paintings from which Material Characterization of Green Areas was Performed.

Artist	Painting's Title/No. Inventory	Place of Origin	Date
Francisco Henriques	*The Pentecost*/801 pint	S. Francisco Church (Évora, Portugal)	1508–1511[a]
Francisco Henriques	*Our Lady of the Snows*/358 pint	S. Francisco Church (Évora, Portugal)	1508–1511[a]
Francisco Henriques	*The Gathering of the Manna*/92 pint	S. Francisco Church (Évora, Portugal)	1508–1511[a]
Francisco Henriques	*Martyrs of Morocco*/89 pint	S. Francisco Church (Évora, Portugal)	1508–1511[a]
Francisco Henriques	*Abraham and Melquisedec*/93 pint	S. Francisco Church (Évora, Portugal)	1508–1511[a]
Francisco Henriques	*Christ in the Garden*/97 pint	S. Francisco Church (Évora, Portugal)	1508–1511[a]
Francisco Henriques	*The Descent from the Cross*/95 pint	S. Francisco Church (Évora, Portugal)	1508–1511[a]
Master of lourinhã	*Saint Claire and Saint Coleta* /1823 pint	Madre Deus Monastery (Lisbon, Portugal)	c. 1515–1520[b]
Master of Lourinhã	*St. Jerome in the Desert*/52 pint	Penha Longa Monastery (Sintra, Portugal)	c. 1520[d]
	Abraham and Melquisedec		
	Last Supper		
	Mass of Saint Gregory		
	The Gathering of the Manna		
Portuguese/Flemish school	*The Annunciation*	Cathedral of Funchal (Madeira, Portugal)	First half of the 16th century[c]
	The Nativity		
	The Pentecost		
	The Assumption of the Virgin		
	Christ in the Garden		
	The Calvary		
	The Descent from the Cross		
	The Resurrection of Christ		

[a]Caetano (1998).
[b]Casa perfeitíssima (2009–2010).
[c]Ferreira (1963).
[d]Carvalho (2011).

X-ray spectra and two-dimensional compositional maps. The images allowed identification of the underlying layers, the chemical elements present, and their distribution. When combined with optical properties (color, morphology) obtained by optical microscopy, SEM-EDX proved to be an important tool for identification of the pigments present.

In order to confirm the mineralogical phases of the green pigments, micro-X-Ray diffraction (μ-XRD) was performed using a BRUKER AXS D8 Discover diffractometer (Bruker AXS, Karlsruhe, Germany) with a Cu Kα radiation source and a BRUKER LynxEye energy-dispersive one-dimensional detector. The diffractogram was obtained in the interval 5–60^o 2θ, step of 0.05o, time per step of 4 s. The identification was performed with EVA software using the ICDD PDF X-ray patterns database.

Results and Discussion

Identification

Cross-sections of selected green areas were first observed by optical microscopy in order to evaluate the presence of pigment mixtures, the sample's morphology, and its stratigraphy. The green pigment particles (Fig. 1) showed characteristic tabular and elongated morphology (Eastaugh, 2004) suggesting well-crystallized particles, in agreement with the known morphology of brochantite. However, one has to take into consideration that when brochantite appears as crystals that are not well-formed, it can be easily mistaken and misidentified as malachite (Makreski et al., 2005). Therefore, elemental and structural techniques should be used to distinguish between these two minerals. In fact, ongoing studies (Campbell, forthcoming) have revealed the use of bronchantite in the 16th-century paintings from The Netherlands that was overlooked or wrongly identified in previous analytical studies.

Complementing optical microscopy analysis, SEM-EDX on the samples provided additional information about the particle morphology, size, and distribution. SEM-EDS showed well-crystallized green minerals suggesting they were of a natural origin, rather than a synthetic or degradation product (Figs. 2a–2c). Moreover, elemental analysis confirmed the correlation between copper and sulphur (Fig. 2d) indicating a copper sulphate-based pigment.

The green anhydrous basic copper II sulphate, $Cu_4(SO_4)(OH)_6$, naturally occurring as the mineral brochantite, can be easily identified by IR spectroscopy (Fig. 3) owing to its characteristic doublet bands ν(OH) hydroxyl stretching bands) at 3,587 (m) and 3,565 (m) cm^{-1} and to its sulphate $\nu(SO_4)$ antisymmetric stretching bands at 1,121 (m) and 1,088 (m) cm^{-1}. Other bands arising owing to typical ν(OH) hydroxyl stretching mode appear at 3,402 (sh), 3,385 (s), and 3,274 (w) cm^{-1}. The fingerprint region reveals the δ(OH) hydroxyl bending modes of brochantite at: 990 (m), 943 (m), 849 (sh), 780 (m), and 732 (m) cm^{-1}. On the other hand, the band at 873 (s) cm^{-1} can be due to the δ(OH) bending mode of the mineral brochantite or a carbonate out-of-plane bending vibration arising from the lead carbonate also present in this mixture. The spectrum contains not only bands due to the pigment (brochantite), but also bands of linseed oil, lead white (probably added as pigment or siccative), and traces of a proteinaceous media. However, the characteristic bands of brochantite are clearly visible in the spectra and they are very similar to theoretical (Schmidt & Lutz, 1993) and experimental results (Van Der Marel & Beutelspacher, 1976; Stoch et al., 2001; Makreski et al., 2005; Correia, 2010).

In general, brochantite in artworks is usually observed as an impurity and is associated with malachite (Correia, 2008). However, no evidence of malachite was found in the spectra of green samples from these paintings where brochantite was identified. This tends to support the thesis that the artist deliberately used brochantite as a pigment, opposite to the idea that we might identify brochantite as a degradation product of other pigments. In the artworks from Frei Carlos, the presence of malachite is only observed as an impurity associated with azurite, which tends to indicate a natural

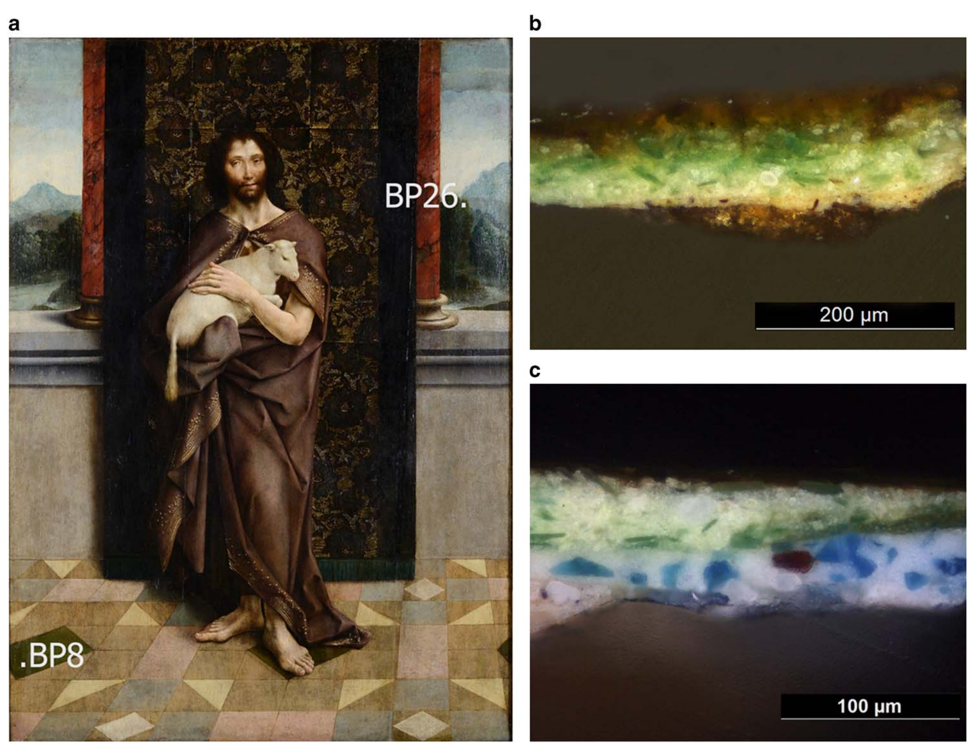

Figure 1. a: The *Good Shepherd* by light photography showing the point sampling (#BP8 and #BP26) and cross-sections with an optical microscope (**b**) #BP8, and (**c**) #BP26.

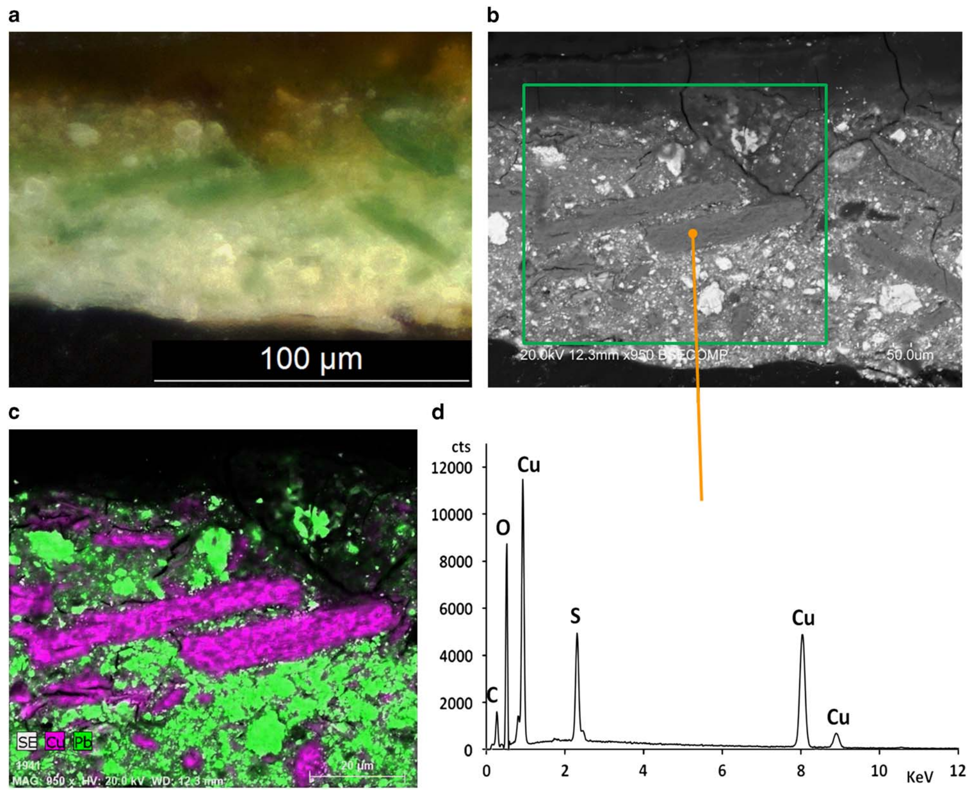

Figure 2. Detail of sample #BP8 revealing green pigment (brochantite) by optical microscopy (**a**) and scanning electron microscopy: backscattered electron image (**b**) energy-dispersive X-ray spectroscopy (EDS) elemental mapping (**c**) and EDS spectrum of a particle (**d**).

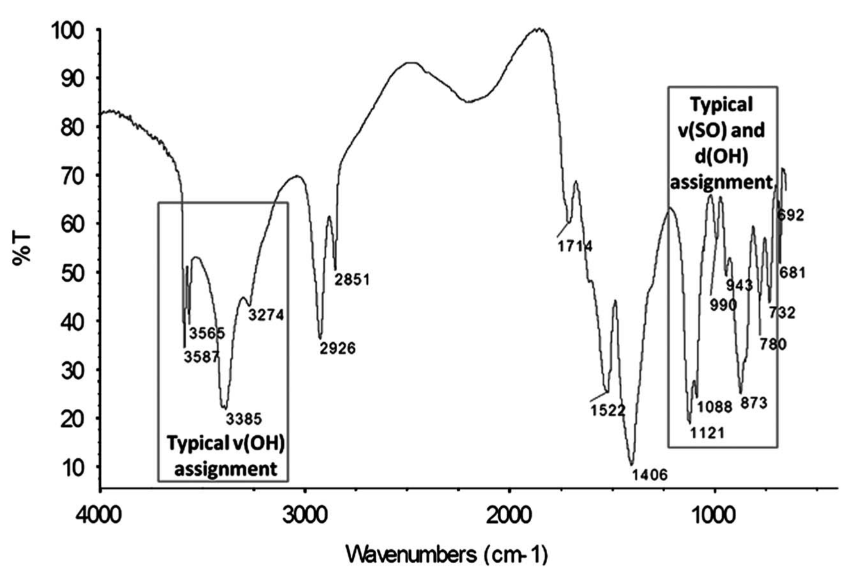

Figure 3. Fourier-transform infrared-spectroscopy spectrum showing typical assignment of brochantite (#BP8).

origin of azurite rather than a possible degradation of malachite (Feller & Roy, 1993).

The Raman spectrum of the low wave number region of the green pigments studied (Fig. 4) shows high similarity with published brochantite spectra (Schmidt & Lutz, 1993; Burgio & Clark, 2001; Bouchard & Smith, 2003; Frost, 2003; Frost et al., 2004; Makreski et al., 2005). This spectral region is characterized by the most intense Raman band at 974 cm^{-1}, which is associated with the ($\nu - 1$) sulphate symmetric stretch. In the region between 1,200 and 1,050 cm^{-1} there are two weak bands at 1,099 and 1,077 cm^{-1} associated with the (ν–3) sulphate anti-symmetric stretching mode. The (ν–4) mode is represented by the Raman bands at 609 and 620 cm^{-1}. According to the literature (Martens et al., 2003;

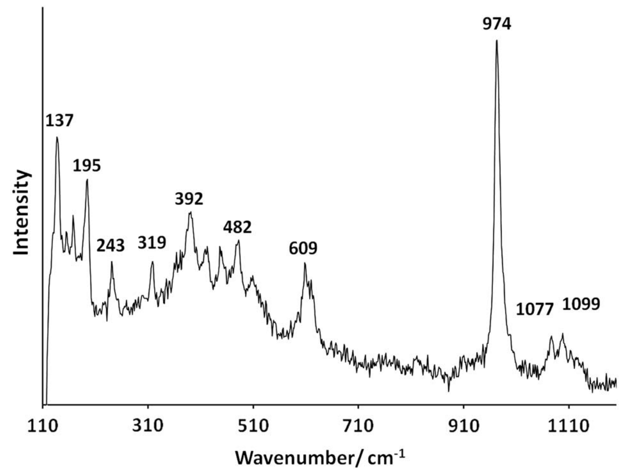

Figure 4. Raman spectrum showing typical assignment of brochantite (#CM19).

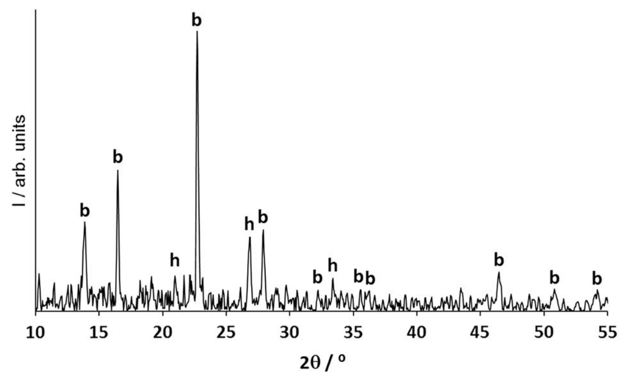

Figure 5. Micro-X-ray diffraction pattern of green layer exhibiting the peaks of brochantite (green pigment) and hydrocerussite (lead white).

Makreski et al., 2005), the bands in the region 509–309 cm^{-1} could be due to the overlapping of Cu-O stretching modes or the (ν–2) mode of the sulphate group. Moreover, at lower frequencies, the bands are very difficult to assign as they are generally associated with characteristic bands of copper sulphate minerals (Martens et al., 2003) and to lattice vibrations.

However, we must mention that there is some discussion going on about the tentative assignments of the brochantite Raman bands. There are several related minerals, such as dolerophanite $Cu_2O(SO_4)$, antlerite $Cu_3(SO_4)(OH)_4$, posnjakite $Cu_4(SO_4)(OH)_6$ (H_2O), langite $Cu_4(SO_4)(OH)_6$ $2(H_2O)$, and wroewulfite $Cu_4(SO_4)(OH)_6$ $2(H_2O)$ (Frost, 2003; Martens et al., 2003; Pérez-Alonso et al., 2006) that show similar Raman bands. Therefore, μ-XRD was applied to characterize crystalline phases in the pigment layer (Fig. 5). This revealed the characteristic XRD peaks of brochantite, hence confirming the data from the previous techniques.

Occurrence

The positive identification of brochantite used as a pigment in several paintings attributed to the Frei Carlos' workshop is listed in Table 1. There is a significant predominance of brochantite in landscapes (vegetation and rocky areas) where the hue is often modified by mixing this mineral with different amounts of lead white ($2PbCO_3{\cdot}Pb(OH)_2$), lead tin yellow type I (Pb_2SnO_4), and azurite ($CuCO_3$ $2Cu(OH)_2$). Generally, the rocky areas show an enrichment in lead tin yellow added to brochantite and lead white, while azurite usually appears only as a trace mineral. Sometimes in the rocky areas, small amounts of yellow ochre (goethite or limonite, associated with a silicate matrix) were also detected. Traces of antlerite are also present sometimes, probably as an impurity, along with brochantite (Frost, 2003). The use of brochantite is also relatively common in paintings in which floor tiles are present such as *Good Sheppard* (Fig. 1), *Appearance of Christ to Virgin,* and *Virgin with a child and an angel*. The stratigraphic analysis, combined with material characterization of green floor tiles revealed relatively similar pigment mixtures, mainly composed of brochantite and lead white, some traces of lead tin yellow, and azurite. The use of brochantite in related paintings is also restricted to landscapes, floor tiles and some other green details (see Table 1), although it is also possible to find a green hue composed of a mixture of blue and yellow pigments for similar purposes. However, brochantite was not detected in areas with more iconographic significance, e.g., green draperies of main figures where an organic copper green pigment is present as a glaze (probably verdigris). These results may indicate a trend of hierarchical use of these green pigments.

Comparable green areas of several paintings attributed to Francisco Henriques and Master of Lourinhã, were also analyzed (see Table 2), in order to try to identify similar approaches between these Portuguese-Flemish masters. The fact that brochantite was not identified in paintings attributed to other 16th-century Portuguese-Flemish masters, suggests that this mineral was only used in the Espinheiro workshop and can therefore be considered as a characteristic feature of the Frei Carlos technique.

Although the use of this green copper-sulphate mineral is not common in easel paintings, it was found in 16th-century Flemish paintings (Campbell, forthcoming). This could be related to this research considering Frei Carlos' Flemish origin (Couto, 1955). On the other hand, studies have shown that brochantite was also used as a green pigment, in the 15th-century Italian easel paintings (Martin & Eveno, 1992; Martin et al., 1995; Bersani et al., 2008) in other European workshops.

Nevertheless, one has to take into consideration that the use of copper minerals as pigments was not only due to the master's influence but also to their availability through the copper European trade (Westermann, 1999) or by local/regional production.

The relationship between this particular copper sulphate and to the copper trade is not well-known since these pigments correspond to a particular product in copper ores, formed in special environmental conditions (arid climates) (Zamana & Usmanov, 2007; Zittlau et al., 2013) with no known mention to it in the 15th and 16th century treatises making comparisons nearly impossible. Moreover, and in the particular case of the Frei Carlos workshop, one has to take the abundance of Portuguese copper ores in the Southern Portugal Iberian Pyritic Belt (Fernandes & Gaspar, 2012), which has the ideal conditions for the formation of this type of copper minerals, into consideration. This abundance, together with the discrete use of this pigment by the Frei Carlos workshop in specific motifs of the paintings also raises the hypothesis of a local/regional source of supply of this pigment.

Conclusion

This paper reports the application of a multi-analytical study, including surface examinations and elemental and structural analytical tools, in the study of 16th-century Portuguese-Flemish paintings attributed to the Master Frei Carlos workshop. The work focuses, in particular, on the characterization of an unusual green pigment, namely brochantite ($Cu_4(SO_4)(OH)_6$).

The use of this pigment in the works attributed to the Frei Carlos workshop seems to be related to a hierarchical use of green pigments as it is present in landscapes and floor areas, but absent in areas with more iconographic importance. The fact that this pigment has not been found in other 16th-century Portuguese or Portuguese-Flemish paintings may raise the hypothesis of the exclusive use of this material by the Frei Carlos workshop, which could give a distinctive material signature to this Master.

The use of brochantite by Espinheiro's workshop could be related to the master's influence and its availability through the copper European trade. It may also be that this workshop had access to local sources of this green pigment, owing to the proximity to local/regional copper mines, while other workshops, mainly from the Lisbon area, had access to pigments coming from traditional trade routes. Further studies will be performed to ascertain the material's provenance and pigment source.

The discovery of this unusual green pigment, brochantite, on the 16th-century Portuguese-Flemish paintings attributed to the Master Frei Carlos workshop and also the new findings on its use by other Netherlandish painters (Campbell, forthcoming) could establish a new perspective on the use of this pigment workshop practice in Portugal and in Europe.

Acknowledgements

The authors wish to acknowledge the Fundação para a Ciência e Tecnologia for financial support (PhD grant SFRH/BD/66068/2009 and project ONFINARTS—PTDC/EAT-HAT/115692/2009) through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund. The authors wish to thank to CHARISMA project Archlab application for financial support allowing the collaboration with the scientific team of the National Gallery in the Project MystiCa and to Marika Spring and Rachel Billingue for scientific support. The research team also wishes to thank Elisabeth Martin for data and to the HERCULES Lab and José de Figueiredo Lab teams for collaboration, especially to the physics Maria José Oliveira. The authors also wish to thank the Évora Museum and National Ancient Art Museum (Lisbon), in particular to art historians Joaquim Caetano and José Alberto Seabra, for granting access to the paintings and technical collaboration.

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