Le vert et le rouge: A study on the materials, techniques and meaning of the green and red colours in medieval Portuguese illuminations

Dissertação para obtenção do Grau de Doutor em Conservação e Restauro

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Resumo

Nesta tese será apresentado o estudo sistemático da cor no conjunto de manuscritos Românicos portugueses que enquadram as coleções do Lorvão, Sta. Cruz e Alcobaça. Com base no estudo dos materiais e técnicas de pintura utilizadas na produção deste conjunto de manuscritos, pretendeu-se identificar possíveis influências das culturas árabe e judaica na sociedade cristã dos séculos XII-XIII, assim como a relação entre estes três scriptoria e as respectivas casas-mãe.

O estudo dos manuscritos de Alcobaça colocou esta coleção como uma das mais consistentes e de maior qualidade no contexto das coleções europeias de manuscritos iluminados. A identificação de gesso como carga na formulação das tintas carmim sugere uma ligação entre Alcobaça e a sua casa-mãe de Claraval, que em muito deverá ter ultrapassado a influência na ornamentação e no sistema iconográfico de Alcobaça.

A relação entre scriptoria e outros centros europeus de produção de manuscritos teve como base o estudo detalhado das tintas verdes e vermelhas presentes nas três coleções de manuscritos. O estudo baseou-se na caracterização das formulações dos ligantes utilizados na produção das tintas vermelhas e na caracterização das especificidades das tintas verdes. O vermelho é uma cor omnipresente na iluminura medieval, ao passo que as formulações das tintas verdes podem ser muito localizadas e idiossincráticas, tornando-se num importante marcador para a identificação de artistas, centros de produção, períodos ou países. Este estudo baseou-se na combinação de dados de µ-FTIR com metodologias quimiométricas, no estudo de tratados medievais e em reconstruções históricas de pigmentos e tintas. O estudo das tintas vermelhas permitiu, pela primeira vez, caracterizar formulações proteicas utilizadas como ligantes em iluminuras medievais (como a mistura de cola de pergaminho e clara de ovo). A técnica de ELISA permitiu a quantificação de clara de ovo em três micro-amostras representativas de cada scriptorium. No que diz respeito ao verde-garrafa, foi possível estabelecer uma relação entre o colapso da banda de absorção atribuída ao proteinato de cobre, as alterações moleculares na proteína e a falta de coesão e adesão ao suporte exibida por estas tintas. Por fim, a análise da utilização da cor nas Hagiografias do Lorvão, Alcobaça e Sta. Cruz evidenciou uma extensa utilização de verde, vermelho e azul nas iluminuras destes manuscritos, sugerindo a influência da cultura árabe na produção destes manuscritos. O estudo efectuado sobre o Libro de como si facem as cores sugeriu uma partilha de conhecimento entre judeus e cristãos.

Palavras-chave: iluminura medieval, vermelhão, verde-garrafa, ligantes proteicos, quimiometria, µ-FTIR.
Abstract

Colour plays a crucial role in the interpretation of an artwork. In this thesis will be presented a systematic study of colour in Portuguese Romanesque manuscripts from the Lorvão, Sta. Cruz and Alcobaça collections. By studying the materials and painting techniques used to produce these illuminated manuscripts, the aim was to recognize possible influences of Muslims and Jews on Christian society, as well as the relation between the three scriptoria and their Mother Abbeys.

This study of the materials and paint formulations of the Alcobaça collection has placed it as one of the most consistent and high quality Romanesque collections of illuminated manuscripts in the European context. Moreover, it suggested that the relation of Alcobaça with its Mother Abbey of Clairvaux, might well have exceeded the influence on the ornamentation and on the iconographic systems, and influenced the use of the materials and paint formulations in Alcobaça.

Red and green paints were chosen for studying the use of binding media formulations and the specificities behind their production, and through this being able to study the relation between scriptoria and other European centres for manuscripts’ production. Red is ubiquitously present in medieval illumination, whereas green paint formulations can be very localised and idiosyncratic, becoming a useful indicator of specific artists, workshops, periods or countries. This study combined µ-FTIR with chemometrics methodologies, the study of medieval treatises and historically accurate paint reconstructions. Red paints allowed, for the first time, to characterize the use of proteinaceous binding media formulations (such as the mixture of parchment glue and egg white) in medieval illuminations. ELISA antibody-antigen assay quantified egg white in three red microsamples representative of each scriptorium. Concerning bottle-green paints, it was possible to establish a relation between the characteristic copper-proteinate band, the molecular changes in the protein and the macroscopic degradation alterations exhibited by these bottle-green paints. Finally, the analysis of the colour use on the Hagiographic readings of the Lorvão, Alcobaça and Sta. Cruz collections revealed an extensive use of green, red and blue paints to produce these illuminations, suggesting the high fingerprint of Christian and Islamic cultures in Portuguese Romanesque illuminations. The approach to the Portuguese medieval recipe book Libro de como si facem as cores suggested the sharing of knowledge that co-existed between Christians and Jews.

Keywords: medieval illuminations, vermilion, bottle-green, proteinaceous binders, chemometrics, µ-FTIR.
## Symbols and Notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \nu_{\text{asym}} )</td>
<td>Asymmetric stretching vibration</td>
</tr>
<tr>
<td>( \nu_{\text{sym}} )</td>
<td>Symmetric stretching vibration</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Bending vibration</td>
</tr>
<tr>
<td>( \mu)-EDXRF</td>
<td>Micro-energy dispersive X-ray fluorescence spectroscopy</td>
</tr>
<tr>
<td>( \mu)-FTIR</td>
<td>Micro-Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>( \mu)-Raman</td>
<td>Micro-Raman spectroscopy</td>
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<tr>
<td>AD</td>
<td>Abbreviation for Anno Domini used in the Gregorian Calendar to refer to the current era</td>
</tr>
<tr>
<td>BC</td>
<td>Abbreviation for Before Christ used in the Gregorian Calendar to refer the years before the start of the current era</td>
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<tr>
<td>XRD</td>
<td>Micro-X-ray diffraction spectroscopy</td>
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<tr>
<td>Sta. Cruz</td>
<td>Santa Cruz collection</td>
</tr>
<tr>
<td>ANTT</td>
<td>Arquivo Nacional da Torre do Tombo</td>
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<tr>
<td>BNP</td>
<td>Biblioteca Nacional de Portugal</td>
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<tr>
<td>BPMP</td>
<td>Biblioteca Pública Municipal do Porto</td>
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<tr>
<td>BnF</td>
<td>Bibliothèque nationale de France</td>
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<tr>
<td>BNT</td>
<td>Bibliothèque nationale de Troyes</td>
</tr>
<tr>
<td>ELISA</td>
<td>Enzyme Linked Immunosorbent Assay</td>
</tr>
<tr>
<td>( f. )</td>
<td>Folio (manuscript page)</td>
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<tr>
<td>Gen</td>
<td>Book of Genesis</td>
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<tr>
<td>(^1)H-NMR</td>
<td>Proton Nuclear Magnetic resonance</td>
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<tr>
<td>HPLC-DAD</td>
<td>High performance liquid chromatography-diode array detector</td>
</tr>
<tr>
<td>ICOM-CC</td>
<td>International Council of Museums – Committee for Conservation</td>
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<tr>
<td>Mt</td>
<td>Saint Mathews (Evangelist)</td>
</tr>
<tr>
<td>(^1)H-NMR</td>
<td>Proton Nuclear Magnetic resonance</td>
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<tr>
<td>PC1</td>
<td>First Principal Component</td>
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<td>PC2</td>
<td>Second Principal Component</td>
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<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
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<td>Term</td>
<td>Definition</td>
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<td>--------</td>
<td>------------------------------------------------</td>
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<tr>
<td>PLSR</td>
<td>Partial Least Squares Regression</td>
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<tr>
<td>SE</td>
<td>Spiritual Exercises</td>
</tr>
<tr>
<td>SEM-EDS</td>
<td>Scanning electron microscopy and energy dispersive X-ray spectrometry</td>
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<tr>
<td>v</td>
<td>Verso (of the folio)</td>
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<td>wt</td>
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* Saint Ignatius of Loyola (SE, 230-237).
In the beginning God created the heavens and the earth.

The earth was without form, and void; and darkness was on the face of the deep.

And the Spirit of God was hovering over the face of the waters.

Then God said, "Let there be light"; and there was light.

Gen 1-5

1. Introduction

1.1. Preamble

Medieval manuscripts are among the most important and valuable testimonies of medieval Art [Pächt 1986; Miranda 1999; Afonso 2011]. In Portugal, it was during the 12th-13th century that medieval manuscript production had its flowering period [Miranda 1996; Melo et al. 2011]; a period marked by profound changes in the Portuguese borders, with Christians fighting to reconquer the southern Portuguese territory, at the time under the Muslim rule, Figure 1.

In this context, the strategic establishment of medieval monasteries close to the Portuguese borders with the Muslim territory had an important role both in peacekeeping and in articulating the social order [Mattoso 1985; Mattoso 1993a]. Nevertheless, these monastic
men showed a clear respect for the mozarabs\(^1\) and for the Islamic culture [Mattoso 1985]. To promote the establishment of monasteries in strategic regions according to the King’s interests, the religious orders were commonly endowed with royal donations of lands, money or general supplies that were used in the daily subsistence of the monastery [Mattoso 1993a].

Throughout the Early Middle Ages, reading and writing was not a universal knowledge. In fact, in the Portuguese Romanesque period, even the nobility depended on the reading and writing knowledge of the monks [Mattoso 1993b]. During the 12\(^{th}\)-13\(^{th}\) centuries, manuscript production was mainly restricted to the monasteries [Miranda 1996; Nascimento 1999]. Nevertheless, illumination (and metalwork) was considered the most valued artistic activity [Afonso 2011]. Inherent to the writing production there was an important aesthetic concern, demonstrated by the illuminations that were frequently accompanying the texts. If in the earliest illuminations, as those produced during the early 12\(^{th}\) century, the line drawing is dominant over the painting, with the course of the time there was an inversion, with line drawings becoming restricted to the outlines, with the paintings having the main role on the illumination, Figure 2 [Mattoso 1999a]. Colour appears as a fundamental element in codex organisation, providing sense and beauty to the written word [Melo et al. 2011].

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\(^1\) Mozarabs is the term generally used to designate someone who was not of pure Arab descend, but that was introduced among the Arabs, speaking their language and imitating their manner of appearance [Hitchcock 2008]. The term mozarabs is also used to refer to the so-called Christians of the Muslim Iberian Peninsula.
Colour production in medieval illuminations was a complex process. Producing high-quality colour paints required the use of high-quality materials, of high-quality paint formulations and the mastery of the drawing and painting techniques. For this the financial resources of the monastery and the knowledge of how to prepare the materials and paint formulations were of extreme importance. By studying the materials and technology underlying its production, new specificities can be found, namely those related to the use of specific formulations, or to the sharing of knowledge between the production centres (the religious monasteries) and other cultures. A more in-depth understanding of the specificities of Portuguese medieval illuminations production will contribute to its valorisation, namely in the European context, at the same time that new findings in the relation between Christians, Muslims and Jews will become apparent. Moreover, by characterizing the specificity of medieval paints formulations, new inputs will be derived to contribute to these important testimonies of medieval culture and art, at the same time that new inputs to the conservation and restoration of illuminated manuscripts will be assessed.

This chapter aims to introduce the reader to the research methodology followed in this dissertation for the study of the materials, paintings techniques and meaning of coloured paints in Portuguese Romanesque illuminations, with a special emphasis on the specificities behind green and red paints (section 1.2). Furthermore, it is aimed to introduce the study of Romanesque manuscripts’ materials that have been developed by the scientific community in the last two decades (section 1.3) and to the specificities of Portuguese Romanesque manuscripts’ illuminations that have been highlighted by our research team in the last six years (section 1.3). To introduce the reader to the Portuguese Romanesque manuscripts’ illuminations two approaches will be presented: the context of their production (the sharing of cultures and knowledge in early medieval Portugal – section 1.4.1; and the monasteries where these manuscripts were produced - section 1.4.2), and the main specificities behind the production of these manuscripts (materials, drawing and painting techniques used for their production – section 1.5.2; and the use of colour in the context of the manuscripts’ production – section 1.5.3).

### 1.2. Research objectives and methodology

The present work is founded in two main objectives: the analysis of the specificities behind the production of Portuguese Romanesque illuminations, and the analysis of the
specificities of the use of colour in the context of the Portuguese Romanesque *scriptoria*. For the first propose, it will be considered the study of the materials and painting techniques used to produce a set of 12th-13th century manuscripts from the Alcobaça collection. Besides, by studying the specificities behind their production, an important contribution to the contextualization of these manuscripts in the European context will be provided. With the study of the red and green paints’ formulations present in the Portuguese Romanesque manuscripts it is aimed to infer on the sharing of knowledge and techniques between *scriptoria* and/or other cultures (namely between Christians, Jews and Muslims). Also, it is aimed to identify the possible use of specific formulations that might characterize the Portuguese Romanesque illuminations’ production (namely the use of specific binding media formulations). Finally, the analysis of the specificities of the use of colour will allow inferring on the importance of the bottle-green colour in the context of the Romanesque Portuguese *scriptoria* as well as on the Romanesque Portuguese culture.

1.2.1. Research design

The research design was founded in three main approaches: the analysis of the drawing techniques, the characterization of the materials and painting techniques, and the study of the colour constructions and colour extent of use, *Figure 3*.

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*Figure 3.* Schematic representation of the research design followed in this Dissertation.

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2 The Lorvão, Santa Cruz de Coimbra and Alcobaça collections constitute the three main Portuguese Romanesque collections of illuminated manuscripts. The study of the Lorvão collection was part of Ana Claro’s PhD dissertation [Claro 2009], and the study of the Santa Cruz de Coimbra collection is part of the PhD research of Rita Castro, still in progress (please see section 1.3).
The study of the drawing techniques and colour constructions and colour extent of use was restricted to the *Hagiographic readings* from the Lorvão, Santa Cruz de Coimbra and Santa Maria de Alcobaça collections. The reason for choosing this set of manuscripts for establishing a systematic relationship between *scriptoria* will be discussed later (*section 1.5.1*). Concerning the study of the materials and painting techniques of Portuguese Romanesque illuminations, the focus was to the Alcobaça collection, as the two remain collections are part of other PhD dissertations (please see *section 1.3*). Nevertheless, for the study of the green and red paints’ formulations, it was included the Romanesque manuscripts of the Lorvão, Santa Cruz de Coimbra and Alcobaça collections. The materials and painting techniques were characterized following a systematic approach based on the analytical results of the study of the coloured paints’ illuminations, on the study of contemporary written sources for the production of materials and techniques for illuminations, and on historical accurate reconstructions. Concerning the analysis of the drawing techniques and the colour construction, these were base on the analysis of the illuminations and of the materials used in the paints’ production. Finally, the colour extent of use was performed by mapping each colour paint present on the illuminations of the *Hagiographic readings* from the Lorvão, Sta. Cruz and Alcobaça collections.

### 1.3. The study of medieval manuscripts’ materials

Medieval manuscripts have been extensively studied in the last decades from an art history perspective. Nevertheless, it was in the last two decades, with the development of new non-invasive analytical techniques, that new insights into the materials used to produce medieval illuminations were achieved. A new approach to the study of the painting techniques used to produce medieval illuminations became attainable. By gathering the analytical results of painting materials, together with the information from medieval written technical sources which describe the production of paints, it becomes possible to proceed with accurate paint reconstructions, and through this, understanding how these medieval illuminations were produced. Furthermore, by characterizing the materials used in Portuguese medieval manuscripts production, an important contribution to the medieval art history field will be provided, namely on the sharing of scientific knowledge and techniques between the three main cultures at the time: Christians, Muslims and Jews. Moreover, by knowing the materials from these illuminations are made, important contributions for understanding the degradations mechanisms that might be occurring can
be achieved. Within these new findings, a new *modus operandi* for the manuscripts conservation may be proposed, ensuring their safeguarding for future generations.

In the last two decades, important contributions have been performed on the study of the materials used to produce Romanesque medieval illuminations, essentially based on inorganic pigments’ identification. In 1995, Robin Clark published an important work on the identification of pigments on two 13th century Italian manuscripts (an *Antiphonal* and a *Choir Book*), and on the 13th century French *Lucka Bible* [Clark 1995]. Based on Raman analysis, identified on the *Antiphonal* was the use of lapis lazuli and malachite; on the *Choir Book*, lapis lazuli was applied over azurite, creating an interesting effect, and reflecting the illuminator’s economical concern with minimizing the use of the more expensive mineral, lapis lazuli. Concerning the *Lucka Bible*, the presence of lead white, vermilion, red lead, lapis lazuli, azurite and orpiment was identified [Clark 1995]. In 1999, Claude Coupry published the analytical study of a set of nine Normand manuscripts produced at the scriptorium of the Trinité de Fécamp Abbey between the end 10th - middle 12th centuries (conserved at the Bibliothèque nationale de France, BnF) [Coupry 1999]. Based on Raman spectroscopy analysis of these manuscripts dated from the end of 10th century, the use of indigo (indigotin) as a major source was identified. For the rest of the manuscripts, lapis lazuli replaced the primacy of indigo as blue source. Other pigments were identified such as red lead, massicot, orpiment and lead white. A certain deep-saturated organic green was analysed, but no conclusions were achieved. A progressive replacement of red lead by vermilion with time was observed. Unfortunately no likely justification for such changes was presented. Interesting to note is the fact that, for the lettering, pure vermilion paints were consistently used. After the year 1070, the combination of red-blue colours became a characteristic amongst the manuscripts produced at the Fécamp Abbey [Coupry 1999]. In 2001, Mark Clarke published an important review on the analysis of European medieval manuscripts, highlighting the most used analytical techniques, general works on pigments history, the history and development of pigment analysis, and the most interesting published results on manuscripts analysis until 2001 [Clarke 2001]. Later, in 2004, Clarke would publish an important paper on the study of Anglo-Saxon early medieval manuscripts from the 7th-11th century using micro-Raman spectroscopy and near-infrared imaging. Within these techniques it was possible to have results mainly for inorganic pigments: minium, verdigris, carbon black and orpiment were the main pigments used to produce the
manuscripts; the organic indigo (indigotin) was found in the earliest examples, and shellfish purple and lead white in some of the most luxurious manuscripts [Clarke 2004].

As stated by Clark in his work published in 1995 “The lack until recently of techniques for pigment analysis which can not only be carried out in situ, but are reliable, sensitive, and non-destructive has greatly restricted the number of significant studies which could be carried out on medieval manuscripts. Much important information of social and/or technological nature thus remains to be revealed” [Clark 1995]. In the last years, the development of new in situ techniques allowed for an improvement on the number of analytical studies of medieval manuscripts. The study of early medieval manuscripts left its comprehensive character, to become more focused. Several studies were published since then concerning specific manuscripts (such as the analysis of the Book of Kells, Ireland, circa 800 AD) based on micro-Raman analysis, which indentified the extensive use of red lead, orpiment, carbon black, indigo, purple (orcein) and gypsum, and mixtures of orpiment and indigo (vergaut), gypsum and indigo, and gypsum and purple [Bioletti et al. 2009]); specific degradation phenomena (such as the study of red lead based paints in the Lorvão Apocalypse (Portugal, 1189), where our team identified galena as the major degradation product, proposing for the first time the red lead degradation mechanism present in that manuscript [Miguel et al. 2009a]); or the study of specific colourants used in manuscript production (such as the identification of a specific dye, e.g. lac dye, based on the development of a microspectrofluorimetry approach [Melo and Claro 2010]). Recently, some studies have followed as modus operandi the combination of analytical results with accurate paint reconstructions based in medieval written technical sources, as a way to better characterize the painting techniques used to produce early medieval manuscripts [Miguel et al. 2009b; Claro 2009; Miguel et al. 2011; Oltrogge 2011].

In the last six years, an interdisciplinary team of chemists, biochemists, informaticians, art historians and conservators under the leadership of Maria João Melo (Conservation Scientist) and Adelaide Miranda (Art Historian) began a systematic study on the colour of Portuguese medieval illumination [Iluminuras 1, 2, 3]. This study concerns a set of 38 manuscripts from the scriptoria of São Mamede do Lorvão (nine manuscripts), Santa Cruz de Coimbra (fourteen manuscripts) and Santa Maria de Alcobaça (fifteen manuscripts), (see Appendix I). Besides characterizing the paints’ formulations, our team aims to recognize possible influences of Muslims and Jews on Christian society, based on the
analysis of the materials and techniques used to produce these Romanesque manuscripts. Also, by studying the extent of use of each colour, the team aims to propose a meaning for its usage. The Lorvão collection was part of the PhD thesis of Ana Claro entitled “An interdisciplinary approach to the study of colour in Portuguese manuscript illuminations” [Claro 2009], whose research took place in the framework of the research project entitled with the same name [Iluminuras 1]. For the first time a systematic study of the materials and painting techniques used to produce 12th-13th century manuscripts from the Lorvão collection was presented. The study of the Santa Cruz de Coimbra collection is part of the PhD research of Rita Castro, still in progress, and the study of the Santa Maria de Alcobaça collection is part of this PhD dissertation.

The present PhD dissertation was carried out in the framework of two research projects: The identity of Portuguese medieval manuscript illumination in the European context (PTDC/EAT/65445/2006) [Iluminuras 2], and Colour in medieval illuminated manuscripts: between beauty and meaning (PTDC/EAT-EAT/104930/2008) [Iluminuras 3]. For the first time, a full characterization of the materials and painting techniques used to produce 12th-13th century manuscripts from the Santa Maria de Alcobaça collection is presented (see Chapter 2). Moreover, a systematic study was carried out on the specificities of red and green paints’ formulations on Portuguese Romanesque illuminations from the Lorvão, Santa Cruz de Coimbra and Santa Maria de Alcobaça collections - le vert et le rouge (see Chapter 3). Green is one of the most important colours which concerns the identity of Portuguese medieval illumination and the influences it has integrated. It presents important specificities that will allow the determination of possible relations with other centres for the production of medieval illuminations. Also, despite presenting a beautiful deep glassy saturated bottle-green appearance, it is suffering a serious loss of cohesion and adhesion to the support. Studying the specificities of its formulation becomes essential for identifying the origin of this problem, and thus being able to contribute to its conservation in the future (see Chapter 3). Red is ubiquitously present in medieval illumination. It could be mined as cinnabar, or synthesized as vermilion. Its study will be important for understanding the influence of other cultures, namely the Arabian culture that might be behind its production, and for the study of the

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3 The systematic study of these deep-glassy dark green paints was started by the research team under the leadership of Maria João Melo and Adelaide Miranda. The team named this colour as “verde garrafa” (bottle-green) due to its visual resemblance to green glass bottles.
binding media formulation (see Chapter 3). By understanding the scientific knowledge behind pigments production and the circulation of materials and technical knowledge during early medieval period in Portugal, evidence for the *convivencia* between Christians, Muslims and Jews will be strengthened. Furthermore, by studying the similarities between different *scriptoria* (as between the monasteries of Lorvão and Alcobaça) new evidence for their relations will be accessed. Finally, with the study of the formulations’ specificities for the colour paints that are suffering a worrying degradation process, we aim to hopefully inspire new methodologies for their conservation.

### 1.4. The context of the Portuguese Romanesque manuscripts production

#### 1.4.1. Early Medieval Portugal: Sharing of cultures and knowledge

The history of early medieval Portugal is strongly related with the history of the early medieval Iberian Peninsular. For nearly eight centuries, Christians, Jews and Muslims lived together and contributed to the political, religious, cultural, linguistic and ethnic diversity of the contemporary Portuguese and Spanish society [Constable 2012]. The presence of Muslims dates back to the year of 711, when the Berber army, under the Arab leadership of General Tariq, invaded the south of the Iberian Peninsula (at the time part of the Visigothic kingdom). At the time, the Iberian Peninsula was occupied by a Catholic Christian majority and a substantial minority of Jewish people, also known as Sephardic Jews, from *Sepharad*, the Hebrew word for Spain [Gerber 1992]. Both Christians and Jews were, at the time, under the Visigothic rule [Fletcher 1992]. The evidences for the Jewish presence in the Iberian Peninsula dates back to the pre-Christian era. It is believed that most arrived during the Roman period, either voluntarily or as slaves brought from the Middle East after the defeat of Judea in 70 AD [Fletcher 1992]. Another reason for the Jewish displacement and their arrival in the Iberian Peninsula was the Islamic invasion of the region comprising the Byzantine Empire between the 7th-12th centuries; many of them had to flee their homeland, having to settle in the Iberian Peninsula [Fletcher 1992]. It took only four years for Muslims to control the territory of the Iberian Peninsula, with exception to the Basque Country, Cantabria, Galicia and Asturias (in the northern Pyrenees) that remained under the Christian domain [Fletcher 1992]. Muslims would subsist in the Iberian Peninsula for more than seven centuries. The Christian *reconquest* of the occupied territories started from Asturias, and gradually advanced towards Andalusia, ending with Muslims expulsion from Granada, in 1492 (from 1264 – the year of the *reconquest* of
Guadalquivir region - to 1492 – the year of Muslims expulsion from Granada by the troops of Isabel la Católica, Queen of Castille - the region of Granada remained under the Muslim rule [Ladero-Quesada 2003]). During the period of Muslim occupation, Jews and Christians became to be known as “People of the Book” (dhimmi), affording the permission to practice their faith under the Muslim rule. Likewise, during the 12th-13th centuries, and after the fall of Muslim occupation in most of the Peninsula territory, Muslims and Jews enjoyed a certain degree of protection, in a period of tolerant coexistence – the convivencia. During this period, Christians, Jews and Muslims lived in mutual cooperation. However, over the years, religious intolerance increased, with Muslims being forced to convert to Christianity. If some joined the Christian rule (the so-called mouriscos), others left the Iberian Peninsula [Constable 2012]. The period of convivencia was extremely fruitful both in the establishment of new commercial networks, namely those routes supported by the Muslims and the Jews, and in the remarkable spreading of scientific knowledge and state-of-the-art technology. By joining Christian, Jewish and Muslim cultures, the Iberian Peninsula embraced the cultural legacy of the Greeks and Roman texts, and the Asian cultural heritage brought through the Muslims culture; with new routes for commercial trades, Muslims occupation allowed the Iberian Peninsula to take part in a new world trade that was extended even to China, that at the same time released the transmission of scientific and cultural knowledge from the Islamic Middle East and Central Asia, allowing the contact of the Iberian Peninsula with Chinese knowledge [Lombard 1971; Melo et al. 2011].

There are several testimonies from the Portuguese convivencia during the 12th-13th centuries. The society, as a whole, would integrate the convivencia multicultural heritage, and the new religious orders (Benedictines, Augustinians and Cistercians) were not exceptions. New materials and techniques were now available for illuminated manuscript production, together with new elements that could integrate the iconographic program of the scriptoria. One of the most interesting cases is related to the iconographic elements present on manuscripts produced in religious monasteries. As an example are two manuscripts from the Lorvão collection, De Avibus and the Lorvão Apocalypse. Here the iconography clearly points to the information of Muslim and Jewish cultures by the illuminator, as in the characteristic semi-circular round arches that characterize the Islamic architecture in “The Dove and the Hawk” (Lorvão 5, f.5) of De Avibus, or in the pileum
ornated with red strokes in the “The victory of the Lamb over the Beast” (*Lorvão 43, f.191*) of the *Lorvão Apocalypse*, an iconographic element that might allow the identification of these characters as Jewish, *Figure 4*.

*Figure 4. Left*, Detail from *Lorvão 5, f.5* (*De Avibus*, 1183-1184) with the *Dove and the Hawk* placed under the characteristic semi-circular round arches that characterize the Islamic architecture; *right*, detail from *Lorvão 43, f.191* (*Lorvão Apocalypse*, 1189) with two men using a *pileum cornutus*. Photos © ANTT.

### 1.4.2. The Portuguese medieval monasteries of São Mamede do Lorvão, Santa Cruz de Coimbra and Santa Maria de Alcobaça

During the Romanesque period, the three main Portuguese *scriptoria* were placed at São Mamede do Lorvão, Santa Cruz de Coimbra and Santa Maria de Alcobaça monasteries, all placed in the middle centre of Portugal, *Figure 5*.

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4 The characteristic Jewish cone-shaped pointed hat.
Figure 5. The Portuguese monasteries of São Mamede do Lorvão, Santa Cruz de Coimbra and Santa Maria de Alcobaça, and the French monasteries with whom they were associated with (Mother Abbeys) – [adapted from Melo et al. 2011].

The monastery of São Mamede do Lorvão was founded near Coimbra, in the margins of the Mondego River and surrounded by a dense forest, Figure 5. There is no precise information on when this monastery was founded. Based on recent studies on the Chartularium Laurbanense (Cartulary of Lorvão), Aires do Nascimento proposes the year of 857 for its foundation, while Fernández Catón proposes the year of 917 [Mattoso 2009]. In a recent study on the Chartularium Laurbanense, the commercial relations of the monastery with the Islamic community are evident (for instance, according to the Cartulary, in 1017 the monastery purchased lands to the Muslim Zuleiman Iben Giaru and in 1019 to the Muslim Mahomad, who at the time lived nearby the monastery’s lands [Nascimento 2008]). The Lorvão monastery played an important role before the Portuguese Kingdom was founded, with important contributions to the development of the surrounding populations, including the construction of important infrastructure, such as mills, bridges, and roads [Nascimento 2008]. Also, and according to contemporary Chronicles, the Benedictine monks from Lorvão were in the basis of the enterprise for the conquest of Coimbra to the Muslims, in 1064 [Nascimento 2008]. In 1206 the Lorvão monastery became a female Cistercian monastery, when Dona Teresa, daughter of the Portuguese King D. Sancho I, joined the monastery with her nuns, after the annulment of her marriage with King Alfonso IX of León [Nascimento 2008]. It is believed that from this moment on the monastery would no more have a scriptorium, even though it continued
enriching its library. For the medieval period, the collection has 18 manuscripts, of which two are particularly significant for the history of Portuguese illumination\(^5\) – the *Lorvão Apocalypse* (*Lorvão* 43, 1189) and the *De Avibus* of Hughes de Fouilloy (*Lorvão* 5, 1183-1184), conserved at the Portuguese National Archives (*Arquivo Nacional da Torre do Tombo*, ANTT) [Miranda *et al.* 2008; Melo *et al.* 2011].

The monastery of Santa Cruz de Coimbra was funded in 1131 under the Rule of St. Augustine. Its foundation had the commitment of D. Afonso Henriques, the first King of Portugal, who donated the royal baths for the establishment of the monastery. In 1131 the court moved from Guimarães to Coimbra, and Santa Cruz acquired a special role on the Kingdom. The monastery was related with Saint-Ruf d’Avignon monastery in France (founded in the 6\(^{th}\) century), *Figure 5*. According to Agostinho Frias, whose work is cited by Miranda [1984], the first books produced at Santa Cruz *scriptorium* must have been copied by the canons Domingos and Pedro Salomão, who were tasked to copy the manuscripts prescribed by the Augustinian Rule and the *Lietbert Customary* of Saint-Ruf for the regular life of Augustinian canons. In 1139, these two canons would travel to Rome to copy the first manuscripts that would comprise the core of Santa Cruz library [Miranda 1996]. From the set of 99 medieval manuscripts kept by the Biblioteca Pública Municipal do Porto (BPMP), 35 belong to the 12\(^{th}\)-13\(^{th}\) century and must have been produced in Santa Cruz [Melo *et al.* 2011].

The monastery of Santa Maria de Alcobaça was established in 1153\(^6\). Its foundation was part of the expansion plan of the Cistercian order for the 12\(^{th}\) century [Miranda 1984]. Similar to Santa Cruz de Coimbra, Alcobaça monastery also benefited from D. Afonso Henriques’ donations and protection [Miranda 1984]. Situated in the centre of Portugal, it was related to the French Cistercian Monastery of Clairvaux (founded in 1115), *Figure 5*. By following Saint Benedict’s rule, the Cistercian “white monks” from Alcobaça lived a life of austerity in food, clothing and liturgical practices [Miranda 1984]. The value given to manual work, as recommended by Saint Benedict, was reflected in the dedication of these monks to agriculture, importing new teachings from Burgundy that, at the time, by

\(^5\) Both manuscripts present a detailed colophon with authorship, date and place of production – the *Lorvão scriptorium*.

\(^6\) Alcobaça is the 53\(^{rd}\) daughter monastery of Clairvaux [Miranda 1984]. At the time of its establishment in 1153\(^6\), Clairvaux was already affiliated with 167 monasteries spread all over Europe, from Ireland, to England, Sweden, Germany, South Italy and Spain [Miranda 1984].
using new technical approaches, was improving agricultural productivity. By working their lands, and by influencing the people from nearby lands for agriculture, Alcobaça would promptly achieve its economic independence from Royal donations [Miranda 1984]. In 1248 the Bishop of Lisbon authorized the “white monks” to build four new churches in their lands, evidence of the population growth around Alcobaça and confirming their social development. This supports the idea that in the first quarter of the 13th century, Alcobaça was already a well-established monastery, with some financial sustainability, contrary to other monasteries from the north of Portugal [Miranda 1984]. It is thus justified to assume the existence of adequate financial resources for acquiring high quality materials for the production of manuscripts and for its illuminations, as will be presented (see Chapter 2). According to Miranda, the quality of the Alcobaça armarium might be equivalent to those from other important European monasteries; and is certainly an important collection among the Cistercian armaria [Miranda 1984]. After the extinction of the religious orders in Portugal in 1834, the collection of manuscripts from the Alcobaça monastery was transferred to the Portuguese National Library (Biblioteca Nacional de Portugal, BNP), where it remains [Mattoso 1993c; Cepeda et al. 2001]. From the set of 456 manuscripts produced during the Middle Ages kept at the BNP, circa 160 manuscripts are from the 12th - early 13th centuries [Miranda 1999; Melo et al. 2011].

Of all the early medieval Portuguese monasteries, Santa Cruz de Coimbra and Santa Maria de Alcobaça monasteries had undoubtedly a major role for the establishment of Portugal, both from a political point of view, and in the establishment of its intellectuality. Also, concerning Romanesque medieval manuscripts, few examples have come down to us, with Santa Cruz de Coimbra and Santa Maria de Alcobaça being the best collections of illuminated manuscripts that survived until the present day [Miranda 1999]. The construction of the armarium7 of Santa Cruz de Coimbra and Santa Maria de Alcobaça was most probably established with manuscripts produced in their own scriptoria. Many of these must have been copied from originals present in their parent abbeys, and in this they contributed to the circulation of manuscripts and scribes between those monasteries and the monasteries with whom they were associated with.

7 Term commonly used to refer a monastic library.
1.5. Portuguese Romanesque illuminations

The set of 38 manuscripts from the three monasteries of São Mamede do Lorvão, Santa Cruz de Coimbra and Santa Maria de Alcobaça manuscripts studied by our research team in the last six years were selected in the framework of the research projects [Iluminuras 1, Iluminuras 2 and Iluminuras 3]. The selection was performed based on the chronological period established (Romanesque period) and on the interests of its artistic and chromatic features.

1.5.1. The Manuscripts

Of all the manuscripts, only six present a colophon with the date originally included by the author (Lorvão 5, 1183/84; Lorvão 43, 1189; Lorvão 50, 1184; Sta. Cruz 4, 1139 Oct. 25; Sta. Cruz 27, 1179, June; and Alcobaça 410, 1257).

The São Mamede do Lorvão (Lorvão) collection stands out for the small number of manuscripts (18 manuscripts) and for its heterogeneity.

Concerning the collections from the monasteries of Santa Cruz de Coimbra (Sta. Cruz) and Santa Maria de Alcobaça (Alcobaça), both present an important set of manuscripts from the Latin Patristics8 [Melo et al. 2011]. From these early Christian authors, Saint Augustine and Saint Gregory are the most represented in Alcobaça, while Saint Augustine and Saint Isidore are the most represented in Sta. Cruz (where is also possible to find copies of the writings of Saint Ambrose, Saint Gregory, Bede and Saint Cassian) [Melo et al. 2011]. Nevertheless, Alcobaça possesses a significant higher number of the Latin Patristics texts, when compared with Sta. Cruz collection (for example, there are circa twenty texts by Saint Augustine) [Melo et al. 2011]. Concerning the encyclopaedias, both Sta. Cruz and Alcobaça collections present the most emblematic works from early medieval period: Saint Augustine (De doctrina Christiana), Saint Isidore (Etymologicarum), Bede (De Rerum Naturam) and Hugh of Saint Victor (Didaskalion).

Another important group of manuscripts present in Alcobaça, though less significant than in Sta. Cruz, is hagiography. According to François Dolbeau [cited in Miranda 1984, p.19], this set of manuscripts present in Alcobaça9 is one of the most important remaining hagiographic collections from the 12th century, and therefore constitute an important link

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8 The Latin Patristics are the first Church theologians, also known as the Church Fathers.

9 The Legendarium from Alcobaça comprises a set of five manuscripts: Alcobaça 418-422 [Miranda 1999].
to the history of the first Cistercians legendaries. The liturgical books, represented by the *Psalters* and *Missals*, are also fairly significant in Sta. Cruz and Alcobaça collections, either by number or quality of illuminations. Due to its dimensions and high care with execution and ornamentation of its illuminations, the Bibles were certainly important manuscripts for both libraries. Interesting to note that in Sta. Cruz, the two Bibles only present the Old Testament (the New Testament is absent in this library), while in Alcobaça both Old and New Testaments are present. Finally, the presence of grammars, such as the work by Papias and others, in the *armarium* from Alcobaça is justified by the great importance given by the Cistercians to the literacy of the monks, since only one mastering reading could be able to study in deep the Holy Scriptures, and thus better know the Word of God [Miranda 1984].

All the three collections have a copy of the *De Avibus* by Hughes of Fouilloy (*Lorvão* 5, 1183-1184; *Sta. Cruz* 34, 1176-1225; and *Alcobaça* 238, 13th century). In Clairvaux there is a copy attributed to the 12th century (*Troyes, Ms 177*). The *De Avibus* is a medieval text that was meant to be a behavior model for the lay-brotherhood community, explaining to them the mysteries of incarnation using birds as examples [Miranda et al. 2010]. It was probably written in Picardy, France, in about 114010 [Miranda et al. 2010].

From the Lorvão collection were chosen a set of nine manuscripts concerning the Iberian monachism11 period of the monastery until the Cistercian period12, from the Sta. Cruz collection were chosen a set of fourteen manuscripts, and from the collection of Alcobaça a set of fifteen manuscripts (see Appendix I).

- *manuscripts selected for establishing a systematic relationships between scriptoria*

For establishing a systematic relationship between *scriptoria* based on the analysis of manuscripts, it becomes fundamental to analyse comparable manuscripts, meaning manuscripts produced during a same period and with a comparable importance for the

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10 Hugh of Fouilloy was a prior at Saint Nicholas of Regny, a small community that depended on the Augustinians of St. Laurent, near Amiens, France.

11 *Monachism* is a way of life in which one consecrates all his life to *God cause*, looking Him in a lifetime of dedication and interiorization. The *Iberian monachism* played an important role on establishment of Christianity in Iberian Peninsula.

12 The Cistercian period begun in 1206, when the Lorvão monastery became a Cistercian feminine monastery.
armarium. Traditionally, the Hagiographic readings are manuscripts with an important place in the armarium of a monastery. It contains the narrative readings on the lives and martyrdoms of the Saints, and was read in the Divine Office or as a source of study by the monks [Brown 1994]. The Hagiographic readings encompasses the Passionarium, Martirologium and Legendarium [Pallazo 1993, p.156]. Concerning the Hagiographic readings from the Lorvão, Sta. Cruz and Alcobaça collections, they were all produced in the same period. The Lorvão collection presents one Passionarium produced in circa 1140 (Lorvão 16); the Sta. Cruz collection has two volumes of the Legendarium from the early-13\textsuperscript{th} century (Sta. Cruz 20 and Sta. Cruz 21); while in Alcobaça the Legendarium produced in the 12\textsuperscript{th}-13\textsuperscript{th} century is presented throughout five volumes (Alcobaça 418-422). This disparity in the number of volumes might be related either to the disappearance of other existing volumes in Lorvão and Sta. Cruz, or to the importance that Hagiography had on Bernadine’s spirit, namely on acting on monks’ behaviour throughout the narration of miraculous and exemplary deeds. Another important set of manuscripts to be compared are the copies of De Avibus from the Lorvão (Lorvão 6, 1183/84), Sta. Cruz (Sta. Cruz 34, 1176-1225) and Alcobaça (Alcobaça 238, 12\textsuperscript{th}/14\textsuperscript{th} century) collections.

1.5.2. The production of Portuguese Romanesque illuminated manuscripts

a) Medieval recipe books for illuminations

Medieval manuscript production made use of ancient traditions for the production of materials, as the De architectura by Vitruvius (1\textsuperscript{st} century BC) or the Historia Naturallis by Plinius (also known as Pliny the Elder) (1\textsuperscript{st} century) [Eastaugh 2004, p.91; Melo et al. 2011]. Afterwards, during the 9\textsuperscript{th}-12\textsuperscript{th} centuries an important set of recipe books for the production of materials and artistic techniques integrate the scriptoria, including the Mappae Clavicula (9\textsuperscript{th}-12\textsuperscript{th} century) or De diversis artibus (12\textsuperscript{th} century) by Theophilus [Clarke 2001b, p.15; Melo et al. 2011]. Concerning the presence of such treatises in Portuguese medieval scriptoria, much must have been contributed by the relations between the Portuguese monastic centres for the production of manuscripts and its Mother Abbeys, namely those between the Augustinians monks from Sta. Cruz and Saint-Ruf d’Avignon; and between the Cistercians monks from Alcobaça and Clairvaux (see Figure 5). If for the Mappae Clavicula (9\textsuperscript{th}-12\textsuperscript{th} century) there are references for its presence in the library of Sta. Cruz (it is referred to in a list of books lent to master Egídio from the monastery of São Vicente de Fora, in Lisbon, in the year of 1218) [Nascimento et al. 1997, p.XCIII]); for De diversis artibus by Theophilus (12\textsuperscript{th} century) its likely presence in Alcobaça might
be suggested by the painting technique used on the flesh painting’s technique of *Alcobaça 446, f.96v* (*Etymologiae, 13th century* - *Figure 6* - that closely follows the instruction by Theophilus on Chap. 3-9 [Hawthorne 1963, pp.17-18] for the flesh painting of a face [Miranda 2010].

*Figure 6*. Details from *Alcobaça 446, f.96v* (*Etymologiae, 13th century*), showing the painting technique referred by Theophilus on *De diversis artibus* for painting a face. Photos ©BNP.

Other medieval treatises for the production of materials and techniques for illumination were very likely present in the Lorvão, Sta. Cruz and Alcobaça monasteries. The *De Clarea* of the so-called “Anonymous Bernensis” (11th-12th century) - a short treatise comprising 5 *folia* mainly concerning the preparation of egg yolk and glair (egg white) for writing and for book’s ornamentation [Thompson 1932; Clarke 2001b] - was possibly known by the illuminators from these monasteries, mainly due to the wide usage of glair on the paints production and to the use of specific formulations for glair, such as the addition of a small amount of yolk to glair (see *Chapter 3*). Another example is the *Libro de como si facem as cores* (ms. Parma 1959), the oldest known Judaeo–Portuguese medieval treatise on the art of illumination, written in Portuguese, but using the Hebrew alphabet [Afonso 2010; Strolovitch 2010]. It is attributed to the 15th century [Afonso 2010], although based on linguistic analysis Ivo Castro states that the first version could date from the 13th - 14th century [Castro 2010], with some of the processes described in the

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13 Nevertheless, this modelling system was universal throughout Romanesque Europe. Theophilus describes it with very detailed instructions, but illuminators could have learned this technique from each other or from other sources.
treatise reflecting even older traditions [Afonso 2010]. The treatise describes the making of synthetic pigments, lakes and clothlets, the manufacture of glue, the tempering and application of colours, and the techniques of applying gold leaf [Miguel et al. 2012]. As part of this PhD research recipes from the *Libro de como si facem as cores* for producing copper-based pigments and vermilion were reproduced as accurately as possible, and compared with the analytical results of red and green paints from the Lorvão, Sta. Cruz and Alcobaça collections. Important findings and conclusions regarding the specificity of this treatise were made, and will be presented towards *Chapter 3*.

It is possible that many other sources for the production of materials used on illuminations may have existed but are now lost, namely oral sharing of knowledge that had never been recorded. For this reason, the study of medieval recipe books must be complemented by accurate reconstructions of the recipes and the analysis of the materials and techniques used to produce contemporary manuscripts. Only thus it becomes possible to realise how realistic and specific a recipe is, and how far it might have been used for producing materials for illuminations. In this sense, the *Art and Technological Source Research Working Group* of the ICOM-CC have performed an important work in the last years, with important discussions and conclusions on this approach [Clarke et al. 2005; Kroustallis et al. 2008; Hermens et al. 209; Eyb-Green et al. 2012].

**b) Coloured paints in Portuguese Romanesque illuminations**

A medieval coloured paint essentially comprises a colourant, for example a pigment or an organic dye, and a binder. Pigments can have their origin either from ground minerals, or as synthesized compounds. Natural dyes could be used either as a lake pigment (prepared by precipitating the dye extract with inorganic salts as alum (KAl(SO$_4$)$_2$·12H$_2$O) [Kirby 2005]), or as a pure dye, as for indigo or lac dye [Melo 2009]. A binder, as a protein or a polysaccharide, is responsible for the cohesion of the pictorial layer as well as for its adhesion to the support, parchment in this case. Other additives may be used to improve the performance of the paint. For
example, fillers (or extenders) may be used to enhance the mechanical properties of the paint as well as the film opacity. For some paints, a final layer could be applied as a varnish or coloured glaze.

Portuguese Romanesque illuminations made use of the most important materials used in the European production of the 12th-13th century medieval illuminations [Melo et al. 2011]. In the last six years our research team have identified the use of the most high quality sources for white, yellow, orange, red, blue, green, black and gold colours in the Portuguese medieval palette, Figure 8. Lead white was the white pigment used par excellence as pure paint, but also for highlighting other colours (such as blue and deep organic reds) and for lightening colours. Orpiment was occasionally used as pure paint\textsuperscript{14}; and in one notable occurrence it was found mixed with indigo to produce dark green paints\textsuperscript{15}. Organic yellow sources might have been used in Portuguese Romanesque illuminations, although its use has not yet been identified\textsuperscript{16}. Red lead is present as pure paint, or applied below other colours to produce volume effects. Vermilion red is widely present in the letterings as in red paints. Its production and specificities will be presented in detail in Chapter 3. Lac dye was applied as a single reddish colour, for shading red lead and, mixed with vermilion to produce dark reds\textsuperscript{17}. Lapis lazuli was used as pure paint, although it was found mixed with azurite, lead white for lightened shades, or indigo for darkened shades. Indigo is widely present, both as a pure paint, or mixed with lapis lazuli for darkening blue shades. Malachite was occasionally found in Portuguese medieval illuminations.

\textsuperscript{14} Orpiment was only identified as pure paint in Lorvão 43 (Lorvão Apocalypse, 1189), Sta. Cruz 1 (Bible, 1151-1200), Sta. Cruz 4 (Homiliarium, 1139), Alcobaça 249 (Missal, 13\textsuperscript{th} century) and Alcobaça 410 (Liber qui dicitur Angelus, 1219) [Melo et al. 2011; Muralha et al. 2012].

\textsuperscript{15} Orpiment was found mixed with indigo on a deep green in Alcobaça 249, f.125v (Missal, 13\textsuperscript{th} century), please see Chapter 2. Moreover, it was also found mixed with red lead in Lorvão 43 in a proportion ranging between 1.2-4.2% (wt%) [Miguel et al. 2009a].

\textsuperscript{16} Fading and degradation of yellow organic dyes are extremely sensitive to ageing, restricting their identification as sources of yellow in medieval manuscripts [Clarke 2011].

\textsuperscript{17} The indication for the presence of lac dye was showed by infrared spectroscopy and microspectrofluorimetry. These results were recently confirmed by Raman microscopy by Rita Castro, and will be published soon.
illuminations\textsuperscript{18}. Black was produced by using vegetable and/or animal carbon black pigments, whereas gold was rarely used in Portuguese Romanesque illumination\textsuperscript{19}.

\textbf{Figure 8.} Colourants and colour patterns in Portuguese medieval illuminations.

The Portuguese Romanesque Illuminations presents in its colour \textit{palette} a characteristic deep glassy saturated green, \textit{Figure 8}. Because of its resemblance to the green glass bottles, it was named in Portuguese \textit{verde garrafa}, bottle-green. This copper-based paint is found ubiquitously in all manuscripts, and was consistently applied as a single colour

\textsuperscript{18} From the 38 manuscripts, malachite was only detected in two \textit{folia}: Lorvão 17, f.169v (Livro das Calendas, attributed to the 13\textsuperscript{th} century) and in the \textit{Palm tree of Lorvão 5}, f.20v (\textit{De Avibus}, 1183-1184) [Claro 2009].

\textsuperscript{19} Gold was identified in \textit{The Creation} (f.95v) of Lorvão 5 (\textit{De Avibus}, 1183-1184) applied straight over the parchment and in the \textit{Lorvão 50} (\textit{Psalms}, 1184), applied on a preparatory layer (not yet characterized) [Melo et al. 2011].
It has a glassy fractured appearance under the microscope and under cross-polarized light these bottle-greens appear as a non-crystalline structure [Miguel et al. 2009b]. Micro-Fourier transform Infrared spectroscopy (μ-FTIR), points to the presence of a copper proteinate [Miguel et al. 2009b]. Copper proteinates have also been identified in illuminations by other authors, namely in the deep green colour of a German manuscript [Scott et al. 2001a] and in a Venetian manuscript, both from the 15th century [Gilbert et al. 2003]. However, no further conclusions on its formulations were presented. Claude Coupry identified the presence of a copper-based pigment on which the analysis by Raman microscopy only allowed an inference as to its organic origin [Coupry 1999]. Within this PhD research, new and important results on the characterization and formulation of these bottle-green paints were achieved. The bottle-green colour paint will be thoroughly explored in Chapter 3. More details on the colourants used in Portuguese Romanesque illuminations can be found in Appendix II.

c) Extenders and special paint formulations
Chalk was frequently identified in Portuguese Romanesque illuminations as extender. Gypsum appears occasionally mixed with deep organic reds (most probably lac dye) in three manuscripts from the Alcobaça collection20 (see Chapter 2). Besides the use of extenders, other special paint formulations were also identified, namely in red paints. As vermilion was a very expensive pigment (see Appendix II), mixing other pigments would save on its use. In Portuguese medieval manuscripts we have found vermilion mixed with the less expensive red lead in the more extensive areas of red paint, such as the Lorvão Apocalypse (Lorvão 43, 1189) [Miguel et al. 2009]. These mixtures were made in such proportions that would not change the colour hue, but allowed the illuminator to save on the use of the most valuable pigments of the medieval palette.

d) Binding media
The analysis of the Portuguese Romanesque illuminations showed the consistent use of a proteinaceous binding media on its production [Melo et al. 2011]. Proteinaceous binding media such as animal glues (for example, parchment and casein glues), egg yolk and/or egg white (also known as glair) were the most common used proteinaceous binders for

20 Gypsum was identified in deep organic reds from Alcobaça 249 (Missal, 13th century), Alcobaça 358 (Sermones de Tempore, 12th century) and Alcobaça 419 (Legendarium, 12th-13th century), please see Chapter 2.
medieval illuminators paint [Muñoz-Viñas 1999], Figure 9 (see Appendix II). The recipes and detailed procedures for its reproduction are described in Appendix III.

*Figure 9.* The most common proteinaceous binders used in medieval illumination. *Left,* casein glue; *centre,* egg (egg yolk and/or egg white); *right,* collagen-based glue.

Combinations of these proteinaceous binders and/or specific formulations may also be considered. The *De Clarea* of the so-called “Anonymous Bernensis” (Berne A.91.17, 11th-12th century) refers the use of glair “to temper vermilion, minium, saffron, and dragonsblood, and azure (…)” [Thompson 1932, p.19]. Moreover, the “Anonymous Bernensis” refers the addition of a small amount of yolk to glair to get a good paint lustre in such amount that “according to your wish, so that it will shine, or not shine; or, wherever it is not shiny enough, or wherever it is too much so” (Thompson 1956, p.60). Such formulation were found and characterized in this thesis (see Chapter 3). Other additives could be used to improve glair plasticity. Earwax is referred in some medieval treatises as in the aforementioned *De Clarea*, the *Ashmole Manuscript 750* (15th century) or the *Ashburnhamiana Manuscript 349* (15th century), which recommend adding a small amount of earwax to egg white to keep the air bubbles from forming during beating and improving the paint plasticity, thus transforming the egg white into a useful binder [Thompson 1956, p.60-61; Clarke 2001b, pp.70, 95]. According to Thompson, “this curious bit of knowledge spread all over Europe, and affected the practice of illuminators everywhere” [Thompson 1956, p.61]. Nevertheless, our studies were not conclusive on the use of earwax in binding media formulation. Other additives, as sugar or honey, could also be mixed with glair to prevent it from completely drying out and becoming brittle, and more importantly, to improve its viscosity and its flexibility, preventing its cracking [Thompson 1956, p.61]. However, the analyses of Portuguese Romanesque illuminations do not indicate its use.

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21 Interesting to note that this recommendation was expressed to temper vermilion based paints and to prepare gold grounds.
Binding media, the "invisibles" components of a paint colour, have an important role both on the paint’s stability as on its influence on the final colour perception [De la Roja et al. 2007]. Also, binding media play a key role in the colour changes over time as well as on the conservation condition of the paint. The characterization of proteinaceous binders in artworks has become an important subject for the conservation scientist. Raman microscopy, μ-FTIR, Near-infrared fiber-optic reflectance spectroscopy (FORS), Gas Chromatography-Mass Spectrometry (GC-MS), Matrix Assisted Laser Desorption/Ionization (MALDI), Immunofluorescence microscopy (IFM) and Enzyme-linked immunosorbent assay (ELISA) antibody-antigen assays are techniques that have been successfully used to characterize binders in artworks [Nevin et al. 2007; Bacci et al. 2001; Colombini et al. 2010; Kirby et al. 2011; Heginbotham et al. 2004; Vagini et al. 2008; Mazurek et al. 2008 and Cartechini et al. 2010]. Nevertheless, all these studies concerned the analysis of paintings and the identification of proteinaceous binders (but not its quantification in the paint’s formulation). The use of chemometrics methodologies for a deeper analysis of proteinaceous binders in artworks has been tested by some authors (such as Jurado-López et al. 2004; Miliani et al. 2007; Romero-Pastor et al. 2011); however none of these works concerned the study of proteinaceous binders in medieval illuminations, or the characterization of binder formulations. Within the present work it was possible to assess, for the first time, the characterization of the binding media used to produce medieval illuminations. Our approach focused on combining infrared spectroscopy data and chemometrics methodologies. Moreover, an ELISA antibody-antigen methodology was optimized and applied on a set of historical micro-samples from Portuguese Romanesque illuminations, allowing for new and unique results (see Chapter 3).

e) Drawing techniques and colour construction

Drawing and colour are undoubtedly the two main influences on the readability of an illumination. From the three sets of manuscripts, Alcobaça presents the collection in which the drawing assumes the major role on the image composition [Miranda 1984]. The characteristic elaborate drawing style from Alcobaça is fairly based on the palmette and the rinceaux²², providing an impressive idea of dynamics and movement [Miranda 1984],

²² The palmette resembles the fan-shaped leaves of a palm tree, and its use as drawing ornamentation dates back to the Ancient Egypt. It was also widely used on Greek and Roman art decoration; the rinceaux is a form of ornament consisting on a patterning of fine intertwined foliate branches, conferring an image of movement and maze to the illumination [Brown 1994].
whereas for the other *scriptoria* this drawing technique becomes less exuberant. For such characteristic much have influenced the relation with Clairvaux, the *Mother Abbey* of Alcobaca. During the regency of the Cistercian Order by the English Abbot Etienne Harding\(^{23}\), the characteristic dynamic and movement of the early medieval Celtic manuscripts influenced the drawing decorations in Clairvaux [Miranda 1984, p.152]. However, by the time of Abbot Etienne Harding’s death in 1134, the Cistercian *scriptorium* of Clairvaux starts to follow a monochromatic austerity, restricting the decoration to the major initials. In this context, the Alcobaca *scriptorium* starts to follow Clairvaux in its austerity [Miranda 1984, p.152]. Decoration became restricted to the major initials, as this same dynamic and movement became the main characteristic of Alcobaca’s illuminations [Miranda 1984, p.152]. This subject will be discussed in *Chapter 2*.

Our studies on the Lorvão, Sta. Cruz and Alcobaca collections demonstrated that colour construction was mainly achieved by making use of pure colours that could be applied as layers to create visual effects – the *matiz*, *Figure 10*.

*Figure 10*. Details of Painting techniques on manuscripts from São Mamede do Lorvão, Santa Cruz de Coimbra and Santa Maria de Alcobaca monasteries. *From left to right, Lorvão 15, f.11; Lorvão 15, f.50; Lorvão 5, f.16; Lorvão 50, f.1v and Lorvão 15, f.26; Sta. Cruz 20, f.173v; Sta. Cruz 1, f.37; Sta. Cruz 34, f.94v; Sta. Cruz 20, f.191 and Sta. Cruz 21, f.19; Alcobaca 421, f.181; Alcobaca 347, f.3; Alcobaca 249, f.125v; Alcobaca 446, f.96v and Alcobaca 410, f.131.*

In the Lorvão collection two distinct kinds of construction of colour were discerned. For the manuscripts produced before the Cistercian period (before 1206), with the exception of

\(^{23}\)Third Abbot of the Cistercian Order. Of English origin, he lived between 1108-1133 [Miranda 1984, p.152].
De Avibus (Lorvão 5, 1183/1184), the construction of colour was based on the use of pure
colour paints and colour contrasts. On the other hand, for the manuscripts produced during
the Cistercian period, we have found that colour construction is mainly based on the matiz
of lac dye (that could be applied over red lead or vermilion to create darken reddish and
orange shades) and indigo (over lapis lazuli, for bluish darken shades), complemented with
lead white’s highlights [Melo et al. 2011]. In Alcobaça the matiz and volumetry achieve its
highest splendour, in letters full of volume and exuberance. Alcobaça reflects the
Byzantine influence, also present in manuscripts from the same period produced in Italy,
Catalunya, Bourgogne and Champagne [Melo et al. 2011]; and the matiz technique
generalized in the Clairvaux scriptorium based on developing volume and a diversity of
shades in one letter, mostly at an ornamental level. Again for this, should have contributed
the relations between Alcobaça and Clairvaux (see Section 1.4.2) [Melo et al. 2011]. If the
Rule of St. Benedict (followed by the Cistercians monks from Alcobaça) was based on
austerity and sobriety, the fact is that the Alcobaça monks applied monochromatism very
seldom, and used the matiz technique in letters full of dynamic and movement [Melo et al.
2011], Figures 10. Concerning the Sta. Cruz collection, we have found that the
illumination readability becomes more dependent on the delicacy of the drawing lines and
on the colour contrasts mainly between pure blue-red-green colours (mainly based on lapis
lazuli, vermilion/deep organic red and bottle-green based paints) [Melo et al. 2011],
Figures 10. This subject will be discussed in Chapter 3.

1.5.3. The use of Colour in the context of Portuguese Romanesque illuminations

Colour plays a crucial role in the interpretation of an artwork. In medieval
illuminations, the use or non-use of colour might reflect a special meaning that must be
considered. Also, the choice of a specific colour for composing the illumination was
not a frivolous choice, not just because the costs of using some of the pigments should
justify their use, but also because there could be specific meanings for colours that should
be taken in account. Good illustrative examples are the illuminations present in the *Lorvão Apocalypse* (*Lorvão* 43, 1189), *Figure 11*. To produce its 88 images, the illuminator made use of contrasting and bright colours for the backgrounds and transparent bodies, which appear to exalt the spirituality present in the text [Miranda et al. 2008]. Moreover, the use of a palette restricted to yellow, orange and red – the *colours of Light* – (the illuminator rarely uses black and brown) shows the importance of colour in the interpretation of the text [Miranda et al. 2008]. Somehow, the illuminator expresses through these three colours the message of *Revelation* present in this Commentary on the *Book of Apocalypse*, and simultaneously through the unpainted bodies (transparent bodies) he evidences the importance of spirituality over the worldly matters [Miranda et al. 2008].

The study of the extent of use of a certain colour in a manuscript was first performed by the research team under the leadership of Maria João Melo and Adelaide Miranda. The study concerned the analysis of the extent of use of each colour in the *De Avibus* of the Lorvão, Sta. Cruz, Alcobaça and Clairvaux *scriptoria*. For the first time, a systematic approach was followed for studying the extent of use of colour in medieval manuscripts. It was possible to achieve interesting results using this approach, as it was possible to verify that the distribution of colours in the copy of Alcobaça is identical to the one of Clairvaux, corroborating the similarity of its iconographic programme [Melo et al. 2011].

To infer the relation between the extent of use of a certain colour in an illumination and its possible meaning in the context of the manuscript, it becomes essential to consider the history and Cultural traditions behind each colour. Red, green and blue colours were consistently used in Portuguese Romanesque illuminations, and the analysis of the extent of use on the *Hagiographic readings* of the Lorvão, Alcobaça and Sta. Cruz collections showed that these were the three most used colours in this set of manuscripts. These results will be presented and the possible meaning for the use of these three colours discussed in *Chapter 3*.

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24 Tables, schemes and marginal elements are included in this count.
- **A brief overview on the history and cultural traditions behind red, green and blue colours**

- **Red**

“So God created Man in His own image” (Genesis 1, 27). The symbolism of red dates back to the Beginning of Time. According to the Hebrew tradition, the first man, Adam, was fashioned from red clay, and *adama* signifies in Hebrew *land* or *man* or *red*. In Latin, *adamus* translates into “man of red earth” [Varichon 2006]. Red symbolizes strength, life, and passion. In classical Arabic, the red colour was commonly ascribed to ardour, intensity and violence [Varichon 2006]. For producing red hues, the pre-historic man commonly used red ochres (pigments), that naturally occur disseminated through rock or earth [Eastaugh *et al.* 2004]. Due to its abundance in Nature, it was and is the cheapest among all red pigments. Therefore, red ochre pigments were the most frequent source for red pigments used by painters throughout the ages, although not commonly used on manuscripts’ production. However, it was only with cinnabar (red (II) mercury sulphide) that magnificent bright red hues were achieved. Cinnabar might be considered the “Red King” [Ball 2001]. Plinius (Roman, 1st century) refers its high price and frequent adulteration with red lead (a cheaper pigment). Until at least the 11th century “it remained as costly to cover the page with vermilion as with gold” [Ball 2001], therefore its use was mostly restricted to the *scriptorium* and the extent of usage a reflection of the financial resources of the monastery. It is thus expected that cinnabar/vermilion use was more related to its bright red hue, than to special meanings behind its use.

- **Green**

The meaning of Green becomes more committed with the socio-cultural context of its use. In fact, it is common to ascribe the meaning of green to instability, to something that changes without prediction. For Michel Pastoureau, green represents everything that changes and that is ephemeral. In the feudal world, it was on a green meadow where the Lords used to face in the legal duels. For this reason, green becomes the colour of hazard, of game, of destiny, of luck, of money and of chance [Pastoureau 2004, Pastoureau *et al.* 2007]. On the other hand, for the Arabic-Islamic civilization, green acquires an overwhelmingly positive connotation, as it is the colour that characterizes the Muslim

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25 The principal colouring matter in red ochres is the naturally occurring iron (III) oxide, Fe₂O₃, known as hematite [Eastaugh *et al.* 2004, p.200].

26 *Cinnabar* is the mineral form of red mercury (II) sulphide. When obtained by synthesis, red mercury (II) sulphide gets the name *vermilion* [Eastaugh *et al.* 2004, p.386].
religion. According to Islamic tradition, when the archangel Gabriel appeared to Mohamed, the Prophet was dressed in green, and the archangel’s wings were green as well [Varichon 2006]. Also, the Prophet’s successors wear green turbans and in paradise Allah welcomes the souls of martyrs who fly to him in the form of green birds [Varichon 2006]. Moreover, for the inhabitants of the Arabian Desert, God made plants green and the sky blue to make things easier visually for His creatures, because these two colours were both so beneficial to visualize [Varichon 2006]. Therefore, for the Portuguese Romanesque context it becomes fundamental to take account of the strong influence of Islamic culture on the 12th-13th century when attempting to infer on the meaning of the green colour on a certain manuscript, please see Section 1.4.1.

- Blue

The blue colour had a significant change in its symbolism throughout history. The Romans ascribed blue to the enemy: Celtic and Germanic barbarians used to colour their skin with woad before going to battle. This bluish-grey tint gave to these northern barbarian warriors a ghostly appearance, which terrified the soldiers of the Roman Empire [Pastoureau 2002, Varichon 2006]. During the 12th century, the increased popularity of the Virgin Mary and the fact of the Virgin’s mantle begin to be painted in blue, strongly contributed to that an inversion on blue’s paradigm. The reason for this change has had various justifications by the authors who write about colour, its history and symbolism. Blue is the colour of sky, and therefore it has alongside been ascribed with heaven. For some authors, blue became the colour of mourning in medieval times; as by wearing blue, one testifies his assurance that the deceased has gone to heaven. For this reason, the Virgin’s mantle began to be painted in blue: as a sign of Her close-relation with Heaven and with the Divine [Ball 2001, Pastoureau 2002, Varichon 2006]. Others suggest a simpler explanation: as Virgin Mary was the most precious symbol of Church’s faith, it was logical that it would be used the most expensive materials on Her representation. In earlier Byzantine art, the artist represented the Virgin Mary with a purple mantle (at the time the most expensive dye, reserved for the most important people). In 12th-13th century Europe, ultramarine blue was the most expensive of all pigments, not only because it was brought overseas from Afghanistan, but also due to its costly purifying procedures. Therefore, ultramarine blue began to be used to paint the Virgin Mary’s mantle [Finlay 2004]. As people began to associate blue with the Virgin Mary, it began to be spread all over the Church as a symbol of Heaven and the Divine. Aiming to embrace to herself this Divine role in society, the
nobility promptly adhered to blue. From this period on, the blue colour evoked royalty and nobility, fidelity and peace [Varichon 2006]. For Arab-Islamic culture, blue represents Nature, cold and the sky; but was also seen as the colour of the sinful ones. The Koran characterizes the guilty excluded from paradise at the Last Judgement as “blue” [Varichon 2006]. Moreover, during the medieval period, blue was the obligatory colour worn by Jews and Christians living in Islamic territory [Stillman 2006]. The use of lapis lazuli as blue source on medieval illuminations and, above all, the extent of its use, was an unquestionable financial investment for the *scriptorium*. To afford the use of lapis lazuli, it was common to restrict its use to the most important and emblematic manuscripts, as this was the most expensive pigment of the medieval palette.
I wish therefore that before everything else a man should know himself, because not only usefulness but right order demand this. Right order, since what we are is our first concern; and usefulness, because this knowledge gives humility rather than self-importance, it provides a basis on which to build. For unless there is a durable foundation of humility, the spiritual edifice has no hope of standing.

Saint Bernard of Clairvaux, Sermon 36 on The Song of Songs, Chp5

2. Alcobaça and its collection

This chapter aims to present the main findings on the study of the materials and painting techniques used for the production of a set of 15 manuscripts from the Alcobaça collection from the 12th-13th century. For details of the manuscripts examined see Appendix I. The analysis of the manuscripts took place in a mission to the Biblioteca Nacional de Portugal in May 2009. Within these results will be examined the existence of a privileged relationship with Clairvaux, how this relationship influenced the use of the materials and painting techniques in Alcobaça scriptorium, and how different it was from the remaining Portuguese scriptoria, particularly from the Lorvão scriptorium (the only other Portuguese collection that has the characterization of the materials and techniques used for the production of illuminated manuscripts, already published as part of the doctoral thesis of Ana Claro [Claro 2009]).

2.1. The manuscripts from Alcobaça

Of the 15 manuscripts selected for this study (see Appendix I), only 4 present a colophon referring to their authorship (Alcobaça 360 by Frater Martinus of the Cistercian Order; Alcobaça 410 by Frater Egidius de Leirena; Alcobaça 412 and Alcobaça 427 by Johannes Pecatoris), two refer the date of its production (Alcobaça 410 in March 1219 and Alcobaça 412 in 1257); and eleven refer to having been produced in Sancte Marie de Alcubacia (Alcobaça 249, 347, 358, 402, 410, 412, 419, 421, 426, 427, and 433) [Miranda 1984; Cepeda et al. 2001].
All the manuscripts are written in Latin with Carolingian calligraphy. With exception of *Alcobaça 249* (Figure 12, left) that was written in flowing text, the remaining 14 manuscripts are written in two columns (Figure 12, right).

![Figure 12. Left, Alcobaça 249, f. 124v, (Missal, 13th century); right, Alcobaça 360, f.2 (Homiliae in Leviticum, 13th century). Photos © BNP.](image)

The number of lines ranges between 25 and 60. With the exception of seven manuscripts (*Alcobaça 347, 405, 419, 421, 426, 433 and 446*) which present a constant number of lines; all the rest vary the number of lines throughout the manuscript. *Alcobaça 419* and *Alcobaça 421* are part of the five-volume *Legendarium* (*Alcobaça 418-422, 12th-13th century*); *Alcobaça 433* is part of the three-volume *Lectionarius cisterciense* (*Alcobaça 432-434, 1170-80/1201-1250*) according to the Divine Office of the Cistercian Rule.

### 2.2. The illuminations from Alcobaça

- **Drawing and painting techniques**

The study of the drawing and painting techniques results in a useful tool for characterizing the artistic and technological knowledge of a *scriptorium*. Moreover, it allows for establishing possible relations and influences between *scriptoria*.

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27 According to Adelaide Miranda, *Alcobaça 433* was produced in 1170-80 [Miranda 1984, p.77]; for the *BNP catalogue*, its production is placed in 1201-1250 [Cepeda *et al.* 2001].
The decoration in the manuscripts from Alcobaça is strongly restricted to the major initials, at the same time that the *dynamic* and *movement* becomes its major characteristic. Its elaborate drawing style is based on the *palmette* and the *rineaux*[^28], *Figure 13*. Concerning the drawing technique itself, a careful observation under magnification of the illuminations from Alcobaça does not indicate the use of a stylus and/or a compass. Nevertheless, the similarities of several letterings, with slight changes on the decoration, might suggest the use of a template by the illuminator as in *Alcobaça 421, f.25v*, *Figure 14*.

A comparative study of initials from the *Passionarium* from Lorvão and the *Legendaria* from Sta. Cruz and Alcobaça *scriptoria* highlighted interesting features concerning ornamentation. In the *Passionarium* from Lorvão are commonly found the zoomorphic initials, partly composed of animal forms, *Figure 15, left*. For the Sta. Cruz’s

[^28]: The *palmette* resembles the fan-shaped leaves of a palm tree, and its use as drawing ornamentation dates back to the Ancient Egypt. It was also widely used on Greek and Roman art decoration; the *rineaux* is a form of ornament consisting on a patterning of fine intertwined foliate branches, conferring an image of movement and maze to the illumination [Brown 1994].
Legendarium, both zoomorphic and anthropomorphic ornaments are present, together with the palmette and the rinceaux ornamentation, Figure 15, centre. Regarding Alcobaça ornamentation, its most emblematic characteristic is, undoubtedly, the extensive use of the palmette and the rinceaux, Figure 15, right, that becomes much more elaborated than the one found in Santa Cruz’s Legendarium. Also, the presence of different drawing techniques in a period close to the establishment of the monastery might indicate that the first illuminators from Alcobaça were already using a consummate art, since there is no evidence for a drawing evolution during this period [Miranda 1984].

Concerning the four copies of De Avibus, it was verified that for both Lorvão and Sta. Cruz representations, the hawk is represented inside a circular frame painted in blue (lapis lazuli), a colour that symbolizes the noble and celestial world and also has an heraldic meaning [Miranda et al. 2010]. Concerning Alcobaça and Clairvaux, the hawk is represented inside a square frame and painted in a deep saturated green (bottle-green colour); here the drawing dominates the representation, while for Lorvão and Sta. Cruz, the painting dominates the composition Figure 16. In Chapter 3, the meaning of green and blue usage in Portuguese Romanesque illuminations will be discussed.

29 In the context of the De Avibus, the hawk represents the knight; and the dove represents the monk [Miranda et al. 2010].
Moreover it was possible to find clear similarities between the manuscripts of Lorvão and Sta. Cruz, and between the ones from Alcobaça and Clairvaux, its Mother Abbey. This reflects, on the one hand, the fact that manuscripts were circulating between the Lorvão and Sta. Cruz monasteries probably due to their vicinity; but that, on the other hand, the Cistercian monastery of Alcobaça was not part of this Portuguese network and was connected to Clairvaux [Miranda et al. 2010].

2.3. Colour in the Alcobaça collection: materials and paint formulations
The analysis of the set of 15 manuscripts from the Alcobaça collection hereby presented took place on a Mission to the Portuguese National Library (Biblioteca Nacional de Portugal, BNP) in May 2009, Figure 17.

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*Figure 16. From left to right, the Hawk as depicted in De Avibus in top) Lorvão (Lorvão 5, f.16 and Santa Cruz de Coimbra (Sta. Cruz 34, f.92); bottom) Alcobaça (Alcobaça 238, f.206v) and Clairvaux (MS 177, f.139) monasteries. Photos © ANTT, ©BPMP, © BNP and ©BMT 30.

30 Bibliothèque Municipale de Troyes.*
The analysis of the materials used to produce the illumination paints of the Alcobaça manuscripts will be presented in this Section as well as in Appendix VI-VII. A consistent use of rose and grey colour paints was found, mostly achieved by mixing vermilion or indigo with lead white, such as in Alcobaça 410 and in Alcobaça 249, respectively, Figure 18a. Rose is also found in the matiz of lac dye, by mixing this dye with lead white, as in Alcobaça 427 (Figure 18b). Some dark blue shades were accomplished by mixing carbon black with indigo. Lapis lazuli was the chosen pigment for the blue colour, being ubiquitous in this collection; indigo was used for darkening blue shades (in Alcobaça 249 and Alcobaça 427) and lead white for lightening its hue (such as in Alcobaça 360) - Figure 18c; and azurite was only found in the lettering of one of the latest manuscripts (Alcobaça 433) - Figure 18d. The remaining colour palette comprises vermilion, orpiment (occasionally present in three manuscripts, Alcobaça 249, Alcobaça 410 and Alcobaça 446), red lead, bottle-green – Figure 18e - and two organic dyes (with a yellowish and dark red hue), not yet characterised – Figure 18b. Additionally, a certain brownish hue is also still uncharacterized - Figure 18f. Whites were obtained with lead white; and blacks with carbon blacks of animal and vegetable origins, as with carbon mixed black paints (a mixture of carbon black with iron-gall ink). Calcite was consistently used as extender, with exception to the deep red organic paints in Alcobaça 238, Alcobaça 249 and Alcobaça 419 that present gypsum mixed with a small amount of calcite as extender.

31 As aforementioned in Chapter 1, the indication for the presence of lac dye was showed by infrared spectroscopy and microspectrofluorimetry. These results were recently confirmed by Raman microscopy by Rita Castro, and will be published soon.
The consistent detection of calcium (Ca), iron (Fe) and potassium (K) from the parchment on the µ-EDXRF analysis of the colour paints may induce the thin layer thickness of these paints from the Alcobaça collection.

Figure 18. The colour on the Alcobaça collection. Details from some of the illuminations: a) Alcobaça 427, f.115v (magnification 10x); b) Alcobaça 421, f.181 (magnification 10x); c) Alcobaça 360, f.2 (magnification 20x); d) Alcobaça 433, f.14 (magnification 10x); e) Alcobaça 238, f.225 (magnification 7x); and f) Alcobaça 421, f.193 (magnification 10x).

- analysed folia

From the 15 manuscripts from the Alcobaça collection, a total of 72 folia were analysed in situ by µ-EDXRF and Raman microscopy, Table 1. Magnified observation was also performed in situ, and a set of 76 micro-samples was collected for further analysis, as µ-FTIR spectroscopy. See Appendix IV for the experimental conditions followed for each technique. Appendix V-A shows the images of the illumination and the areas analysed by µ-EDXRF, Raman microscopy and µ-FTIR spectroscopy.

32 Ana Claro, in her PhD dissertation, presented a systematic study on the paint thickness over the µ-EDXRF signal, and concluded that the X-Ray penetrates circa 100 µm in deep on the paint layer [Claro 2009].

33 Besides the areas of analysis indicated in Appendix V-A, µ-EDXRF was also performed in the same areas where micro-sampling took place.
Table 1. Manuscripts analysed from the Alcobaça collection and its date of production; and the folia analysed by µ-EDXRF, µ-FTIR and Raman microscopy.

<table>
<thead>
<tr>
<th>Manuscript</th>
<th>folia analysed</th>
<th>Total folia</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Alcobaça</em> 238 12th-13th century</td>
<td>203, 203v, 206v, 210, 214, 220v, 224v, 225, 226v</td>
<td>9</td>
</tr>
<tr>
<td><em>Alcobaça</em> 249 13th century</td>
<td>91v, 92, 109v, 124v, 125, 125v</td>
<td>6</td>
</tr>
<tr>
<td><em>Alcobaça</em> 347 12th-13th century</td>
<td>3, 57v</td>
<td>2</td>
</tr>
<tr>
<td><em>Alcobaça</em> 358 12th century</td>
<td>1, 36, 115v</td>
<td>3</td>
</tr>
<tr>
<td><em>Alcobaça</em> 360 13th century</td>
<td>1, 2, 3v, 4v, 10v, 11v</td>
<td>6</td>
</tr>
<tr>
<td><em>Alcobaça</em> 402 12th-13th century</td>
<td>85v, 127v, 201v, 227</td>
<td>4</td>
</tr>
<tr>
<td><em>Alcobaça</em> 405 12th-13th century</td>
<td>3v, 4v, 5</td>
<td>3</td>
</tr>
<tr>
<td><em>Alcobaça</em> 410 March 1219</td>
<td>61, 61v, 111v, 131</td>
<td>4</td>
</tr>
<tr>
<td><em>Alcobaça</em> 412 1257</td>
<td>10, 10v, 11v, 12</td>
<td>4</td>
</tr>
<tr>
<td><em>Alcobaça</em> 419 12th-13th century</td>
<td>1v, 70, 91v, 98, 98v</td>
<td>5</td>
</tr>
<tr>
<td><em>Alcobaça</em> 421 12th-13th century</td>
<td>159v, 181, 193v, 194, 198v, 202, 207v</td>
<td>7</td>
</tr>
<tr>
<td><em>Alcobaça</em> 426 12th-13th century</td>
<td>160v, 161, 251, 251v, 252</td>
<td>5</td>
</tr>
<tr>
<td><em>Alcobaça</em> 427 12th-13th century</td>
<td>115v</td>
<td>1</td>
</tr>
<tr>
<td><em>Alcobaça</em> 433 12th-13th century</td>
<td>4v, 14, 15, 16, 16v, 17, 196</td>
<td>7</td>
</tr>
<tr>
<td><em>Alcobaça</em> 446 13th century</td>
<td>12v, 32v, 33, 33v, 96v, 97</td>
<td>6</td>
</tr>
</tbody>
</table>

2.3.1. Binders and varnishes

Infrared spectroscopy demonstrated the use of a proteinaceous binder on Alcobaça illuminations. The fingerprint for the protein is clearly observed in the infrared spectra by its characteristic polyamide absorption pattern, namely the amide I (stretching band $\nu$(CO) at 1653 cm$^{-1}$), amide II ($\nu$(CN) stretching and $\delta$(NH) bending, 1550 cm$^{-1}$), the $\delta$(CN) bending at 1450 cm$^{-1}$, the $\nu$(OH) and $\nu$(NH) stretching at 3400-3000 cm$^{-1}$ [Stuart et al. 1997; Chalmers et al. 2002], Figure 19a. Additionally, are also observed the characteristic absorptions for the asymmetric methyl stretching, $\nu_{\text{asym}}$(CH$_3$), at 2963 cm$^{-1}$ and for the asymmetric methylene stretching, $\nu_{\text{asym}}$(CH$_2$), at 2935 cm$^{-1}$, and the absorption band at 2875 cm$^{-1}$, assigned to the absorption of the symmetric methyl stretching, $\nu_{\text{sym}}$(CH$_3$).
In Appendix VI are displayed the representative infrared spectra of other paints from the Alcobaça collection where these same features were identified.

*Figure 19*. Infrared spectrum of a red paint from *Alcobaça* 405, f.4v: **a**) concerning the entire wavenumber region (4000-650 cm\(^{-1}\)); **b**) restricting the spectrum to the C-H absorption region (3000-2840 cm\(^{-1}\)). The inset, detail from the area where micro-sampling was performed (magnification 40x).

The same pattern was found in what seems to be a contemporary varnish or glaze present in *Alcobaça* 427, f.115v that closely matches the infrared spectra of egg white, *Figure 20*.

*Figure 20*. Infrared spectra of black) varnish present in *Alcobaça* 427, f.115v; grey) egg white. The inset, detail from the area where micro-sampling was performed (magnification 40x).

The analysis of binding media formulations used to produce red Portuguese medieval illuminations (and, thus, present in Alcobaça illuminations\(^{34}\)) was performed based on the analysis of infrared spectra following a chemometric approach (see Chapter 3 and

\(^{34}\) For this study it was selected a set of infrared spectra from red and blue paints from *Alcobaça* 238, 358, 405, 419, 421, 426 and 433.
Appendix X). Concerning the Alcobaça collections, chemometrics pointed to a consistent use of parchment glue, frequently in the presence of egg white (that can be present as part of the paint formulation or as a varnish), see Chapter 3. ELISA antibody-antigen assay was used on a red microsample from Alcobaça 238, f.206v (De Avibus, 12th/14th century), detecting the presence of egg white. The characterization of the binding media formulation of red paints from the Alcobaça collection will be presented and discussed in Chapter 3.

2.3.2. Extenders

Calcium carbonate (CaCO₃) was consistently used as an extender and was identified, using μ-FTIR, by its characteristic strong absorption band at 1432 cm⁻¹ due to the ν(CO₃²⁻) stretching, together with the sharp peaks of the carbonate group bending δ(CO₃²⁻) at 878 cm⁻¹ and 712 cm⁻¹ [Sagîn et al. 2012], Figure 21. Appendix VI shows representative infrared spectra of other paints from the Alcobaça collection where these same features were identified.

![Figure 21. The use of calcite as extender. Infrared spectrum from a red paint from Alcobaça 419, f.1v. The inset, detail from the area where micro-sampling was performed (magnification 40x).](image)

Gypsum, a dehydrated calcium sulphate (CaSO₄·2H₂O), used as an extender in the deep organic red present in Alcobaça 238, Alcobaça 249 and Alcobaça 419, was also identified by infrared spectroscopy. Its presence was demonstrated by the characteristic stretching bands ν(OH) at 3540 and 3402 cm⁻¹ from the water groups and its respective bending vibrations δ(OH) at 1687 and 1624 cm⁻¹, the sulphate anions stretching broad band ν(SO₄²⁻) at 1137 cm⁻¹ and low intense peak at 1119 cm⁻¹, and its bending band δ(SO₄²⁻) at
672 cm\(^{-1}\) [Mandal et al. 2002], Figure 22a (for other representative infrared spectra of deep organic reds see Figures AP VI.3, AP VI.6 and AP VI.29 in Appendix VI). Raman microscopy identified gypsum in a white paint from Alcobaça 249, f.91v through its most characteristic band at circa 1007 cm\(^{-1}\) (as the band at circa 414 cm\(^{-1}\) has very low intensity, the signal to noise signal does not make it visible in the Raman spectrum) [Muralha et al. 2012], Figure 22b.

**Figure 22.** The use of gypsum as extender. **a**) Infrared spectrum from a deep red colour (*lac colour*) from Alcobaça 249, f.109v (*the inset*, skeletal structure of gypsum showing anion water - adapted from [Mandal et al. 2002], and detail from the area where micro-sampling was performed – magnification 40x); **b**) Raman spectrum of a white paint from Alcobaça 249, f.91v - *black*; and representative Raman spectrum of calcium sulphate (*Sigma-Aldrich, Germany*) - *grey*\(^{35}\).

\(^{35}\) Each spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
2.3.3. Coloured paints

- white

White colour was obtained with lead white (2PbCO₃. Pb(OH)₂), identified by μ-FTIR by the characteristic intense broad band of the ν(CO₃²⁻) stretching at *circa* 1415 cm⁻¹, and the sharp peak of the δ(CO₃²⁻) bending at 682 cm⁻¹ that indicates the presence of basic lead carbonate, and the expected broad absorption due to the ν(OH) stretching at *circa* 3541 cm⁻¹, Figure 23, left (see other representative infrared spectra of lead white-based paints in Appendix VI). Raman microscopy identified lead white through its most characteristic medium-strong band at 1049 cm⁻¹ related to the ν₁ stretching mode of the CO₃²⁻ anion [Gettens et al. 1993a]. Despite being commonly referred to as the presence of a doublet (at 1049 cm⁻¹ and 1053 cm⁻¹), the fact is that typically lead white illumination paints only presents a single low intense band at 1049 cm⁻¹, probably due to a lower spectral resolution, Figure 23, right. μ-EDXRF detected the presence of lead.

*Figure 23. The use of lead white in white paints. Left, infrared spectrum from a white paint from Alcobaça 347, f.3 (the inset, detail from the area where micro-sampling was performed – magnification 40x); right, Raman spectrum from the same white paint (black), and representative Raman spectrum of lead white (Maimeri, Italy) - grey*.³⁶

- yellow: inorganic and organic yellow paints

With the exceptions of Alcobaça 249, f.91v and Alcobaça 410, f.131 where yellow colour was made with orpiment (As₂S₃), the remaining yellow paints have most probably an organic source. Orpiment was identified by Raman microscopy based on its characteristic bands at 154, 201 and 292 cm⁻¹ ascribed to the δ(S-As-S) angle bending and to the bands at 309 and 353 cm⁻¹ attributed to the ν(As-S) stretching [Forneris 1969], Figure 24, right.

³⁶ Each spectrum collected using 632.8nm excitation, a 100x objective and 1.7 mW laser power at the surface sample (accumulation time: 10 s, for five cycles).
Figure 2. The use of orpiment in yellow paints. Left, µ-EDXRF spectrum from a yellow paint from Alcobaça 249, f.91v; right, µ-Raman spectrum from the same yellow paint (the inset, molecular structure of $\text{As}_2\text{S}_3$) - black; and representative Raman spectrum of orpiment (Kremer Pigmente, Germany) - grey.

µ-EDXRF identified the presence of arsenic and sulphur, Figure 24, left. On the infrared spectrum there are no bands ascribed to the absorption of an extender (as calcite, gypsum or lead white), indicating its use as a pure paint (see a representative infrared spectrum in Figure AP VI.6 of Appendix VI).

Concerning the remaining yellow paints, Raman microscopy shows only a high fluorescence background signal, ascribed to an organic dye or pigment. µ-FTIR analysis of yellow organic paints in Alcobaça 421, f.202 and Alcobaça 427, f.115 shows an infrared spectrum with the characteristic polyamide absorption pattern as the $\nu$(OH) and $\nu$(NH) (see Section 2.3.1). It was also possible to identify the presence of calcite (CaCO$_3$) from its characteristics absorption bands at 1432 cm$^{-1}$ and 878 cm$^{-1}$ (the absence of the $\delta$(CO$_3^{2-}$) absorption bending at 712 cm$^{-1}$ – less intense than the 878 cm$^{-1}$ absorption bending – might be due to the low concentration of calcium carbonate on the organic yellow paint [Sagın et al. 2012], Figure 25, left. µ-EDXRF detected the presence of calcium, iron, potassium, sulphur and phosphorous (with an intensity – counts – close to that detected on the parchment), Figure 25, right.

37 Each spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
Orange paints were produced with red lead (Pb₃O₄), a lead(II) lead(IV) tetroxide also known as minium, that was identified by its characteristic Raman spectrum: two intense bands at 548 cm⁻¹ and 122 cm⁻¹ ascribed to the ν(PbO) stretching vibrations, two low-intense bands at 390 cm⁻¹ and 149 cm⁻¹ ascribed to the PbO₂ vibrational modes, and a low-intense band at 223 cm⁻¹ due to δ(PbO₂) bending angle [Edwards et al. 2009; Rada et al. 2011; Rao et al. 1975; Shaltout et al. 2005], Figure 26, left. μ-EDXRF consistently detected the presence of lead, together with calcium, iron, potassium, sulphur and phosphorous (all with an intensity – counts – close to that detected on the parchment), suggesting the absence of an extender in these orange paints. On a certain deep orange paint in Alcobaça 412, f.10v, μ-EDXRF identified the presence of lead and mercury, together with calcium, iron, potassium, and phosphorous (all with an intensity – counts – close to the one detected on the parchment). As Kα(S)≈Mα(Pb), it was not possible to identify the presence of sulphur. However, the presence of such amount of mercury might reflect its use as mercury sulphide (HgS, vermilion), indicating that this dark orange paint might have been prepared by mixing red lead with vermilion, Figure 26, right.
Figure 26. The use of red lead in Alcobaça illuminations. Left, Raman spectrum from an orange paint of Alcobaça 419, f.91v (black) and representative Raman spectrum of red lead (Vaz Pereira, Portugal) - grey; right, μ-EDXRF spectrum of a deep orange paint of Alcobaça 412, f.10v showing the presence of lead and mercury.

In Alcobaça 446, f. 32v, a certain light orange paint was obtained by mixing minium with orpiment. μ-EDXRF identified the presence of arsenic, lead and a higher signal for calcium, when compared with the other orange-based paints (due to the paint thickness, it is always detected the signal from parchment compounds, calcium, iron, potassium, and phosphorous), Figure 27, left.

Figure 27. The use of a certain light orange paint from Alcobaça 446, f.32v. Left, μ-EDXRF spectrum the presence of lead and arsenic; right, Raman spectrum detecting the presence of orpiment.

The presence of orpiment was identified by Raman microscopy due to its characteristic bands at 352, 309, 291, 201 and 153 cm⁻¹ (please see Section 2.3.3 – yellow) [Forneris

38 Each spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).

39 Spectrum collected using 632.8nm excitation, a 100x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
Red lead was identified by its characteristic band at 546 cm\(^{-1}\) (see Section 2.3.3 – orange) [Edwards et al. 2009], Figure 27, right.

**- red: inorganic and organic red paints**

The bright red colour present in Alcobaça was obtained with vermilion (\(\alpha\)-HgS), identified by Raman microscopy through its characteristic bands at 342 cm\(^{-1}\) attributed to the \(\nu\)(Hg-S) stretching, and to the bands at 252 and 284 cm\(^{-1}\) ascribed to the \(\delta\)(S-Hg-S) angle bending [Frost et al. 2010], Figure 28, right. Please see other representative Raman spectra of red paints in Appendix VI.

*Figure 28.* Vermilion based paints in the Alcobaça collection. *Left,* infrared spectrum of a red paint from *Alcobaça* 347, f.3 where calcite is present as extender; *right,* Raman spectrum of the same red paint (black) and representative Raman spectrum of vermilion (Sigma-Aldrich, Germany) – grey.\(^{40}\) The inset, detail from the area where micro-sampling was performed (magnification x40).

With exception to *Alcobaça* 410 (*Liber qui dicitur Angelus*, 1219) that was not analysed by \(\mu\)-FTIR spectroscopy, red paints were analysed in seven of the fourteen remaining manuscripts (*Alcobaça* 238, *Alcobaça* 358, *Alcobaça* 405, *Alcobaça* 419, *Alcobaça* 421, *Alcobaça* 426 and *Alcobaça* 433). \(\mu\)-FTIR analysis shows that, invariably, vermilion was mixed with calcite, CaCO\(_3\) (identified through its characteristic absorption bands at 1432 and 878 cm\(^{-1}\), please see Section 2.3.2), instead of being applied as pure pigment either on red lettering paints or in red illuminations, *Figure 28, left.* For other representative infrared spectra of red paints where chalk was also identified, please see Appendix VI. The exception was a red paint from an illumination on *Alcobaça* 405, f.4v, where vermilion was applied as pure pigment (please see the representative infrared spectra in *Figure AP VI.21* of Appendix VI).

\(^{40}\) Each spectrum collected using 632.8nm excitation, a 100x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
Concerning organic red paints, a deep organic red dye was consistently found. Infrared spectroscopy identified the characteristic absorption bands assigned to the C-H stretching at 2960 cm\(^{-1}\), 2854 cm\(^{-1}\) and 2934 cm\(^{-1}\), that are characteristic of the polymeric chain of shellac, the resin part of lac dye, please see Appendix II [Derrick et al. 1999; Sutherland 2010], Figure 29 (black line). These same features were also found for a deep organic red paint in *De Avibus*, from the Lorvão collection, Figure 29 (grey line). Other representative infrared spectra of deep organic reds found in the Alcobaça collection may be found in figures AP VI.3, AP VI.6, AP VI.29, AP VI.32 and AP VI.44 of Appendix VI. Rita Castro in the framework of her PhD research has just confirmed by Raman microscopy the presence of lac dye as the deep organic red source found in these illuminations. These results will be published soon.

Additionally identified in *Alcobaça 421, f.202* was the presence of gypsum (with its characteristic absorption bands at 3402 cm\(^{-1}\), 1134 cm\(^{-1}\) and 672 cm\(^{-1}\)) and calcite (1432 cm\(^{-1}\) and 878 cm\(^{-1}\)) as extenders, not present in the infrared spectrum from *De Avibus* from the Lorvão collection.

![Figure 29](image.png)

*Figure 29.* Comparison between the infrared spectra of a deep red dye found in the Alcobaça collection (*black line, Alcobaça 421, f.202*) and in *De Avibus* of the Lorvão collection (*grey line, Lorvão 5, f.6*). The inset, detail from the area where micro-sampling was performed (magnification 40x).

- **blue**

In Alcobaça illuminations, blue paints were extensively achieved using lapis lazuli, the most important blue source on medieval art, please see Appendix II. Lapis lazuli (Na\(_8\)Al\(_6\)Si\(_6\)O\(_{24}\)S\(_n\)) was identified by \(\mu\)-FTIR through its characteristic aluminosilicate
matrix absorption: the $\nu_{\text{asym}}(\text{Si-O}_4)$ asymmetric stretching of the internal tetrahedral structure of the aluminosilicate matrix at 1010 cm$^{-1}$, that presents a shoulder at 1140 cm$^{-1}$ linked to the $\nu_{\text{asym}}(\text{S-O})$ asymmetric stretching of linkages between tetrahedra [Miliani et al. 2008], Figure 30, left. Moreover, Raman microscopy clearly identified lapis lazuli based on its characteristic bands: the $\delta(\text{S}_3^-)$ bending at 255 cm$^{-1}$ and 285 cm$^{-1}$, the $\nu(\text{S}_3^-)$ stretching at 544 cm$^{-1}$, and the $\text{S}_2^-$ vibration at 580 cm$^{-1}$ that is accompanied by its overtone band at 1090 cm$^{-1}$ [Hayez et al. 2004], Figure 30, right. For other representative infrared spectra of lapis lazuli based paints, please see Appendix VI.

![Infrared and Raman spectra](image)

**Figure 30.** Lapis Lazuli paints in the Alcobaça collection. Left, infrared spectrum of a blue lettering present in Alcobaça 358, f.115v (the inset, detail from the area where micro-sampling was performed – magnification x40); right, Raman spectrum from a blue paint on Alcobaça 249, f.125v (black) and representative Raman spectrum of lapis lazuli (Kremer Pigmente, Germany) – grey.41

Even though it may be possible to identify by µ-FTIR analysis the presence of the bands ascribed to minerals associated with lapis lazuli, such as calcite, CaCO$_3$ (identified through its characteristic absorption bands 1432 cm$^{-1}$ and 878 cm$^{-1}$, please see Section 2.3.2), the fact is that the relative intensity of its characteristic bands suggests that calcite is present as an extender, and not as an impurity of lapis lazuli, Figure 30, left (please see other representative infrared spectra of blue paints in Figures AP VI.3, AP VI.9, AP VI.32 and AP VI.35 of Appendix VI). Moreover, it was verified that for these blue lapis lazuli based paints a lesser amount of binder is present when compared with other coloured paints of this collection. This fact, together with the grain size of lapis lazuli, contributed greatly to the paints erosion overtime.

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41 Each spectrum collected using 632.8nm excitation, a 100x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for ten cycles).
For lighter blues, Raman microscopy identified the recurrent use of lapis lazuli mixed with lead white, as in *Alcobaça* 427, f.115v (lapis lazuli was identified by its characteristic bands at 255, 544, 580 and 1090 cm\(^{-1}\); and lead white by its characteristic band at 1049 cm\(^{-1}\)), *Figure 31, left*. In the same illumination, dark blue was obtained with indigo, identified by Raman microscopy with its characteristic band at 1571 cm\(^{-1}\) ascribed to the \(\nu(C=C)\) stretching vibrations and its two characteristic bands assigned to the bending vibrations involving the central C=C bonds and the *out-of-plane* bending involving the five membered-ring at 549 cm\(^{-1}\) and 599 cm\(^{-1}\), respectively [Leona *et al.* 2004; Amat *et al.* 2011], *Figure 31, right*.

*Figure 31. Light and dark blue in Alcobaça collection. Left*, Raman spectrum of a light blue paint from *Alcobaça* 427, f.115v demonstrating the use of lapis lazuli mixed with lead white (*the inset, detail from light and dark blue applied in the illumination – magnification 10x*)\(^{42}\); *right*, Raman spectrum from the same *folium* where indigo was used for producing a dark blue paint (*black*) and representative Raman spectrum of indigo (*Sigma-Aldrich, Germany*) – grey\(^{43}\) (*the inset, molecular structure of indigo*).

To darken the blues, lapis lazuli was mixed either with indigo or with a carbon black pigment, as in *Alcobaça* 410, f.131, where Raman microscopy identified the characteristic bands\(^{44}\) ascribed to lapis lazuli (544, 580 and 1090 cm\(^{-1}\)) and to a carbon-based black pigment (1325 and 1580 cm\(^{-1}\), please see below in *Section 2.3.3-black* the Raman microscopy characterization of this pigment), *Figure 32*.

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\(^{42}\) Spectrum collected using 632.8nm excitation, a 100x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).

\(^{43}\) Each spectrum collected using 632.8nm excitation, a 100x objective and 1.7 mW laser power at the surface sample (accumulation time: 10 s, for five cycles).

\(^{44}\) Raman spectrum of a dark blue paint from *Alcobaça* 410, f.131 was subjected to a base line correction.
Figure 3. Blue paint backgrounds in the Alcobaça collection. Left, a detail from Alcobaça 421, f.181 (Legendarium, 12th-13th century); right, a detail from Alcobaça 405, f.3v (Expositio in Leviticum, 12th-13th century) where a particular pure lapis lazuli based paint is present. Photos © BNP.

Out of all the blue paints found in the Alcobaça collection, a particular blue from Alcobaça 405 (Expositio in Leviticum, 12th-13th century) stands out for its brightness and clarity. This is achieved not only by the simplicity of the drawing (that further emphasises the blue hue), but also by the absence of other paint colours on the illumination composition. In Figure 33, this effect is quite visible, especially when comparing the blue paint applied as background in Alcobaça 421, f.181 (Figure 33, left) with in Alcobaça 405, f.3v (Figure 33, right).

Each spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 10 s, for five cycles).
Regarding the formulation specificities of this blue paint, µ-FTIR analysis demonstrated the use of lapis lazuli as blue source, characterized by the band at 1002 cm\(^{-1}\), although it is not evident the presence of the band at 1140 cm\(^{-1}\) (ascribed to the \(\nu_{\text{asym}}(\text{S-O})\) asymmetric stretching of linkages between tetrahedra). Moreover, the presence of a lower amount of binder was apparent, as showed by a lower ratio intensity between the absorption bands of the proteinaceous binder and the aluminosilicate matrix, Figure 34, right. Finally, the absence of calcite as extender was noted (Figure 34, right), an extender commonly found in other lapis lazuli based paints, such as those of Alcobaça 421, f.181, where µ-FTIR identified - besides the bands attributed to lapis lazuli (at 1140 cm\(^{-1}\) and 995 cm\(^{-1}\)) - the characteristic strong absorption bands of calcite at 1430 cm\(^{-1}\) and 877 cm\(^{-1}\), Figure 34, left.

**Figure 34.** Comparing lapis lazuli based paints in the Alcobaça collection: left, infrared spectrum of a blue paint from Alcobaça 421, f.181; right, infrared spectrum of a blue paint from Alcobaça 405, f.3v where a particular pure lapis lazuli based paint is present. The inset, details from the areas where micro-sampling was performed – magnification x40.

In the set of manuscripts from the collection of Alcobaça whose analysis are here presented, lapis lazuli was consistently used as the only blue pigment. The exception was found for a certain manuscript, Alcobaça 433 (Lectionnarius cisterciense), with some of the blue lettering painted with azurite, Figure 35.

Azurite, \(\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2\), was occasionally identified in blue lettering of Alcobaça 433 by µ-FTIR through its characteristic absorption bands ascribed to the bending

**Figure 35.** Alcobaça 433, f.4v
Photo © BNP.
modes of carbonate $\delta(\text{CO}_3^{2-})$ at 817 and 837 cm$^{-1}$, the two $\nu_3$ asymmetric modes of the carbonate at 1415 and 1504 cm$^{-1}$, and the stretching vibration of the hydroxyl unit $\nu$(OH) at 3430 cm$^{-1}$ [Frost et al. 2007], Figure 36a. Moreover, Raman microscopy identified azurite by its characteristic bands at 82, 250, 403, 839 and 1098 cm$^{-1}$ [Mattei et al. 2008; Frost et al. 2002], Figure 36b. The bands observed at 82, 250 and 403 cm$^{-1}$ are assigned to the vibrations of the CuO group, namely to the O-Cu-OH bending vibration (250 cm$^{-1}$) and to the Cu-O bond stretching (403 cm$^{-1}$) [Mattei et al. 2008; Frost et al. 2002].

![Figure 36. Azurite in Alcobaça collection. a) infrared spectrum of a blue paint from Alcobaça 433, f.14; b) Raman spectrum of a blue paint of Alcobaça 433, f.4v (black) and representative Raman spectrum of azurite (Kremer Pigmente, Germany) – grey](image)

Each spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
The bands observed at 839 and 1098 cm\(^{-1}\) are assigned to vibrations of the carbonate group, namely to the *out-of-phase* bending mode of the carbonate group (839 cm\(^{-1}\)) and to the symmetric stretching vibration of CO (1098 cm\(^{-1}\)) [Mattei *et al.* 2008; Frost *et al.* 2002].

Regarding the discrepancy in the allocation of the date of production for *Alcobaça 433*\(^{47}\), the *BPN catalogue* refers to it as having been produced in Alcobaça in 1201-1250 [Cepeda *et al.* 2001]. On the other hand, Adelaide Miranda in her Master dissertation assigns its production to 1170-80 [Miranda 1984, p.77]. It is well established that azurite started to be used later on than lapis lazuli. Thus, is not reasonable that from a set of fifteen manuscripts all produced in a same period; azurite has been used in only one manuscript. Besides, from manuscript pagination, is unlikely that these letterings were introduced in the manuscript in a latter period. A detailed observation of all the *folios* of the *Alcobaça 433* showed that in fact this manuscript is a compilation of two distinct set of texts. The first is in line with the materials and painting techniques found for the 12\(^{th}\) century manuscripts from the Alcobaça collection, whereas in the second set the calligraphy and lettering decorations reminds those found in the French manuscripts from Clairvaux from the 13\(^{th}\) century. It was in this second set of texts that azurite was identified. It is thus very likely that the first set of texts were produced in Alcobaça in 1170-80 as suggested by Adelaida Miranda [Miranda 1984, p.77], whereas the second set of texts was produced in Clairvaux between 1201-1250, as referred in the *BNP catalogue* [Cepeda *et al.* 2001].

- **green**

Green is an important colour in Romanesque Portuguese manuscripts, particularly a certain deep green colour (CIELAB colour measurements, \(L^* = 35.75, \ a^* = -9.99, \ b^* = 7.58\) \(^{48}\)), *Figure 37*. Under polarised light it appears as a non-crystalline structure. \(\mu\)-

\(^{47}\) As aforementioned, *Alcobaça 433* is part of the set of eleven manuscripts presenting a colophon referring to have been produced in *Sancte Marie de Alcubacia* [Miranda 1984; Cepeda *et al.* 2001].

\(^{48}\) D65 illuminant and 10\(^\circ\) observer angle.
EDXRF identified the presence of copper and a small content of zinc, suggesting the use of a copper alloy such as brass, in the production of this synthetic copper pigment, Figure 38, right.

µ-FTIR allowed characterization of its most characteristic fingerprint: the copper proteinate (copper complex with the protein-based binder) indicated by a broad band at circa 1648 cm$^{-1}$. In Figure 38, left is shown the two patterns found for the copper proteinate band: a full broad band that is usually accompanied by changes on the C-H stretching absorption region (3000-2840 cm$^{-1}$) – black line - apparently dependent on bottle-green’s macroscopic changes (as the loss of cohesion and adhesion increases, the most altered is the C-H stretching absorption region); and a situation where this complexation is not yet completed – green line. Other representative spectra of bottle green paints may be found in Appendix VI. The bottle-green paints formulation will be deeply characterized in Chapter 3.

![Figure 38. Bottle-green paints in the Alcobaça collection. Left, infrared spectra from two different areas of a bottle-green paint microsample from Alcobaça 433, f.15; right, µ-EDXRF spectrum from the same paint. The inset, detail from the area where micro-sampling was performed – magnification 40x.](image)

A dark green hue made by mixing orpiment with indigo was found in Alcobaça 249, f.125v (Missal, 13th century). Raman microscopy showed the bands at 291, 309 and 353 cm$^{-1}$ for orpiment; and at 549, 599 and 1571 cm$^{-1}$ for indigo, Figure 39. Besides the presence of this dark green hue, this illumination stands out for its very expressive rinceaux and its size (it occupies circa 2/3 of the folium pagination) – please see Figure 54-right.
From the analysis of the set of manuscripts here presented, it was possible to characterize two origins for the carbon black paints. Raman microscopy allowed characterization of a black paint from *Alcobaça 249, f.125v* based on its characteristic broad doublet at 1580 cm⁻¹, assigned to the sp² C–C bonds, and at 1325 cm⁻¹ assigned to the sp³ C–C bonds of graphite [Rada et al. 2011], *Figure 40 (black line)*. The intensity ratio of these two bands suggests that this carbon is most probably of vegetal origin (carbon blacks of vegetable origin display a more intense contribution from the sp² C–C bonds of graphite, when compared to carbon black of animal origin, which presents a larger contribution from the sp³ C–C bonds of graphite), *Figure 40 (light green and grey lines, respectively)*. Moreover, the lack of the feature at *circa* 960 cm⁻¹ corresponding to a symmetric stretching from the PO₃²⁻ ion, which is typical of the calcium phosphate traces present in animal black, is not present on this carbon black [Weerd et al. 2004].

*Figure 39. Infrared spectrum of a dark green paint produced by mixing orpiment with indigo on Alcobaça 249, f.125v*. The inset, detail from the area where micro-sampling was performed – magnification 40x.

- *black*

49 Spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
Figure 40. Raman spectra of a black paint from Alcobaça 249, f.125v (black line), and of commercial Ivory black pigment (grey line) and Vine Black pigment (light green line)\textsuperscript{50} - both commercial pigments acquired from Kremer Pigmente, Germany.

\textmu FTIR identified the use of a carbon black of animal origin on Alcobaça 347, f.3, showed by the stretching vibrations of calcium carbonate at 1415 and 877 cm\textsuperscript{-1} (please see Section 2.3.2) characteristic of carbonated hydroxyapatite (resulting from the calcination of bones), and a strong band at 1035 cm\textsuperscript{-1} ascribed to the phosphate group (PO$_3^{2-}$) that characterizes the calcium phosphate traces commonly present in animal black [Sagîn et al. 2012; Tomasini et al. 2012], Figure 41, left. Other representative infrared spectra of black paints may be found in Figures AP VI.15, AP VI.21 and AP VI.32 of Appendix VI. \textmu EDXRF analysis identified in some black contours (as in Alcobaça 421, f.202) the presence of iron (with lower elemental ratio of counts for Ca/Fe than the ones found for the writing ink), suggesting the use of a carbon-mixed paint, probably produced by mixing a carbon black pigment with iron gall ink, Figure 41, right. Other representative \textmu EDXRF spectra of black paints are displayed in Appendix VI.

\footnote{Each spectrum collected using 632.8nm excitation, a 100x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).}
Together with grey, rose is one of the most characteristic colours from the Alcobaça palette\textsuperscript{51}, Figure 42. From the analysis of this collection, two different formulations were identified for the production of rose colour paints: one consisting of a mixture of an organic red dye (not yet characterized) with lead white; and another, which was characterized by Raman microscopy, consisting of a mixture of vermilion with lead white (vermilion was identified by its characteristic Raman bands\textsuperscript{52} at \textit{circa} 340 cm\textsuperscript{-1} and \textit{circa} 250 cm\textsuperscript{-1}, and lead white by its characteristic Raman band at 1049 cm\textsuperscript{-1} [Frost \textit{et al.} 2010; Gettens \textit{et al.} 1993a]), Figure 43.

\textsuperscript{51} Rose and grey colours are emblematic not for being widely present in the manuscripts from Alcobaça collection, but because they are almost absent in the manuscripts from the Lorvão and Sta. Cruz collections.

\textsuperscript{52} Raman spectrum of a rose paint from \textit{Alcobaça} 410, f.131 was subjected to a base line correction.
Grey hues were characterized in *Alcobaça 427, f.115v* where µ-FTIR identified the presence of lead white (towards its characteristic absorption bands at 3538, 1415 and 680 cm\(^{-1}\) [Gettens *et al.* 1993a]) and indigo (namely \(\nu(C=O)\) stretching at 1628 cm\(^{-1}\) and a band at 1317 cm\(^{-1}\) attributed to the \(\nu(C-C)\) stretching of the six-membered ring [Leona *et al.* 2004]), *Figure 44a*. Raman microscopy identified the characteristic Raman bands of indigo at 1571, 549 cm\(^{-1}\) and 599 cm\(^{-1}\) [Leona *et al.* 2004; Amat *et al.* 2011] and the band at 1049 cm\(^{-1}\) that characterizes lead white, *Figure 44b.*

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53 Spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
Figure 44. The use of grey colour as a mixture of indigo with lead white. a) Infrared spectra of black) a grey paint from Alcobaça 427, f.115v, and grey) of indigo (Sigma-Aldrich, Germany) (the inset, detail from the area where micro-sampling was performed – magnification 40x); b) μ-Raman spectrum from the same grey paint (the inset, molecular structure of indigo).

- brown

Brown is seldom present in the Alcobaça collection. From the set of fifteen manuscripts selected for this study, brown was identified in six manuscripts: Alcobaça 238, Alcobaça 358, Alcobaça 360, Alcobaça 402, Alcobaça 421 and Alcobaça 446, Figure 45.

54 Each spectrum collected using 632.8nm excitation, a 100x objective and 1.7 mW laser power at the surface sample (accumulation time: 10 s, for five cycles).
Brown formulations remain to be characterized. µ-EDXRF analysis proved inconclusive: with exception to *Alcobaça* 446, where µ-EDXRF identified the presence of copper, lead, iron, calcium and potassium on a certain dark brown paint (from the magnified observation it becomes evident that a brownish-green layer - the copper and iron source - was applied over a bright orange layer – the lead source, *Figure 45, d*); the remaining brown paints showed the presence of calcium, potassium, iron, chlorine and sulphur with an intensity close to the one detected for the parchment, which may reflect the use of an organic source for producing this brownish hue. Raman microscopy presented no signal for these paints, and µ-FTIR results were inconclusive. Nevertheless, it is possible to say that some of the brownish paints seem to be inorganic, whereas others (e.g. the transparent brownish in *Alcobaça* 238, f.203v, see *Figure AP VI.3*) have most probably and organic origin.

*Appendix VI* displays the representative spectra of the Alcobaça collection, where each analytical technique was used to characterize the colours found in each manuscript.

### 2.3.4. Other materials present in the manuscripts from the Alcobaça collection

Besides the materials used for coloured paint’s production, there are other materials that display a crucial role in a medieval manuscript: the parchment (the support of the text and the illuminations), the ruling (to guide the handwriting of the text), and the writing inks (without which would not be possible to write the text, the foremost reason for the manuscript’s production).
The type of skin used to produce the Alcobaça manuscripts is undetermined. However, based on colour and follicle pattern, it is possible that a goatskin and/or sheepskin have been used for parchment production.

µ-EDXRF analysis identified the presence of elements usually ascribed to parchment such as calcium (Ca), potassium (K) and iron (Fe), but not so intensely the elements manganese (Mn), chlorine (Cl), sulphur (S) and arsenic (As), with exception to Alcobaça 410 and Alcobaça 426 where arsenic was detected in an elemental ratio of counts for Ca/As of 8 and 120, respectively. Important to note is that no yellow paint was analysed in Alcobaça 426, therefore it is not possible to infer if any orpiment was used in its colour palette. However, the detection of orpiment might be related to its use in parchment production as an insecticide [Eastaugh 2004, p.285], as it was common to spread it over the parchment to avoid the proliferation of microorganisms as fungi.

µ-FTIR analysis identified the characteristic collagen fingerprint, namely its characteristic polyamide absorption pattern at 1635, 1550 and 1450 cm⁻¹, the νasym(CH₃) at 2963cm⁻¹, the νasym(CH₂) at 2935cm⁻¹, an absorption band at 2875cm⁻¹ assigned to the νsym(CH₃), and the OH and NH stretching at 3400-3000 cm⁻¹ [Stuart 2004; Chalmers et al. 2002].

- ruling

The analysis of the ruling by µ-EDXRF identified, besides the presence of calcium (Ca) and iron (Fe) mostly ascribed to the parchment, a small amount of lead (Pb), most probably due to the use of a lead point for ruling⁵⁵, Figure 46.

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⁵⁵ Since the beginning of the 12th century, it became common to use a metal point of lead to rule the parchment [Brown 1994]. Other metal points could also be used for ruling, such as silver points or points made of an alloy of three quarters of lead and one quarter of bronze points [Shailor 1991, p.15].
The inset, detail from the spot of analysis.

- **writing inks**

An iron-gall ink used as writing ink was identified by Raman microscopy\(^{56}\) due to its characteristic bands at 1577 cm\(^{-1}\) (medium), 1475 cm\(^{-1}\) (strong), 1427 cm\(^{-1}\) (shoulder), 1335 cm\(^{-1}\) (medium-strong), and a broad band in the range 640-500 cm\(^{-1}\) [Lee *et al.* 2006]. According to Bicchieri *et al.*, the band centered at circa 572 cm\(^{-1}\) might be ascribed to an iron-parchment complex [Bicchieri *et al.* 2008], *Figure 47*.

\(^{56}\) Iron-gall ink was analysed by Raman microscopy in one manuscript, *Alcobaça 446*; and by µ-EDXRF in the 15 manuscripts, that consistently identified the presence of Iron (Fe).

\(^{57}\) Each spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
Comparing the results for the Raman analysis of the writing ink from *Alcobaça 446, f.32v* and modern iron-gall ink\(^{58}\) applied on parchment, *Figure 47*, it is noticeable that natural ageing or degradation causes an increase in fluorescence of the ink when compared with that found for freshly prepared iron-gall ink, resulting in poorer resolution and broader, weaker bands above a higher fluorescence baseline\(^{59}\) [Lee *et al.* 2006].

- red writing ink

In the Alcobaça manuscripts, besides the capital letter that introduces the text, it is common to find a red written sentence – the rubric\(^{60}\), *Figure 48*.

![Rubric from Alcobaça 238, f.220v.](image)

*Figure 48. A rubric from Alcobaça 238, f.220v. Photo © BNP.*

For the majority of the rubrics analysed by \(\mu\)-EDXRF was found the presence of a small amount of lead (the elemental ratio of counts for Hg/Pb varies between 6-28) in three of the eleven manuscripts where red rubrics were analysed by this technique. It was not possible to conclude based on \(\mu\) -EDXRF results whether the lead has a lead white source.

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58 Iron-gall ink was reproduced using gallnuts (*Zecchi*, Italy), a homemade wine, an iron salt (iron sulphate - *Aldrich*, Germany) and Arabic gum (*Zecchi*, Italy), following the recipe described in the *Padova manuscript* [Merrifield 1999, p.676]. Afterwards, it was applied on parchment with a pen nib. After *circa* 1 month, it was analysed by Raman microscopy.

59 Raman spectrum of iron-gall ink from *Alcobaça 446, f.32v* was subjected to base line and smooth corrections.

60 *Rubric* derives from the Latin word for red, *rubrica*, as a red ink was commonly used for its writing [Brown 1994]. This title, chapter heading or instruction is not strictly part of the text, but has the main role of helping to identify the text components, separating two subjects on the text by introducing with a one-summary sentence the subject of the following paragraph.
or a red lead source. Moreover, on the red rubric where μ-EDXRF detected mercury and lead, Raman microscopy only identified the characteristic bands ascribed to vermilion. If red lead was present in these paints formulations, even in a low percentage, it would probably be better identified by Raman microscopy, than lead white, whose characteristic bands present lower Raman intensities. It is probable that a small amount of lead white was mixed with vermilion as extender. Another possibility for the small amount of lead white might result from brush contamination or from vermilion adulteration, but for this conclusion the results of μ-FTIR analysis would have been crucial.

2.4. Conservation condition

- Bindings

From the three main Portuguese medieval collections (Lorvão, Sta. Cruz and Alcobaça), Alcobaça is the only presenting manuscripts with original bindings from the 12th-13th century [Nascimento et al. 1984]. From the set of 15 manuscripts here presented, three of them present original bindings (Alcobaça 347, 358 and 426), and five present contemporary bindings (Alcobaça 405, 412, 419, 421 and 446) [Cepeda et al. 2001], Figure 49.

![Figure 49. Original binding, Alcobaça 426, 12th-13th century](image)

Photo by Ana Lemos.

Regarding the conservation condition of the bindings of the manuscripts from the Alcobaça collection, besides some degradations related to binding ageing, it may be

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61 Besides the use of calcite or lead white as extenders, it was common to mix vermilion with red lead (Pb₃O₄) for larger painted surfaces in such proportion that the final red colour is not changed [Claro 2009]. This allows the artist to save one of the most valuable pigments in the medieval palette, vermilion (HgS).
referred the mutilation and absence of some folia\textsuperscript{62}, and the parchment deterioration caused by humidity\textsuperscript{63} [Cepeda et al. 2001]. A systematic assessment of the conservation condition of these parchments is in progress as part of the research project [Iluminuras 3] and of the PhD thesis of Rita Castro.

- Paints degradation over time

Paint degradations are more related to the loss of cohesion and adhesion to the support of bottle-green paints (Figure 50a), the whitish efflorescence over a yellow orpiment based paint on Alcobaça 249, f.91v (Figure 50b), and the lead based pigments’ blackening, lead white (present in two manuscripts, Alcobaça 249, f.91v and Alcobaça 446, f.96v) and red lead (Alcobaça 360, f.2), Figure 50c and 50d, respectively.

\textbf{Figure 50.} Degradation patterns found in Alcobaça collection: \textbf{a}) loss of cohesion and adhesion to the support of bottle-green paints (Alcobaça 351, f.1; magnification 50x); \textbf{b}) whitish efflorescence over an orpiment based paint (Alcobaça 249, f.91v; magnification 32x); \textbf{c}) lead white blackening (Alcobaça 446, f.96v; magnification 16x); and \textbf{d}) red lead blackening (Alcobaça 360, f.2; magnification 80x).

- Bottle-green paints

The bottle-green paints are suffering from extensive degradation as indicated by a severe loss of cohesion and adhesion to the support. Nevertheless, this has not affected the

\textsuperscript{62} In Alcobaça 238 some folia were cut; in Alcobaça 410 and Alcobaça 412 some folia were mutilated; and in Alcobaça 402 are missing the last three folia.

\textsuperscript{63} In Alcobaça 410 this degradation becomes more evident.
brightness or the intensity of the deep green (CIELAB colour measurements, L*=35.75, a*= -9.99, b*= 7.5864). It seems like it has only affected the invisible component of the paint: the binder. Moreover, contrary to what is commonly found for other copper based pigments applied over parchment, in the bottle-green paints there is no evidence for the copper corrosion of parchment.

The bottle-green paints’ formulation will be discussed in Chapter 3, with a comparative study of the bottle-green infrared spectra and its relation to the macroscopic degradations for the Lorvão, Sta. Cruz and Alcobaça scriptoria.

- Whitsish efflorescence

A certain whitish effloresce over a yellow orpiment based paint was found in Alcobaça 249, f.91v. μ-FTIR analysis showed a significant alteration in the protein fingerprint, namely in the C-H absorption region (3000-2840 cm\(^{-1}\)) and in the Amide absorption region (1740-1495 cm\(^{-1}\)), Figure 5. It is possible that the bands at 873 cm\(^{-1}\) and 811 cm\(^{-1}\) are assigned to the presence of arsenolite, an arsenic trioxide (As\(_2\)O\(_3\)), resulting from orpiment oxidation. This oxide is found in nature, as an oxidation product of arsenic bearing sulphides [Miguel et al. 2009a].

![Infrared Spectrum](image_url)

**Figure 5.** Infrared spectrum of a whitish efflorescence present over a yellow orpiment based paint in Alcobaça 249, f.91v. The inset, detail from the area where micro-sampling was performed – magnification 32x.

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64 D65 illuminant and 10º observer angle.
In a study on the red lead degradation found in the Lorvão 43, simulation studies of the reaction of red lead (Pb₃O₄) with orpiment (As₂S₃) in water have shown that galena (PbS) and lead arsenate ((AsO₄)₂Pb₃) are the main degradation products for this reaction [Miguel et al. 2009a]. Also identified was the presence of As₂O₃, most probably due to the reduction of arsenate ion in water [Miguel et al. 2009a]. Further ageing studies involving orpiment degradation must be performed to be able to propose the mechanism responsible for this whitish efflorescence.

- Lead white and orpiment degradations

Lead white blackening was observed in two manuscripts, Alcobaça 249 (f.91v) and Alcobaça 446 (f.96v). Raman microscopy identified galena, a lead sulphide (PbS), as the degradation product of lead white, and a band at \textit{circa} 810 cm\(^{-1}\) indicating the presence of an arsenate-based species. Moreover, it was also identified an intense broad band at \textit{circa} 339 cm\(^{-1}\) in Alcobaça 446, f.96v, most likely due to an orpiment-based solid phase in agreement with the reduction of orpiment or the arsenate-based species, Figure 52 [Muralha et al. 2012].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig52.png}
\caption{Raman spectra of lead white degradation in: (A) Alcobaça 249, f.91v, showing galena (i-iii), the arsenate band (i), and the sulphate band associated with galena laser-induced degradation (ii); (B) Alcobaça 446, f.96v, showing (i) orpiment-based solid-phase compound, (ii) orpiment-based solid phase compound with the main bands of orpiment, and (iii) orpiment (from Alcobaça 249, f.91v).}
\end{figure}

From the analysis of a lead white degraded microsample from Alcobaça 249, f.91v it was verified that the bands ascribed to lead white are still present (namely the band at 1049 cm\(^{-1}\), Figure 52A-(i)), but now two large broad bands appear at \textit{circa} 200 and 440 cm\(^{-1}\), corresponding to the main spectral features of galena (Figure 52A-(i) and 65

\[65\] Each spectrum collected using 632.8nm excitation, a 50x objective and 1.7 mW laser power at the surface sample (accumulation time: 5 s, for five cycles).
Figure 52A-(ii), where a reference spectrum for galena is shown. The spectra of galena modifies as the laser degradation starts, shifting the broad band at 454 cm\(^{-1}\) to lower wavenumbers, as already observed by Batonneau et al. [Batonneau et al. 2000]. A band from lead sulphate (PbSO\(_4\)) is also emerging in the region between 960-980 cm\(^{-1}\), revealing that galena is already suffering a laser-induced degradation (Figure 52A-(ii)).

In a microsample from Alcobaça 446, f.91v, the Raman spectra showed an intense broad band at circa 339 cm\(^{-1}\) (Figure 52B-(i)) and on a few spectra the peaks corresponding to orpiment (at 154, 292, 309 and 353 cm\(^{-1}\), Figure 52B-(ii)). To better visualize these feature, a representative spectrum of orpiment acquired on Alcobaça 249, f.91v, Figure 52B-(iii) is shown. This broad band at circa 339 cm\(^{-1}\) was also observed on a study by Rochette et al. [Rochette et al. 2000], who attributed it to an orpiment-based solid phase forming after 330h of artificially reduction of arsenate by H\(_2\)S. However, without further analysis it is not possible to postulate if either orpiment or the arsenate species reacted with a sulphide compound and an intermediate species is being observed by Raman microscopy.

- **Red lead degradation**

A certain orange degradation was found on Alcobaça 360, f.2, that under magnified observation, appears to migrate from the parchment to the paint surface, Figure 50d. Raman microscopy identified the characteristic bands ascribed to red lead (548, 390, 223, 149 and 122 cm\(^{-1}\) [Edwards et al. 2009; Rada et al. 2011; Rao et al. 1975; Shaltout et al. 2005], see section 2.3.3-orange), and \(\mu\)-EDXRF only detected lead (Pb) and the elements assigned to the parchment, as calcium (Ca), potassium (K) and iron (Fe). It was not possible to identify the presence of any sulphur-containing pigments, nor the presence of arsenic on the parchment\(^{66}\), which could be reacting with red lead and producing galena (as happens with the red lead degradation found on Lorvão Apocalypse [Miguel et al. 2009a]). Further studies must be performed in order to identify the sulphur source of this degradation, as the presence of traces of the action of microorganisms that are often responsible for the increment of sulphur content on the parchment.

- **Previous interventions**

The illuminations do not demonstrate any apparent intervention, with exception to Alcobaça 421, f.202 (Legendarium, 12\(^{\text{th}}\)-13\(^{\text{th}}\) century) that presents a varnish whose

\(^{66}\) To prevent the development of microorganisms, it was common to spread a small amount of orpiment on the parchment.
infrared spectrum displays the characteristic absorption fingerprint of a collagen-based glue, Figure 53.

**Figure 53.** Black, infrared spectrum of a varnish found in *Alcobaça 421, f.202*; grey, infrared spectrum of parchment glue. The inset, detail from the area where micro-sampling was performed – magnification 10x.

µ-FTIR analysis identified the characteristic collagen fingerprint, namely its characteristic polyamide absorption pattern as the Amide I (\(\nu(\text{CO})\) at 1635 cm\(^{-1}\)), Amide II (\(\nu(\text{CN})\) and \(\delta(\text{NH})\) at 1550 cm\(^{-1}\)), the \(\delta(\text{CN})\) at 1450 cm\(^{-1}\), the \(\nu_{\text{asym}}(\text{CH}_3)\) at 2963 cm\(^{-1}\), the \(\nu_{\text{asym}}(\text{CH}_2)\) at 2935 cm\(^{-1}\), an absorption band at 2875 cm\(^{-1}\) assigned to the \(\nu_{\text{sym}}(\text{CH}_3)\), and the OH and NH stretching at 3400-3000 cm\(^{-1}\) [Chalmers *et al.* 2002; Stuart 2004].

Considering that the varnish is locally present on a restricted part of the illumination and that it was not found present as a varnish with a same infrared fingerprint in the remaining illuminations analysed in this work, it is reasonable to consider that this might have been applied subsequently to the production of the illumination.

### 2.5. Comparing the Alcobaça and the Lorvão collections

The present section aims to establish a comparison between the Alcobaça and the Lorvão collections, not just considering the aesthetic characteristics of both collections, but making use of the main findings of the study of the materials and paintings techniques used to produce the two set of manuscripts that had previously been subject of study within the framework of the research projects [*Iluminuras 1; Iluminuras 2; Iluminuras 3*]. Moreover,

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67 Parchment glue was reproduced following a recipe from *Libro de como si facem as cores* [Strolovitch 2010, p.235], please see Appendix III.
to be able to proceed with this comparison, it is essential to make use of Ana Claro’s PhD dissertation [Claro 2009], where the main results for the study of the materials and painting techniques used to produce a set of 9 manuscripts belonging to the Lorvão collection are systematically presented. From this set of manuscripts preserved at the ANTT (Arquivo Nacional da Torre do Tombo), only 3 present a colophon with their date of production: the Lorvão Apocalypse (Lorvão 43, 1189), the De Avibus (Lorvão 5, 1183-84) and the Enarrationes in Psalmos of Saint Augustine (Lorvão 50, 1184). The remaining manuscripts are attributed to the 12th-13th century, please see Appendix I.

By comparing the Lorvão and the Alcobaça collection, the first main evidence is the difference in consistency of each collection: the Lorvão collection presents a considerable heterogeneity of the drawing and painting techniques; whereas in Alcobaça the palmette and the rinceaux ornamentation are reliably present in the collection, as well as a great homogeneity of the painting techniques. Afterwards became apparent the presence of more extensive areas painted with red lead, vermilion and indigo in the Lorvão collection, not so often found in the Alcobaça collection. Red lead becomes less used in extension for the Alcobaça collection, and indigo becomes restricted for the matiz and highlights that are used to give volume and to create a greater visual impact, which so well characterizes the Alcobaça collection, Figure 54.

Figure 54. The use of indigo in the Lorvão and Alcobaça collections. Left, the extensive use of indigo in Lorvão 16, f.73, (Passionarium, circa 1140); right, the use of indigo to produce a deep green or a matiz of blue in Alcobaça 249, f.125v (Missal, 13th century). Photos © ANTT and © BNP.
On the other hand, a certain deep organic red dye (most probably *lac dye*) and lapis lazuli were used to paint larger areas in Alcobaça than in the Lorvão collection. Contrary to what was found for the Lorvão collection in which, for the same folia, whenever pure lapis lazuli was applied in the illumination, azurite was also found in minor initials [Claro 2009, p.64]; in Alcobaça azurite only appears in the lettering of a certain manuscript, *Alcobaça 433* (*Lectionnarius cisterciense*, 1178-80/1201-1250), and never combined with lapis lazuli.

Concerning the use of orpiment, it was extensively used for producing a yellow paint in a particular manuscript from the Lorvão collection, *Lorvão 43* (*Lorvão Apocalypse*, 1189) [Claro 2009], while in Alcobaça it was identified in two manuscripts produced during the 13th century, *Alcobaça 249* (Missal, 13th century) and *Alcobaça 410* (*Liber qui dicitor Angelus*, 1219), Figure 55.

![Figure 55. The use of orpiment in the Lorvão and Alcobaça collections. From left to right: Lorvão 43, f.120, (Lorvão Apocalypse, 1189), Alcobaça 249, f.91v (Missal, 13th century) and Alcobaça 410, f.131 (Liber qui dicitor Angelus, 1219). Photos © ANTT and © BNP.](image)

Despite having been used in only one manuscript from the Lorvão collection, the fact is that the painted area with orpiment is much larger in *Lorvão Apocalypse*, than in the two Alcobaça manuscripts (*Alcobaça 249* and *Alcobaça 410*). Also interesting to notice is that

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68 However, the low concentration of azurite did not allowed to conclude if it was present as an impurity or if it was added with the purpose of using a less amount of lapis lazuli (one of the most expensive pigments of the medieval palette) [Claro 2009, p.64].
both manuscripts from Alcobaça were produced circa 50-70 years later than the Lorvão Apocalypse\textsuperscript{69}, and that the manuscripts produced at the same time present as yellow source colour an organic yellow, not yet characterized. Nevertheless, it is important to refer the importance of yellow in the context of the Iberian Apocalypse manuscripts, which might well have contributed to the extension of use of orpiment in the Lorvão Apocalypse. In this sense, it is more expectable that the Lorvão Apocalypse presents a larger extent of use of orpiment due to the Iberian tradition of this manuscript, rather then to the importance of orpiment in the scriptorium. Concerning the specificities on the paints’ formulations, the most interesting to note were the inorganic and organic red paints’ formulations. Ana Claro refers the systematic use of pure vermilion paints for the letterings and red writing inks, and the use of vermilion mixed with an extender (as lead white, red lead or calcite) for the illuminations [Claro 2009, p.61], a system that was not verified for Alcobaça manuscripts, as aforementioned. Nevertheless, it is important to note that the Lorvão red paints where vermilion was found mixed with red lead as extender was in the Lorvão Apocalypse, where it occupies extensive areas (for some cases almost half of the folium); and that such extensions of red paints are not present in the manuscripts of Alcobaça. Furthermore, from three Portuguese collections so far analysed (Lorvão, Sta. Cruz and Alcobaça), it was in Alcobaça and, more specifically, on the deep red organic paints that was first identified the use of gypsum mixed with a small amount of calcite as extender on a paint formulation. According to Isabel Pombo Cardoso, the most common sources for medieval gypsum were Spain, France, Germany, Italy and Northern Africa; whereas there are no references for sources of good quality gypsum in the Portuguese territory at that time [Pombo Cardoso 2010]. The presence of gypsum in the manuscripts from Alcobaça suggests the relation of this scriptorium with its Mother Abbey of Clairvaux in France, that apparently might well have exceeded the influence on the ornamentation and on the iconographic systems, to influence also the use of the materials and paints formulations in Alcobaça. Nevertheless, it would be of extreme importance to be able to compare the materials and paints formulations of contemporary manuscripts from Alcobaça and Clairvaux.

\textsuperscript{69} The Lorvão Apocalypse is unique in the Portuguese artistic context. It presents a colour palette mainly restricted to yellow, orange and red (the illuminator seldom uses black or brown), despite other manuscripts produced in the same period in the Lorvão scriptorium presenting a rich palette of colour, where it is possible to be found the best pigments and organic colourants available at the time. From the 69 illuminations present on the Lorvão Apocalypse, 18 are full page illuminated, presenting large yellow, orange or red painted areas [Miguel et al. 2009a].
Finally, it is important to refer the importance of the study of the materials used to produce the paint and the new findings that were possible to achieve throughout it. A good example is the comparison between the Lorvão 15 (Gradual, 1201-1250) and the Alcobaça 427 (Bible, 12th-13th century), Figure 56.

![Figure 56](image)

Even if at first glance, the similarities between the two manuscripts are notable (namely the extensive use of the *rineaux* and the four-coloured *rubrica*), the analysis of the paint formulations strengthened the similarities between these two manuscripts, such as the use of indigo and lead white for the *matiz*, that was not identified following such formulation in any other manuscript from the Lorvão, Sta. Cruz or Alcobaça collections. Within these results, it was possible to bring new insights that supports the possibility of these two manuscripts have been produced in the same *scriptorium*, most probably in the Alcobaça *scriptorium*.

**2.6. Final remarks on the Alcobaça collection**

From the study of the Alcobaça collection hereby presented it is possible to conclude that in the Alcobaça’s *scriptorium* monochromatism was applied as an exception and, when used, it was applied in letters full of volume and exuberance. The ornaments present a
more restrictive palette in the oldest manuscripts (as in Alcobaça 358), diversifying later in the liturgical manuscripts, as in the Missals (Alcobaça 249), or in the great Bible (Alcobaça 427) and in the Legendarium (Alcobaça 419 and Alcobaça 421).

The molecular analysis of the colour palette of the Alcobaça collection permitted the conclusion that the best colourants available during medieval times were used: vermilion, red lead (*minium*), orpiment, a deep red organic dye (most probably *lac dye*), lapis lazuli, indigo, lead white, carbon and bone black, as well as a synthetic copper green (the so-called bottle-green). Azurite was solely used in the lettering of one manuscript (Alcobaça 433). This specificity supported the idea of the art historians that this manuscript comprises two different sets of texts, one produced in Alcobaça in 1170-80 [Miranda 1984, p.77], and another in Clairvaux between 1201-1250 [Cepeda *et al.* 2001].

In the Alcobaça illuminations, lapis lazuli was the colour for blue and was usually used as a pure pigment; darker blues were obtained by mixing lapis lazuli either with indigo or with a carbon black pigment, and lighter blues by mixing it with lead white. A deep saturated green - bottle-green - found ubiquitously in all manuscripts, was always applied as a single colour. Reds were obtained with vermilion often mixed with an extender, such as calcite and, less frequently, with lead white. Dark reds are quite present in large painted areas, and could have been obtained from an organic dye such as *lac dye*. The whites and lights were applied using lead white, and for the black colour, both carbon black and bone black were used. Red lead was less used for painting large areas (when compared with the Lorvão collection). However, the characteristic visual effect produced by applying a deep red organic dye over a red lead layer found for the Lorvão manuscripts is also found in some of the Alcobaça manuscripts (as in Alcobaça 446). Orpiment was less often employed than in the Lorvão collection. Other shades of yellow and brownish colours were also found in the studied manuscripts, but so far their characterization was not possible. At last, rose and grey colours, the most emblematic colours from Alcobaça, were mostly achieved by mixing vermilion or indigo with lead white, as in Alcobaça 410 and in Alcobaça 249, respectively; or sometimes achieved by mixing a deep red organic dye with lead white as in the *matiz* of *lac dye*, or carbon black with indigo, as in Alcobaça 427 and in Alcobaça 421. The use of gypsum as extender suggests that Clairvaux might well have

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70 Again, becomes important to stress that rose and grey colours are emblematic not for being widely present in the manuscripts from Alcobaça collection, but because they are almost absent in the manuscripts from the Lorvão and Sta. Cruz collections.
exceeded the influence on the ornamentation and on the iconographic systems of Alcobaça, to influence also the use of the materials and paints formulations in its scriptorium.

Finally, it is fundamental to refer the very good conservation condition of the Alcobaça collection. Besides being the only Portuguese collection (and one of few European collections) where it is still possible to find 12th-13th century manuscripts with original binding, its coloured paints present a very good conservation condition, with exception (as aforementioned) of the bottle-green paints that present a serious loss of cohesion and adhesion to the support, to the whitish efflorescence over a yellow orpiment based paint (Alcobaça 249), to the darkening of lead based pigments, as lead white (in Alcobaça 249 and Alcobaça 446) and red lead (Alcobaça 360), and to a likely product of the orpiment reduction reaction by a sulphide source (Alcobaça 446).
Every valley shall be lifted up,  
and every mountain and hill be made low;  
the uneven ground shall become level,  
and the rough places a plain.  

Isaiah 40, 4

3. **Le vert et le rouge**

Red and Green are important colours in the context of Portuguese Romanesque illuminations. Red is ubiquitously present and red paints display a very good conservation condition; green is widely used in Portuguese Romanesque illuminations with a deep green glassy appearance (named in Portuguese “verde garrafa”, bottle-green), of which molecular analysis showed its specificity among the green sources commonly used for illumination paint production. The study of the specificities of the use and production of these red and green colours was the main subject of this research. For the study of the importance of red and green in Portuguese Romanesque context, the use of colour will be discussed in the Lorvão, Sta. Cruz and Alcobaça collections through the study of colour in their Hagiographic readings\(^{71}\).

3.1. **The use of colour in the Lorvão, Sta. Cruz and Alcobaça collections**

The analysis of the use of colour in the three collections was based on a comparative study of the five Hagiographic readings produced in the Lorvão, Sta. Cruz and Alcobaça scriptoria (Lorvão 16, Sta. Cruz 20, Sta. Cruz 21, Alcobaça 419 and Alcobaça 421), Figure 57. For this analysis two approaches were followed: one focused the analysis on the colour schemes used in the illuminations, the other the extent of use of each colour in the manuscripts. For this analysis a set of 172 letterings and initials from the five manuscripts\(^{72}\) were considered.

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\(^{71}\) As aforementioned in Chapter 1, the use of the Hagiographic readings (a term that includes the Passionarium and the Legendarium) for the establishment of a systematic relationship between drawing and painting techniques was based on two main reasons: its transversal importance on the armaria of the monasteries, and the fact that these manuscripts were produced in the same period.

\(^{72}\) 25 letterings and initials from the Lorvão 16; 10 from the Sta. Cruz 20; 45 from the Sta. Cruz 21; 38 from the Alcobaça 419; and 54 letterings and initials from the Alcobaça 421.
Figure 57. From left to right, major initials in the Hagiographic readings from Lorvão 16, f.59v (Passionarium, 1140); Sta. Cruz 20, f.152 (Legendarium, 13th century); Sta. Cruz 21, f.262v (Legendarium, 13th century); and Alcobaça 419, f.35v (Legendarium, 12th-13th century) and Alcobaça 421, f.193v (Legendarium, 12th-13th century). Photos © ANTT, © BPMP and © BNP.

a) Colour schemes in the Hagiographic readings from the Lorvão, Sta. Cruz and Alcobaça collections

The illuminations from the Passionarium in the Lorvão collection present a colour scheme based on the combination of red-green-blue colours, which is commonly accompanied by a brownish hue, not yet characterized, Figure 57. The fact that paint degradation is more pronounced in this manuscript leads us to consider the hypothesis that this brownish-yellow hue might result from a degradation process of an organic dye [Clarke 2011]. In fact, the conservation condition of the paints of the Lorvão 16 is strongly affecting the interpretation of the colour scheme followed by the illuminator.

The illuminations present in the Legendarium from Sta. Cruz (Sta. Cruz 20 and Sta. Cruz 21) are characterized by a colour scheme based on the combination of red-green-blue-yellow, Figure 57. Although it is not common to characterize an unpainted area as a colour, the fact is that in Sta. Cruz these unpainted areas seem to integrate the colour scheme, enhancing the contrast between the remaining four colours. Moreover, notable is the well-balanced use of each colour on the colour scheme, not so evident in the other manuscript from the Lorvão and Alcobaça collections.

Concerning the illuminations in the Legendarium from the Alcobaça collection (Alcobaça 419 and Alcobaça 421), the colour contrast is less effective, mostly due to a disproportion in the area occupied by each colour in the illuminated initials. The initials present
backgrounds painted in red, deep organic red, blue or bottle-green, being the colour contrast provided by the colour present on the initial’s ornamentation, Figure 57. The most common colour schemes are the lapis lazuli based backgrounds with deep organic red ornamentations; deep organic red backgrounds with bottle green ornamentations; deep red organic backgrounds with lapis-lazuli ornamentations; and vermilion based backgrounds with bottle-green ornamentations.

- **Red and Green as a complementary colour scheme in the Hagiographic readings illuminations**

A complementary colour scheme consists of the use of any two colours that are oppositely positioned on the colour wheel [Feisner 2006, p.75], Figure 58. The use of complementary colour schemes allows for the most intense contrast hues, leading to bright and intense images [Feisner 2006, p.75].

Red and green are oppositely placed in the colour wheel, thus are considered complementary colours [Feisner 2006, p.19, 75]. Besides, red is a warm colour, whereas green is cold colour. The red-green colour scheme was only found in the Legendaria from Sta. Cruz and Alcobaça collections. In Figure 59 are displayed the two variants found for this colour scheme: green backgrounds highlighted with red ornamentations (Sta. Cruz 20, f.71), and red backgrounds highlighted with green ornamentations (Alcobaça 421, f.148v).

![Figure 58](image)

**Figure 58.** A contemporaneous 12-colour colour wheel (adapted from [Feisner 2006, p.19]).

![Figure 59](image)

**Figure 59.** The use of the red-green colour scheme the Hagiographic readings from Sta. Cruz 20, f.71 (Legendarium, 13th century) – left; and Alcobaça 421, f.148v (Legendarium, 12th-13th century) - right. Photos © BPMP and © BNP.
The red-green colour scheme creates an impressive colour contrast, promoting a vibrant appearance to the illuminations. Even for the illumination from Sta. Cruz 20, f.71, where a considerable area of green paint has been lost due to its loss of adhesion to the support, this contrast is still observable. In fact, the red-green colour scheme promotes a special striking contrast of colours, placing these initials amongst the most appealing illuminations of the Hagiographic readings from Lorvão, Sta. Cruz and Alcobaça collections.

b) *The extent of colour in the Hagiographic readings from the Lorvão, Sta. Cruz and Alcobaça collections*

The study of the extent of use of a certain colour\(^7^3\) allows to infer its importance on the palette of the scriptorium, or even to propose possible relations between manuscripts [Melo et al. 2011]. The present study was performed on the five Hagiographic readings from the Lorvão (Lorvão 16), Sta. Cruz (Sta. Cruz 20 and Sta. Cruz 21) and Alcobaça (Alcobaça 419 and Alcobaça 421) collections, from which the areas of the main colours used were quantified: red, deep organic red, orange, blue, green, rose and yellow. As the painting materials were previously characterized [Melo et al. 2011], it became possible to associate a molecular palette to these colours, with exception to an organic yellow, a rose and a brownish-yellow hue, not yet characterized. Deep organic red is most probably a lac dye-based paint. In a first analysis, it was possible to verify a consistency between the colours distribution in the manuscripts produced in a same scriptorium, Figure 60. However, it would be necessary to analyse a larger number of manuscripts to validate these results.

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\(^7^3\) The colour mapping was performed using a MATLAB\(^\text{®}\) algorithm developed by Jorge Sarraguça and João A. Lopes from Requimte-FFUP (for more details, please see Appendix IV.3.3).
Also evident is the restriction to using blue, green, red (inorganic and organic) and yellow colours on the illuminations and an unexpectedly rare use of red lead in the palette (only present in the Legendarium from Alcobaça, occupying a maximum of 0.8% of the painted area in Alcobaça 419). It is important to bear in mind the extensive use of red lead in medieval illuminations, namely in Portuguese Romanesque illumination. Moreover,
contemporary manuscripts produced in these same *scriptoria* present a more extensive use of red lead [Melo *et al.* 2011]. Rose was only found in one manuscript (*Alcobaça 419*), in a very low percentage of painted area (*circa* 0.3%). The use of a certain brownish-yellow hue was intensive in *Lorvão 16* (*circa* 42% of the painted area). In the *Legendarium* from Sta. Cruz yellow became less brownish and less used than in the *Lorvão 16* (*circa* 13% in *Sta. Cruz 20* and *circa* 5% in *Sta. Cruz 21*). In the *Legendarium* from Alcobaça the use of yellow became almost residual (*circa* 2% in *Alcobaça 419* and 0.4% in *Alcobaça 421*). Red hues (deep organic red and vermilion) were more extensively used in Sta. Cruz than in Alcobaça. In *Sta. Cruz 21* its use was broader (*circa* 57.8%) than the use of the combination of lapis lazuli and bottle-green (*circa* 38%), whereas in *Sta. Cruz 20* it was interesting to verify an identical use of red hues (*circa* 43%) and of the combination of lapis lazuli and bottle-green (*circa* 44%). In the *Hagiographic readings* from Lorvão and Alcobaça an inversion was verified in the extent of use of the combination of lapis lazuli-bottle green. Moreover, in the *Legendarium* from Alcobaça the bottle-green colour was more extensively used than lapis lazuli. It is interesting to notice in the *Passionarium* from Lorvão the evidence of the amount of lapis lazuli being identical to the bottle-green as if those two colours existed in contrast. We emphasise the use of bottle-green in the five manuscripts, which increases from the Sta. Cruz manuscripts to the Lorvão and to the Alcobaça manuscripts, apparently at the expense of the red, *Figure 60*.

c) The use of colour in the context of the *Hagiographic readings*

The analysis of *Figure 61* allows comparison of colour extent on the five *Hagiographic readings*. The percentage corresponds to the area of each paint colour used on the set of manuscripts from each *scriptorium*. In a first analysis it was interesting to verify a roughly constant extent of use of lapis lazuli for the three *scriptoria* (occupying *circa* 23% of the painted area). Vermilion was more extensively used in Sta. Cruz and less used in Lorvão, whereas deep organic red was only used on Sta. Cruz and Alcobaça (and more extensively used in this last *scriptorium*). The use of bottle-green was more extensive in Alcobaça and

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74 For this quantification only the rose paints were considered, and not the rose hues that are part of the *matiz* of lac dye (as in *Alcobaça 421*, f.193v, please see *Figure 57*).

75 According to Aires A. Nascimento, the *Passionarium* from Lorvão (*Lorvão 16*) may not have been produced in the *Lorvão scriptorium*. The author suggests the Sé de Coimbra *scriptorium* – a place with less tradition in illumination production than the Lorvão *scriptorium* – as a possible place for its production, although he is not definite on this attribution [Nascimento 2002]. This could explain the specificity on the presence of this brownish-yellow, not found in the other *Hagiographic readings*. However, a larger number of manuscripts should be analysed to validate these results.
less in Sta. Cruz. It was very interesting to observe a more extensive use of yellow in the *Passionarium* from Lorvão (*Lorvão 16*, 1140) that is, at the same time, the oldest manuscript from this set of five manuscripts and the only that might reflect a deeper influence of the Iberian tradition [Nascimento 2002].

![Figure 61](image)

*Figure 61.* Colour analysis for the *Hagiographic readings* from the Portuguese monasteries of Lorvão (one manuscript), Sta. Cruz (two manuscripts) and Alcobaça (two manuscripts). The percentage hereby presented corresponds to the area of each paint colour used on the set of manuscripts from each *scriptorium*.

Considering the importance of red and blue colours on the medieval palette, it turns interesting to note a larger extent of use of bottle-green colour in the *Legendarium* from Alcobaça at the expense of red hue (vermilion and deep organic red paints). Also, in the *Hagiographic readings* from the Lorvão and Sta. Cruz *scriptoria* bottle-green was used as extensively as lapis lazuli, suggesting a similar importance of these two colours in these *scriptoria*. Somehow, the meaning of spiritual colour is shared between two colours and two cultures, once for the Christian culture it was ascribed to lapis lazuli, whereas for the Islamic culture was ascribed to green. Concerning the use of vermilion, it is interesting to notice the fact that the oldest manuscripts (those produced in the Lorvão and Alcobaça during the 12th-13th century) present fewer areas painted with vermilion, when compared with the *Legendarium* from Sta. Cruz produced in the late 13th century. In the present case, it is not possible to speak of the progression of blue as a change of paradigm in the history of colour use, as referred by Pastoureau, Gage and Brussatin⁷⁶ [Pastoureau 2002; Gage 2009; Brussatin 1995]. In fact, what was possible to verify was a progression of vermilion over deep organic red and bottle-green. It is not likely that this progression has been assigned to an improvement of the financial resources available in the *scriptorium*

⁷⁶ Nevertheless, a larger number of manuscripts should be analysed to validate these results.
(since the amount of lapis lazuli used on the Hagiographic readings remained constant for the three scriptoria), but to the fact that vermilion was more accessible to be used. Another possibility could be the contact / Islamic influence to have been reduced later on.

3.2. *Le vert in Portuguese Medieval illuminations*

Colour production for medieval illuminations was a complex process and good green colours were not available to the medieval artist; saturated deep colours were difficult to obtain and many were not durable [Miguel *et al.* 2009b]. Green paints could be produced by mixing other pigments (notably orpiment with indigo [Bernasconi *et al.* 1993]) and, eventually, by developing new unique recipes. These new recipes could involve the origin of the raw material, the purification procedure and/or the paint preparation. Perhaps more than any other colour, greens were worked and modified to allow for deep, stable, saturated paints, as the green-colour sources that existed at the time (such as malachite, the basic copper carbonate \( \text{Cu}_2\text{CO}_3(\text{OH})_2 \)) did not present such desirable deep hues. Such new recipes and special formulations could be very localised and idiosyncratic, which is the reason why several authors [Bernasconi *et al.* 1993; Dekeyzer *et al.* 1999; Denoël 2000; Gilbert *et al.* 2003] have pointed out that greens can be useful indicators of specific artists, workshops, periods or countries. Considering the Portuguese Romanesque context, as aforementioned, green has an important place on the colour palette of the Lorvão, Sta. Cruz and Alcobaça scriptoria. At the same time, the consistency on its deep saturated colour for the three scriptoria suggests a well-established procedure for its production that might well characterize the Portuguese Romanesque palette [Miguel *et al.* 2009b]. In this section, the colour and molecular characterization of the bottle-green paints appearing on a set of 22 manuscripts from the Lorvão, Sta. Cruz and Alcobaça collections will be presented and its specificities discussed. Furthermore, a comparison with a bottle-green paint from an 11th-12th century manuscript produced at the Fécamp Abbey (*BnF Latin 5062*)77 will be performed, and the results discussed. The illuminations of this manuscript were analysed by Raman microscopy [Coupry 1999]. Coupry identified the presence of a copper-based compound with characteristic Raman bands that could indicate an organic origin for these bottle-green paints, although she was not able to establish any further conclusions on its composition [Coupry 1999, p. 76]. With our analysis, it was possible to go further in this characterization.

77 The manuscript is preserved at the *Bibliothèque nationale de France*. The sample was kindly provided by Doctor Claude Coupry (CNRS, France).
3.2.1. Specificities of Portuguese medieval bottle-green paints

The Portuguese medieval bottle-green paints present a deep green glassy fractured appearance under the microscope, Figure 6. Despite suffering from extensive degradation, this has not affected the brightness or the intensity of the deep green. It has however affected the binding media. As a result bottle-greens are being lost due to a weakening in the cohesion and adhesion to the support. It is important to note that whenever bottle-green stands out from the parchment, the consequent exposed surface of the parchment does not present an apparent degradation, clearly visible in the detail of the bottle-green paint from the Sta. Cruz 1, f.37 (Figure 6, centre).

![Figure 6. Patterns of bottle-green surfaces found in Portuguese Romanesque manuscripts where it is visible its characteristic lost of cohesion and adhesion to the support. From left to right, Lorvão 15, f.5v (1201-1250; magnification 50x), Sta. Cruz 1, f.37 (1151-1200; magnification 80x) and Alcobaça 360, f.2 (13th century; magnification 50x).](image)

Despite some slight variations on the bottle-greens glassiness (as evidenced in Figure 6), its hue does not vary significantly alongside this set of manuscripts of the Lorvão, Sta. Cruz and Alcobaça collections, Table 2.

| Table 2. CIELAB colour coordinates$^a$ for the bottle-green paints of the Lorvão (Lorvão 13, 13th century), Sta. Cruz (Sta. Cruz 34, 1176-1225) and Alcobaça (Alcobaça 238, 12th/14th century) manuscripts. |  |
| --- | --- | --- | --- |
| Manuscript | L* | a* | b* |
| Lorvão 13, f.44v | 38.49±0.55 | -14.18±0.12 | 11.96±0.40 |
| Sta. Cruz 34, f.94v | 33.35±0.01 | -8.26±0.04 | 6.41±0.01 |
| Alcobaça 238, f.210 | 39.57±0.58 | -8.65±0.33 | 11.66±0.36 |
| verdigris | 59.69±0.04 | -37.51±0.17 | -21.94±0.13 |
| malachite | 59.55±0.01 | -30.36±0.02 | 13.40±0.01 |

$^a$The L* coordinate represents the lightness; the a* coordinate the green-red variation and b* the blue-yellow variation.
Moreover, CIELAB colour measurements reveal the absence of the blue component (evidenced by positive values on the b* component), usually present in other green pigments commonly found in medieval illuminations such as verdigris \(^{78}\), Table 2.

Under the microscope using cross-polarized light these bottle-greens appear as a non-crystalline structure, which strongly restricts its molecular characterization. Therefore, its characterization was restricted to the \(\mu\)-EDXRF, \(\mu\)-FTIR and Raman microscopy analysis that will be later presented.

- \(\mu\)-EDXRF

Micro-EDXRF identified copper (Cu), zinc (Zn) and, in some of the cases, lead (Pb) as the main elements present in this bottle-green colour, pointing to the possible use of brass, a copper zinc alloy, as the starting material for the copper-based pigment (please see Appendix VIII for more details on copper alloys). Other elements such as chlorine (Cl), potassium (K) and calcium (Ca) were also detected, but they are also present in the parchment. The elemental ratio of counts for Cu/Zn and Cu/Pb were seen to be consistent for the manuscripts produced in the Lorvão, Sta. Cruz and Alcobaça scriptoria, suggesting that the same or a similar batch of copper-based pigment was used for the production of the bottle-green paints of each manuscript (see Section VIII.2.2 of Appendix VIII). Lead was seldom detected, suggesting that more often an alloy of pure brass was used in the production of the copper-based pigment (see Section VIII.2.2 of Appendix VIII).

- \(\mu\)-FTIR

Infrared spectroscopy proved fundamental for the characterization of the bottle-green paints from the Lorvão, Sta. Cruz and Alcobaça manuscripts, as it demonstrated the most characteristic specificity of these bottle-green paints: the copper proteinate. The idea of producing these bottle-green paints by merely grinding a synthetic copper pigment (such as verdigris \(^{79}\)) with a proteinaceous binder does not allow to match the infrared fingerprint nor the characteristic colour and glassy appearance of these bottle-green paints.

\(^{78}\) Verdigris (Kremer Pigmente, Germany) and malachite (Zecchi, Italy) paint reconstructions were made using parchment glue as binder applied on parchment (Musée du Parchemin et de l’Enluminure, France). Parchment glue was reproduced following a recipe from Libro de como si facem as cores [Strolovitch 2010, p.235], please see Appendix III.

\(^{79}\) For the use of verdigris and general aspects of its production please see Appendix VIII.
Verdigris displays a characteristic infrared spectrum in which the absorptions of the asymmetric and symmetric stretching of the acetate group appear at circa 1635 and 1422 cm\(^{-1}\), respectively [San Andrés et al. 2010]; the absorptions of the asymmetric and symmetric bending of the methyl group appear at circa 1445 and 1353 cm\(^{-1}\), respectively [San Andrés et al. 2010]; and absorption bands of the O-H stretching are also clearly observed in the 3400–3100 cm\(^{-1}\) region [San Andrés et al. 2010], Figure 63. In this Figure is also shown the infrared spectra for parchment glue (a collagen-based binder) and a paint produced by thoroughly grinding this proteinaceous binder with verdigris. The fingerprint for the collagen is evident in the characteristic polyamide absorption pattern, namely the amide I (CO stretching, 1653 cm\(^{-1}\)), amide II (CN stretching and NH bending, 1550 cm\(^{-1}\)) and CN bending at 1450 cm\(^{-1}\), and also by the OH and NH stretching at 3400–3000 cm\(^{-1}\) [Stuart et al. 1997]. In the infrared spectrum of this green paint obtained by mixing a collagen-based binder and verdigris, the fingerprints for both compounds are maintained, and the spectrum can be read as a sum of the two previously described spectra (Figure 63).

![Infrared spectra of (A) parchment glue, (B) verdigris and (C) verdigris ground with parchment glue applied on a parchment support. The inset, molecular structure of copper acetate monohydrated (adapted from [Kyuzou et al. 2010]).](image)
Other possibilities could be considered to explain the copper-protein complexation and the colour and glassy appearance of these bottle-green paints, such as the influence of time over the reaction. However, it is not to be expected that time might lead to the consistent characteristics observable in the bottle-green paints. In this approach a systematic experimental design was followed based on infrared spectroscopy and on a chemometric approach, resulting in new important information on the specificities of these copper-proteinates.

The infrared spectrum of the Portuguese bottle-green paints is characterized by a broad band at \textit{circa} 1645 cm$^{-1}$ that might have resulted from a collapse of the protein (the binder) amide I and II absorption bands (1653 and 1550 cm$^{-1}$, respectively) and the acetate absorption band (\textit{circa} 1635 cm$^{-1}$) of a verdigris-based pigment, indicating the formation of a copper complex with the protein. Also the protein OH and NH stretching absorption bands display a different absorption pattern, where the NH absorption band (\textit{circa} 3350 cm$^{-1}$) is not so evident [Miguel et al. 2009b]. Figure 64.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Characteristic patterns of bottle-greens infrared spectra from the \textit{Sia. Cruz} 27, f.1 (green) and \textit{Alcobaça} 358, f.1 (black). \textit{Grey line}, a representative infrared spectrum of calcium oxalate (\textit{Fluka, Germany}).}
\end{figure}

\textit{Figure 64} presents two patterns found for the copper proteinate band: a full broad band that is usually accompanied by changes on the C-H stretching absorption region (3000-2840 cm$^{-1}$) – \textit{black line} – apparently related with macroscopic changes in the bottle-green
paints (such as the loss of cohesion and adhesion increases, the most altered is the C-H stretching absorption region); and a situation where this complexation is not yet completed – green line. However, it is important to stress that despite this loss of cohesion and adhesion, even the most altered bottle green paints preserve their deep bright saturated colour. Furthermore, the characteristic absorption bands of calcium oxalate\(^8\) (Ca\(_2\)C\(_2\)O\(_4\)\(n\)H\(_2\)O) at 1322 and 784 cm\(^{-1}\) [Rampazzi et al. 2004] were systematically found in the infrared spectra of the bottle green paints, Figure 64 - grey line. Due to the presence of the copper proteinate band at circa 1645 cm\(^{-1}\) the calcium oxalate band at circa 1640-1620 cm\(^{-1}\) cannot be clearly established.

As aforementioned, the manuscripts from the Sta. Cruz collection were studied in the context of a Molab mission in 2009. In the framework of this mission, it was possible to analyse these bottle-green paints by Fiber-optic FTIR reflectance spectroscopy. Of the analysis of 38 bottle-green paints surfaces, circa 63% of the paints present the characteristic absorption bands of oxalate: C=O stretching, combined with H-O-H bending of crystallization water at 1622 cm\(^{-1}\), and C-O stretching at 1319 cm\(^{-1}\) [Ricci et al. 2006], Figure 65.

\[
\text{Figure 65. Fiber-optic FTIR reflectance spectrum from a bottle-green paint of Sta. Cruz 20, f.138 (13th century).}
\]

\(^8\) Calcium oxalate is a degradative oxidation product of organic materials, as the proteinaceous binder, with calcium compounds, as calcite (CaCO\(_3\)), present on the parchment’s surface as a surface pre-treatment [Rampazzi et al. 2004].
Fiber-optic FTIR reflectance spectroscopy did not allow identification of any further absorption bands ascribed to the molecular structure of these bottle-green paints. Nevertheless, it allowed verification that the bottle-green paints for which were identified the highest intensities for the characteristic absorption bands of oxalate were not those where the greatest macroscopic alteration is observed (loss of cohesion and adhesion to the support). As this is a surface analysis technique, this might suggest that the oxalate is more related to a degradation that is occurring on the bottle-green paint surface, and not to the degradation responsible to the loss of cohesion and adhesion to the support.

Principal Component Analysis (PCA) was applied to the C-H absorption region (3000-2840 cm\(^{-1}\)) and to the proteinate absorption region (1770-1490 cm\(^{-1}\)) of a set of 72 infrared spectra of bottle-green paints from the Lorvão, Sta. Cruz and Alcobaça manuscripts\(^{81}\) (please see representative spectra of bottle-green paints for each manuscript in Appendix VII.1). Additionally included was an infrared spectrum from a bottle-green paint from a manuscript produced in Fécamp Abbey’s scriptorium (BnF Latin 5062, 1078-1108). This approach intended to study if there was a relation between the band ascribed to the copper-protein complexation and the alterations on the C-H stretching absorption region\(^{82}\), if these specificities could somehow discriminate the bottle-green paints between scriptoria, and whether they might be specific for the Portuguese Romanesque scriptoria or not.

\(\text{a) C-H absorption region (3000-2840 cm}^{-1}\)\\n
The infrared spectra analysis of the bottle-green paints restricted to the C-H stretching absorption region allowed identification of two distinct situations: the presence of the characteristic absorption bands of the binder (\(\nu_{\text{asym}}(\text{CH}_3)\) at 2965 cm\(^{-1}\), \(\nu_{\text{asym}}(\text{CH}_2)\) at 2936 cm\(^{-1}\) and \(\nu_{\text{sym}}(\text{CH}_3)\) at 2876 cm\(^{-1}\)), and the situations where the protein has suffered greater alterations and where these characteristic absorption bands are no longer present, Figure 66, right.

\(^{81}\) PCA was applied to infrared spectra of bottle-green paints from 4 manuscripts (6 micro-samples; 8 infrared spectra) of the Lorvão collection, 5 manuscripts (13 micro-samples; 42 infrared spectra) of the Sta. Cruz collection and 12 manuscripts (18 micro-samples; 22 infrared spectra) of the Alcobaça collection. All infrared spectra were pre-processed for baseline slope correction, followed by standard normal variate (SNV) and positivity correction by adding each spectrum to its minimum value. Afterwards, spectra were processed with a Savitzky-Golay filter with 15-points window size, 2\(^{nd}\) order polynomial and 1\(^{st}\) derivative, followed by mean centring (please see Appendix IV).

\(^{82}\) The scores analysis was based on the analysis of the loadings for PC1 and PC2 and of each infrared spectrum.
Figure 66. Left, scores plot of PCA model applied to the C-H absorption region (3000-2840 cm\(^{-1}\)) of the infrared spectra of bottle-green paints from the Lorvão (grey squares), Sta. Cruz (green circles), Alcobaça (black triangles) and Fécamp (red circle) manuscripts. Right, infrared spectra of bottle-green paints from Sta. Cruz 27, f.1 (green) and Alcobaça 358, f.1 (black) evidencing the two distinct patterns found for the C-H absorption region. The PCA scores of both infrared spectra are highlighted by yellow circles (left).

Figure 66 (left) shows the scores plot of the PCA model applied to the infrared spectra of the bottle-green paints from the Lorvão, Sta. Cruz and Alcobaça manuscripts restricted to the C-H absorption region. It was verified that the first principal component (PC1) includes circa 64\% of the variability of the infrared spectra restricted to this wavenumber region. It concerns the presence or absence of the absorption bands of the symmetric and asymmetric stretching of the methyl and the methylene groups: for negative PC1 values, the infrared spectra present no C-H stretching absorption, whereas for positive PC1 values, the C-H stretching absorptions are present. The second principal component (PC2) includes circa 26\% of the variability in the infrared spectra restricted to this infrared region. This variability is ascribed to alterations in the methyl group evidenced by changes in the intensity of the absorption bands of the \(\nu_{\text{asym}}(\text{CH}_3)\) at 2965 and the \(\nu_{\text{sym}}(\text{CH}_3)\) at 2876 cm\(^{-1}\): for negative PC2 values, these two bands show the lowest intensity, whereas for positive PC2 values, they present the highest intensity values. PCA of the infrared spectra restricted to this wavenumber region showed two main clusters concerning: A) the infrared spectra where the characteristic C-H absorption bands are absent; and B) the infrared spectra where these features are present, Figure 66, left. Although it was verified that the majority of the Lorvão infrared spectra present less alterations in this region whereas the majority of the Alcobaça infrared spectra no longer present the bands ascribed to the C-H stretching absorptions (with exception to Alcobaça 412, 426 and 433), it is not possible to make absolute a conclusion on discrimination between scriptoria. Concerning the manuscripts
from Sta. Cruz collection, *Sta. Cruz* 20, 21, 27 and 34 are those that show less changes in this region. Again it would be necessary to analyse a larger number of manuscripts to validate these results.

**b) Proteinate absorption region (1770-1490 cm\(^{-1}\))**

As aforementioned, the infrared spectra analysis of bottle-green paints restricted to the proteinate absorption region (1770-1490 cm\(^{-1}\)) showed two different situations: one situation where a full broad band ascribed to the copper proteinate complexation is present – *black line, Figure 67, right* - and another where this compexation is not yet completed – *green line, Figure 67, right*.

![Diagram](image)

**Figure 67.** Left, scores plot of PCA model applied to the proteinate absorption region (1770-1490 cm\(^{-1}\)) of the infrared spectra of bottle-green paints from the Lorvão (grey squares), Sta. Cruz (green circles), Alcobaça (black triangles) and Fécamp manuscripts (red circle). Right, infrared spectra of bottle-green paints from *Sta. Cruz* 27, f.1 (green) and Alcobaça 358, f.1 (black) demonstrating the two distinct patterns found for the proteinate absorption region. The PCA scores of both infrared spectra are highlighted by yellow circles (left).

The scores plot of the PCA model applied to the infrared spectra of bottle-green paints restricted to this wavenumber region (1770-1490 cm\(^{-1}\))\(^{83}\) is shown in *Figure 67, left*. The first principal component (PC1) includes circa 63% of the total spectral variability and concerns the variability on the broad band at *circa* 1645 cm\(^{-1}\): for negative PC1 values the infrared spectra present a full broad band, whereas for positive PC1 values the complexation is not yet fully present. Concerning the second principal component (PC2), it includes *circa* 18% of the total spectral variability and is related with the variations on the broadening of the three bands (1653, 1624 and 1560 cm\(^{-1}\)), and not to changes in its

\(^{83}\) The scores analysis was based on the analysis of the loadings for PC1 and PC2 and of each infrared spectrum.
intensities: for negative PC2 values the three bands are shaped, whereas for positive PC2 values, they become broadened (please notice that despite PC2 justifies the infrared variability on the broadening of each three absorption bands, the copper proteinate band at circa 1645 cm$^{-1}$ is justified by the variability on PC1). The analysis of the infrared spectra clusters observed in the scores plot revealed two main spectral groups: A) one group where a full broad band ascribed to the copper proteinate complexation is present; and B) another group where this compexation is not yet completed, Figure 67, left. Again, it was not possible to discriminate between scriptoria. However, it was verified that the Sta. Cruz manuscripts’ samples are those on which the copper proteinate band is less fully complexed. Moreover, it was interesting to verify an inconsistency for both volumes of the Legendarium (Sta. Cruz 20 and Sta. Cruz 21, 13th century) on the presence of the full broad proteinate band, for a same manuscript (some paints present a full broad band, whereas others present the broad band not fully complexed), which may reflect an inconsistency in the bottle-green paint’s production or an heterogeneous molecular evolution over time in this paint. The bottle-green paints from Alcobaça presented deeper full broad proteinate bands, with exception to Alcobaça 412, 426 and 433 (an exception that was also verified for the C-H absorption region).

Despite not being possible to establish a discrimination between scriptoria, PCA results indicate a possible relation between the copper proteinate complexation and the alterations on the methyl and the methylene groups of the protein: infrared spectra presenting less collapsed bands present a less altered C-H stretching absorption region, whereas those presenting broader copper-proteinate bands (as those from Alcobaça bottle-green paints) do not show the characteristic bands ascribed to the absorption of the C-H stretching. This relation may well be ascribed to the intervention of both substituent groups on the copper-protein reaction, but also to a relation between the broadening of the copper-proteinate band and the alterations on the molecular structure of the protein, responsible for the cohesion loss of these bottle-green paints.

Concerning the presence of calcium oxalate identified by its characteristic absorption bands at 1322 and 784 cm$^{-1}$ (Figure 64), it was verified that the infrared spectra that presented less alterations on the C-H absorption region and less complexed copper proteinate bands, are those where the oxalate band has higher absorption. Moreover, the Lorvão bottle-green paints presented higher oxalate absorptions, whereas for the Sta. Cruz
and Alcobaça paints the oxalates absorption band at \textit{circa} 1322 cm\textsuperscript{-1} (the most intense band of calcium oxalate) was identified both with higher and lower absorptions.

The analysis of a microsample from a bottle-green paint of an 11th-12th century manuscript produced at the Benedictine Abbey of Fécamp (\textit{BnF Latin 5062}, 1078-1108) showed the same infrared pattern found for the Portuguese Romanesque illuminations: the copper proteinate band at \textit{circa} 1635 cm\textsuperscript{-1}, the changes on the C-H stretching absorption region (3000-2840 cm\textsuperscript{-1}) as shown by the PCA analysis restricted to these to wavenumber regions, please see \textit{Figures 66-67}. Likewise identified was the presence of the characteristic absorption band at 1322 and 784 cm\textsuperscript{-1} of calcium oxalate, \textit{Figure 68}.

![Figure 68. Infrared spectrum of a bottle-green paint from an 11th-12th century manuscript produced at the Fécamp Abbey (\textit{BnF Latin 5062}, 1078-1108) kindly provided by Dr. Claude Coupy. The inset, a detail from where micro-sampling was performed (Photo © Presses Universitaires de Caen).](image)

The noticeable similarities found between the infrared spectra of the bottle-green paints from the Lorvão, Sta. Cruz and Alcobaça collections and the Benedictine Abbey of Fécamp might well indicate a well-established procedure to produce deep saturated glassy greens for illumination during the medieval period, and that apparently it was not restricted to the Portuguese monasteries. If a similar procedure was followed to produce these bottle-green paints it explains the similar degradation patterns found on these paints (both macroscopic and molecular degradations), and the noticeable absence of parchment corrosion underneath the paints, usually ascribed to copper-based paints.
Raman microscopy

A typical verdigris-based compound Raman spectrum is characterised by the bands ascribed to the acetate groups at 2993, 2935, 1412, 1350 and 707 cm\(^{-1}\) [Chaplin et al. 2006; Nakamoto 2009, p.64; San Andrés et al. 2010], Figure 69. Other bands are also present, namely the bands ascribed to the water coordination at circa 320 cm\(^{-1}\) and the vibrations ascribed to the C-C bonds [Chaplin et al. 2006; Nakamoto 2009, p.64; San Andrés et al. 2010], Figure 69.

![Figure 69](image)

**Figure 69.** Representative Raman spectrum of verdigris reproduced following the recipe described in the *Libro de como si facem as cores*\(^\text{84}\). The inset, molecular structure of copper acetate monohydrated (adapted from [Kyuzou et al. 2010]).

For the majority of the Raman spectra of historical bottle-green paints, the obtained spectra exhibit a high fluorescent background obscuring most of the spectral features, rendering it impossible to determine the exact nature of the compound. The analysis of the bottle-green paints from the Lorvão manuscripts by Raman microscopy revealed inconclusive. The analysis by Raman microscopy of a bottle-green microsample from *Sta. Cruz 1, f.2 (Bible, 1151-1200)* show weaker bands at circa 1576, 1524, 1451, 1364, 685 and 350 cm\(^{-1}\), in agreement with some of the spectral features of a verdigris-based compound [Chaplin et al. 2006; Nakamoto 2009, p.58, 64; San Andrés et al. 2010], Figure 70. In addition the stretching vibrational bands of the methyl group, usually three at circa 2930-3020 cm\(^{-1}\)

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\(^{84}\) Spectrum collected using 632.8nm excitation, a 100x objective and 0.17 mW laser power at the surface sample (accumulation time: 30 s, for one cycles).
with one of them being quite strong [San Andrés et al. 2010], are collapsed into one broad band at \textit{circa} 2939 cm$^{-1}$. The observed band at \textit{circa} 1250 cm$^{-1}$ corresponds to the amide III fingerprint of the protein-based binder [Muralha et al. 2012], \textit{Figure 70}.

\begin{center}
\begin{figure}
\includegraphics[width=\textwidth]{raman_spectrum.png}
\caption{Raman spectrum of a bottle-green paint from \textit{Sta. Cruz I, f.2} (Bible, 1151-1200).
}
\end{figure}
\end{center}

The hydroxyacetates and hydrated acetates show characteristic bands in the region between 3050–3650 cm$^{-1}$, providing a fingerprint of the hydroxyl content of the samples [San Andrés et al. 2010]. However in the present results the presence of these bands is not evident. Moreover, the low-intense broad band at \textit{circa} 1451 cm$^{-1}$ might be attributed to a vibrational band from the acetate (COO$^-$) ion [Nakamoto 2009, p.64; San Andrés et al. 2010]. The band at 685 cm$^{-1}$ might be attributed to the O-C-O deformation modes whereas the bands at 1364, 1524 and 1576 cm$^{-1}$ might be ascribed to the carboxilate group [Nakamoto 2009, p.64; San Andrés et al. 2010]. Finally, the broad intense band at 350 cm$^{-1}$ is ascribed to the water coordination [Nakamoto 2009, p.58].

Raman analysis of the bottle-green paints from the Alcobaça manuscripts showed broader bands suggesting higher molecular alterations on these paints, \textit{Figure 71}.
The analysis of a bottle-green microsample from *Alcobaça 238, f.210* (*De Avibus, 12th/14th century*) shows a broad band at circa 2942 cm\(^{-1}\) (that might be ascribed to the collapse of the stretching vibrational bands of the methyl group [San Andrés *et al.* 2010]), another strong broad band at circa 1450 cm\(^{-1}\), and weaker bands at circa 700, 345 and 321 cm\(^{-1}\), again in agreement with some of the spectral features of a verdigris-based compound [Nakamoto 2009, p.58, 64; San Andrés *et al.* 2010], *Figure 71*. However, the strong broad band at circa 1450 cm\(^{-1}\) appears to have a collapsed band at circa 1315 cm\(^{-1}\), all corresponding to vibrational bands from the acetate (COO\(^{-}\)) ion, *Figure 71* [San Andrés *et al.* 2010].

The Raman results corroborate the infrared results previously presented, where a copper proteinate is identified. It also corroborated the molecular alterations that were more pronounced on Alcobaça rather than on Sta. Cruz bottle-green paints. Finally, it was possible to identify for the first time the characteristic vibrational bands from the acetate (COO\(^{-}\)) ions on copper proteinates, suggesting the use of a verdigris pigment as the copper-source used on the production of these bottle-green paints.

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*Spectrum collected using 632.8 nm excitation, a 50x objective and 0.17 mW laser power at the surface sample (accumulation time: 10 s, for three cycles).*
3.2.2. Medieval textual sources on producing synthetic copper pigments

Synthetic copper greens constitute an important subject for art technological source research. There are a considerable number of medieval recipes for the production of copper-based pigments that use very specific medieval terminology and which sometimes lack important information on quantities and temperatures [Oltrogge 2005]. Its reproduction often becomes a laborious and challenging task. In order to cover all reasonable possibilities for the production of copper-based green pigments in medieval times, besides verdigris, other synthetic copper pigments of a blue hue should also be mentioned, such as the copper blue pigment lime blue (copper hydroxide-based pigment), which has already been successfully synthesised based on medieval recipes from the late 11th century in the Mappae Clavicula, to recipes from the 15th century in the Bolognese Manuscript [Krekel et al. 2003]. Another copper blue pigment described in medieval recipe books as the Mappae Clavicula [Smith and Hawthorne 1974, p.21] or the Libro de como si facem as cores [Strolovitch 2010, p.227] is the so-called silver blue, produced from silver coins or silver leaves. In fact, medieval silver was impure and used to contain copper in its composition [Merrifield 1999, p.ccx]; and silver blue was in fact a copper acetate formed from the copper content of the silver used on the recipe [Orna et al. 1980; Orna et al. 1985]. Its production and characterization was widely studied by Orna et al. [Orna et al. 1980; Orna et al. 1985; Orna 1996]. Besides the several recipes for producing lime blue and silver blue, there is a large number of medieval recipes describing how to produce synthetic copper pigments, many differing on the materials used as starting components, leading to the production of different copper complexes. The review published by Scott et al. on copper carboxylates is of considerable importance, as it presents the synthesis and characterization of several basic copper acetates, basic calcium copper acetates and chlorates, using recipes from medieval sources [Scott et al. 2001b]. Other copper sources could have been used for producing green painted illuminations, such as copper sulphates like the mineral posnjakite, CuSO₄·3Cu(OH)₂·H₂O that has already been identified in illuminations from the 14th-15th century [Gilbert et al. 2003]. Other copper-sulphate minerals could have been used as green pigments, such as antlerite [CuSO₄·2Cu(OH)₂], brochantite [CuSO₄·3Cu(OH)₂], langite [CuSO₄·3Cu(OH)₂·2H₂O] [Gilbert et al. 2003].

To fully characterize the bottle-green paints, it was fundamental to identify the copper source used in its production. Considering the evidence from the molecular
characterization of the historical bottle-green paints for the possible use of a copper acetate as the copper source used in its formulation, our approach focused on reproducing synthetic copper-acetate pigments. Nevertheless, other copper sources were tested such as copper chlorides \( (\text{CuCl}_2.2\text{H}_2\text{O}) \), sulphates \( (\text{CuSO}_4.5\text{H}_2\text{O}) \) and carbonates \( (\text{CuCO}_3.\text{Cu(OH)}_2) \), but none led to the bottle-green colour, to its molecular infrared fingerprint nor to its characteristic glassy appearance [Miguel et al. 2009b].

**- reproducing medieval copper-acetate pigments**

A selection of medieval recipes for producing synthetic copper-acetate pigments was reconstructed, following the medieval instructions as accurately as possible, *Table 3*.

*Table 3.* Medieval recipes tested to reproduce the bottle-green colour and main results.

<table>
<thead>
<tr>
<th>Copper complex</th>
<th>Treatise</th>
<th>Variables</th>
<th>Main results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper acetates</td>
<td><em>Libro de como si facem as cores</em></td>
<td>Copper</td>
<td>Bluish-green pigment</td>
</tr>
<tr>
<td></td>
<td>13th-14th century</td>
<td>Vinegar</td>
<td></td>
</tr>
<tr>
<td>Calcium copper acetates*</td>
<td><em>Secretum Philosophorum</em></td>
<td>Copper</td>
<td>Bluish-green pigment</td>
</tr>
<tr>
<td></td>
<td>14th century</td>
<td>Marc⁸⁶</td>
<td></td>
</tr>
<tr>
<td>Basic copper acetates*</td>
<td><em>Mappae Clavicula</em></td>
<td>Copper</td>
<td>Blue-turquoise pigment</td>
</tr>
<tr>
<td></td>
<td>9th-12th century</td>
<td>Vinegar</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lime</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>De diversis artibus</em></td>
<td>Copper</td>
<td>Greenish-blue pigment</td>
</tr>
<tr>
<td></td>
<td>12th century</td>
<td>Vinegar</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Soap</td>
<td></td>
</tr>
</tbody>
</table>

*Procedure according to [Scott et al. 2001b] descriptions. Please find detailed instructions for the four recipes in Appendix VIII.

The recipes that were closest in colour were those from the Portuguese *Libro de como si facem as cores* [Strolovitch 2010, p.228], *Secretum Philosophorum* [Clarke 2009] and *De diversis artibus* [Hawthorne and Smith 1963, p.32], *Figure 72*. However, after being ground, all lost hue and saturation. As the µ-EDXRF analysis of historical bottle-green paints pointed to the possible use of brass for producing the synthetic copper pigment, the reproduction of copper acetates pigments were performed using brass leaves with circa 30% (wt%) of zinc. µ-EDXRF analysis of the copper-acetate pigment produced following the recipe from the *Libro de como si facem as cores* showed an elemental ratio of counts for Cu/Zn close to the ones found for the historical bottle-green paints. Nevertheless, it was

⁸⁶ The refuse of grape skin from the wine-press [Thompson 1956].
verified that the presence of zinc in copper acetate’s composition does not influence either the final colour, the characteristic molecular pattern nor the final glassy appearance of the bottle-green paint’s reconstructions.

Infrared analysis showed strong similarities between the copper-acetate produced by the recipes described in *Secretum Philosophorum* and in *De diversis artibus*, in which were identified the most characteristic verdigris absorption bands at 3457, 3365, 3266, 1635, 1445, 1422 and 1353 cm$^{-1}$ [San Andrés et al. 2010], Figure 72. The pigment produced following the *Libro de como si facem as cores* presented changes in the characteristic ν(OH) at 3457, 3365 and 3266 cm$^{-1}$. Again, the pigment produced following the *Mappae Clavicula* recipe presented the most altered spectrum for the O-H stretching absorption region (3600-3000 cm$^{-1}$), Figure 72. After ground and applied as a paint$^{87}$, the

$^{87}$ Paints were produced with parchment glue that was reproduced following a recipe from *Libro de como si facem as cores* [Strolovitch 2010, p.235] and applied over parchment, please see Appendix III and IV.
four copper salts obtained following the procedures described in *De diversis artibus* by Theophilus, the *Mappae clavicula*, the *Secretum Philosophorum* and the *Libro de como si facem as cores* did not match either the colour or the infrared spectra of the bottle-green found in the Lorvão, Sta. Cruz and Alcobaça manuscripts. As infrared analysis of historical bottle-green paints points to a copper proteinate, complexation with parchment glue was tested over a range of temperatures from 20 to 70°C, and followed by µ-FTIR, with no success. However, from these results it was possible to verify that copper acetates presented the best features for being tested on other approaches for reproducing bottle-green paints, as will be presented.

### 3.2.3. Reproducing bottle-green paints

As none of the previously described reconstructions led to the intended results (that is the deep saturated colour, the glassy appearance and the characteristic molecular fingerprint), new variables were introduced and tested, attempting to reproduce the historical bottle-green paints. Chapter XXVIII of the *Libro de como si facem as cores* reads thus: ‘If you wish to make green and to temper it, add vinegar and green and egg yolk and grind it all together’ [Strolovitch 2010, p.233]88. Based on this information, the influence of vinegar was tested89, as well as the influence of the heating procedure on the copper proteinate complexation. Both parameters proved crucial to closely reproduce the deep-green glassy appearance as well as the characteristic molecular fingerprint of the historical bottle-green paints from the Lorvão, Sta. Cruz and Alcobaça manuscripts. The main finds and specificities of this reproduction will be presented and discussed in the following section.

#### - the role of vinegar on the final colour hue

Several commercial white and red vinegars were used to redissolve verdigris, as well as a number of oak-matured homemade vinegars90 (please see the procedure for redissolving verdigris in *Section VIII.4 of Appendix VIII*). A 50-year-old homemade vinegar enabled us

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88 Other recipe books such as the *Montpellier Manuscript* (14th century) recommend the use of vinegar, wine and a mixture of vinegar and honey for tempering greens [Clarke 2011b, p.113-114]. Our reconstructions using several biological/organic wines did not result in reproduction of the bottle-green paints. The reproductions using a mixture of commercial vinegars and biological honeys did not result in a deep saturated green colour, although it was possible to reproduce the characteristic glassy appearance.

89 Egg yolk was also tested as suggested by the recipe, but no good results were achieved either on reproducing the glassy appearance or the characteristic molecular fingerprint of the historical bottle-green paints.

90 These homemade vinegars were oak matured over one to two years. An older one, aged circa 50 years, was oak matured over circa 30 years, then transferred to an earthenware wine container and stored for circa 10 years, and then further bottle matured for approximately 10 more years.
to reproduce a bottle-green colour paint comparable to the original bottle-green paints, 

Table 4.

Table 4. CIELAB colour coordinates\(^6\) for the bottle-green paints of the Lorvão (Lorvão 13, 13\(^{\text{th}}\) century), Sta. Cruz (Sta. Cruz 34, 1176-1225) and Alcobaça (Alcobaça 238, 12\(^{\text{th}}\)/14\(^{\text{th}}\) century) manuscripts, and for the bottle-green paint’s reconstruction.

<table>
<thead>
<tr>
<th>Manuscript</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lorvão 13, f.44v</td>
<td>38.49±0.55</td>
<td>-14.18±0.12</td>
<td>11.96±0.40</td>
</tr>
<tr>
<td>Sta. Cruz 34, f.94v</td>
<td>33.35±0.01</td>
<td>-8.26±0.04</td>
<td>6.41±0.01</td>
</tr>
<tr>
<td>Alcobaça 238, f.210</td>
<td>39.57±0.58</td>
<td>-8.65±0.33</td>
<td>11.66±0.36</td>
</tr>
<tr>
<td>Bottle-green reproduction</td>
<td>38.45±0.36</td>
<td>-12.15±0.14</td>
<td>5.10±0.15</td>
</tr>
</tbody>
</table>

\(^6\)The L* coordinate represents the lightness; the a* coordinate the green-red variation and b* the blue-yellow variation.

The commercial vinegars are more pure and less complex than homemade oak-matured vinegars. HPLC–DAD\(^{91}\) and \(^1\)H NMR\(^{92}\) analyses of the set of commercial and homemade vinegars allowed to identify possible elements in the 50-year-old homemade vinegar that might play a significant role in the final colour, as the presence of gallic, citric, maleic and formic acids (detected by HPLC–DAD), and a considerable amount of sugars (namely glucose, galactose and fructose) and ethanol (detected by \(^1\)H NMR) \cite{Miguel et al. 2009b}. The presence of gallic acid proved crucial for reproducing the bottle-green colour. In fact, several reproductions using vinegars presenting gallic acid in its composition gave these results, whereas the reproductions using vinegars without gallic acid in its composition did not produce the bottle-green colour. Gallic acid was also tested to dissolve verdigris, demonstrating its contribution on the bottle-green colour reproduction. Moreover, the presence of sugars strongly contributed to the final glassy appearance. Our experimental evidence suggests that the complexation between the copper (II) ion and the phenolic compounds present in oak matured vinegars is responsible for the colour change from the bluish-green colour that characterizes verdigris into a bottle-green paint.

- **the role of the copper-protein complexation in the paint’s transparency**

The copper-protein complexation step showed the crucial role of the binding media on the paint’s transparency. More specifically, it was verified that both heating time and

\(^{91}\) High Performance Liquid Chromatography–Diode Array Detection, HPLC-DAD.

\(^{92}\) Proton Nuclear Magnetic Resonance spectroscopy, \(^1\)H NMR.
temperature during the parchment glue addition to the verdigris treated with the 50-year-old homemade vinegar plays an important role on the copper-binder complexation and to the transparency of the paint. Moreover, it was verified that applying egg white as a varnish strongly contributes to match the glassy appearance and the characteristic absorption bands at 1653, 1560 and 1406 cm\(^{-1}\) of the bottle-green paints, *Figure 7*.

*Figure 7*. Infrared spectrum of synthesised bottle-green paint with verdigris and 50-year-old homemade vinegar and parchment glue applied on a parchment support with egg white applied as varnish. *The inset*, a detail from the reproduced bottle-green paint (magnification 50x).

Besides being possible to match the infrared spectra of the historical bottle-green paints, these reproductions allowed us to go further in the molecular characterization of the historical samples. In fact, the infrared spectra of the historical bottle-green paints consistently displayed a medium-broad band at *circa* 1410-1400 cm\(^{-1}\). This band is commonly attributed to the \(\nu(CO_3^{2-})\) stretching, that could indicate the presence of carbonates as an extender (that was not so likely possible, due to the transparency of these paints and to the low amount of calcium detected by XRF analysis, most probably present on the parchment surface). In fact, it was verified that the band at *circa* 1406 cm\(^{-1}\) that was consistently present for all the infrared spectra of bottle-green paints reconstructions resulted from the complexation of the \(\delta(CN)\) bending of the protein at *circa* 1450 cm\(^{-1}\) with the \(\delta_{asym}(CH_3)\) of verdigris at *circa* 1445 cm\(^{-1}\).

Infrared analysis proved crucial for characterizing the specificities of the historical bottle-green paints. However, it would not be possible to go so far with the characterization of these copper-proteinate paints without an experimental design strongly based on the
analysis of medieval treatises, on the analytical results of the historical paints and on accurate paint reconstructions based on the two previous approaches.

Finally, the heavy *craquelure* pattern and loss of adhesion to the support observed in the bottle-greens is not present in the recently painted bottle greens, as both the extensive *craquelure* and loss of adhesion may be considered natural phenomena of the ageing of a rather thick paint. The deep, homogenous and brilliant green hue displayed by the historical bottle-green paints prompts us to propose that the colour changes during ageing are minor.

### 3.2.4. Final remarks on *Le vert* in Portuguese Medieval illuminations

The study of the bottle-green paints from the Portuguese Medieval illuminations demonstrated the importance of following a systematic approach based on the analytical study of the materials, on the contemporary written sources and on accurate reconstructions based on both, whenever one aims to deeply study a paint formulation; meaning, not only to characterize the materials, but how the paints formulation might have been produced. Considering these bottle-green paints, one must also take into account the influence of time on the paint (in the present case, nine centuries of ageing), that much might have contributed to changes both on a macroscopic level (such as the loss of cohesion and adhesion to the support) as on a molecular level (such as the presence of oxalates or the alterations on the methyl groups observed in these paints). It was a complex work that we do believe has contributed largely to a new overview over the formulations of copper-proteinate bottle-green paints. With our results on the specificities of these paints formulations we do believe that much can now be done on the study of the degradation mechanism of these bottle-green paints as a contribution to its conservation, that needs to be performed.

### 3.3. *Le rouge* in Portuguese medieval illuminations

Red mercury (II) sulphide was the inorganic red source *par excellence* in medieval illumination. It is found in nature as red cinnabar (α-HgS) or, less frequently, as black metacinnabar (β-HgS)

93 [Eastaugh et al. 2008]. When obtained by synthesis, red α-HgS receives the name of vermilion. In this section, the colour and formulation specificities of

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93 For more details on black and red mercury (II) sulphide, please see Appendix IX.
the red paints from 18 manuscripts from the Lorvão, Sta. Cruz and Alcobaça collections will be presented and discussed. For the first time, it was possible to characterize the use of binding media formulations in medieval illuminations. Moreover, the full rationalization will be presented for the recipe mentioned to produce vermilion in the Portuguese medieval manuscript the *Libro de como si facem as cores* [Strolovitch 2010, p.229]. Its particularities will be discussed and compared with what was found for the red paints from the Lorvão, Sta. Cruz and Alcobaça collections. Within this approach, it was possible to go further in the characterization of the solid-state reaction behind the production of vermilion following the *dry process*.

### 3.3.1. Specificities of Portuguese medieval red paints

Red was used in Portuguese Romanesque illumination as writing ink and to paint the *rubricae* and the illuminations. In general, red paints display a very good conservation condition, although under magnification the presence of *craqueleure* is clear, *Figure 74*.

*Figure 74*. A red paint surface from *Alcobaça 419, f.91v* where it is visible the characteristic microscopic *craqueleure* found in the red paint surfaces found in Portuguese Romanesque illuminations. Photos © BNP.

There is no obvious visual colour variation in the red paints, *Figure 75*. However, CIELAB colour measurements reveal notable variations in the yellow component (demonstrated by the variations in the *a* component) that may well indicate paints of different thicknesses.

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94 For more details on vermilion synthesis, please see Appendix IX.
(the CIELAB colour measurements of thicker layers will be less influenced by yellowing parchment than thin layers) Table 5.

![Cedar of Lebanon representation](image)

**Figure 7.5.** Representation of the *Cedar of Lebanon* in the three Portuguese copies of *De Avibus*. From *left to right*, *Lorvão 5*, f.25 (1183/86), *Sta. Cruz 34*, f.94v (1176-1225) and *Alcobaça 238*, f.210 (12th/14th century). *Light-green circles* indicate the areas of colorimetric measurements. Photos © ANTT, ©BPMP and ©BNP.

**Table 5.** CIELAB colour coordinates of red paints from the representation of the *Cedar of Lebanon* on the three Portuguese copies of *De Avibus*.

<table>
<thead>
<tr>
<th>Manuscript</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Lorvão 5</em>, f.25</td>
<td>47.00±0.09</td>
<td>37.25±0.21</td>
<td>29.52±0.21</td>
</tr>
<tr>
<td><em>Sta. Cruz 34</em>, f.94v</td>
<td>51.78±0.69</td>
<td>41.76±0.52</td>
<td>39.87±0.19</td>
</tr>
<tr>
<td><em>Alcobaça 238</em>, f.210</td>
<td>49.17±0.08</td>
<td>38.35±0.23</td>
<td>34.48±0.10</td>
</tr>
</tbody>
</table>

µ-EDXRF consistently detected the presence of mercury (Hg). As Hg(Mα)≈S(Kα), it was not possible to detect sulphur (S). Other elements such as potassium (K) and calcium (Ca) were also detected, but they are also present in the parchment. However, for a significant set of red paints, calcium was detected with higher intensities than in the parchment, suggesting its presence in the paints’ formulation.

**- Raman microscopy**

The bright red colour found in Portuguese Romanesque illuminations was accomplished with vermilion red (α-HgS), as demonstrated by Raman microscopy through its
characteristic bands at 342 cm\(^{-1}\) attributed to the \(\nu\)(Hg-S) stretching, and to the bands at 252 and 284 cm\(^{-1}\) ascribed to the \(\delta\)(S-Hg-S) angle bending [Frost et al. 2010] (for representative spectra of vermilion red, please see Figure 28-right).

- **SEM-EDS**

Three red historical micro-samples from the Lorvão 43, f.200, Santa Cruz 27, f.15 and Alcobaça 238, f.206v were analysed by SEM-EDS for characterizing its morphology and identifying the existence of tracing elements in their composition\(^95\), Figure 76.

![Figure 76. From left to right, Lorvão 43, f.200 (Lorvão Apocalypse, 1189), Sta. Cruz 27, f.15 (Salterium, 1179) and Alcobaça 238, f.206v (De Avibus, 12th/14th century). Light-green circles indicate the areas of microsampling and of colorimetric measurements. Photos © ANTT, © BPMP and © BNP.](image)

The backscattered images of the three red historical samples show a similarity in the morphology of the three samples and the morphology of a red paint produced with cinnabar from Almadén mines\(^96\), Figure 77. The particle size of the historical samples is in consistency with the particles size of cinnabar paint reproductions. Furthermore, the heterogeneity of the particle sizes of the historical samples (sizes vary from circa 0.3 \(\mu\)m to 1.4 \(\mu\)m) suggests that grinding was not very effective, while simultaneously the shape of the particles suggests that a crushing procedure might have been used (the particles appear more to have been crushed than ground), Figure 77.

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\(^95\) Depending on the chemical element, the detection limit of EDS analysis may reach 0.2% (%wt).

\(^96\) The crystal was first ground dry on an agate mortar with an agate pestle for half an hour, and then ground for another half an hour with water to improve the homogeneity of the particles size. To prepare the paint, please see Section IV.1.1 of Appendix IV.
A crystal of red mercury (II) sulphide on which grinding was not effective was isolated in the red paint microsample from Lorvão (Lorvão 43, f.200). It evidences the characteristic laminar fracture that characterizes minerals’ structures, Figure 78.
Figure 78. SEM backscattered images of a localized in fracture crystal of red mercury (II) sulphide in a micro-sample from Lorvão 43, f.200. The unfocused areas are ascribed to the binding media that is surrounding the crystal\textsuperscript{97}.

EDS analysis of the historical red paint micro-samples identified some of the most characteristic elements usually assigned as impurities to cinnabar. Impurities were found locally distributed, in very low concentrations, demonstrating the high purity of the samples. For the three samples were detected the presence of aluminium (Al) and silicon (Si), most probably due to the presence of an aluminosilicate as impurity, together with sodium (Na) and potassium (K) that can be attributed to some clay impurities, see Section VII.3 of Appendix VII. In the red sample from Alcobaça, silicon (Si) was also detected together with a higher amount of oxygen (O) that might be originated from quartz. Moreover, iron (Fe) in its oxidized state was detected in the red sample from Santa Cruz, whereas in the red sample from Alcobaça it was identified together with sulphur (S) in a ratio similar to what found for pyrite (FeS\textsubscript{2}). EDS analysis did not identify the presence of iron (Fe) in the red sample from Lorvão. For representative X-ray spectra, please see Section VII.3 of Appendix VII. EDS analysis of cinnabar from Almadén mines showed an higher content of Magnesium and a lower content of Iron, when compared with the historical red paint samples (for representative X-rays spectra, please see Section VII.3 of Appendix VII.3).

\textsuperscript{97} In backscattered images the compounds with higher molecular weight are shown lighter on a grey scale, than those with lower molecular weight, that appear darker. In this sense, for the same level of analysis, red mercury (II) sulphide particles appear as light grey, whereas the darkened areas (suggesting to be unfocused areas) are ascribed to the binder.
- µ-FTIR

With exception to Lorvão 43 (Lorvão Apocalypse, 1189) where red (II) mercury sulphide was found mixed with red lead for more extensive paintings [Miguel et al. 2009], µ-FTIR analyses showed that for the remaining manuscripts vermillion was applied as a pure pigment or mixed with chalk (CaCO₃)⁹⁸, Figure 79a. Moreover, in the Lorvão collection red mercury (II) sulphide was consistently used as a pure pigment for the red letterings and mixed with an extender in illuminations [Claro 2009]. However for the Sta. Cruz and Alcobaça collections this consistency is no longer present. In some red lettering paints or in red illumination paints it is found as a pure pigment while in others the pigment is mixed with an extender.

![Figure 79. a) Characteristic patterns of reds infrared spectra from the Lorvão 43, f.200 (grey), Lorvão 5, f.25 (red) and Alcobaça 238, f.206v (black); b) Infrared spectra restricted to the C-H absorption region (3000-2840 cm⁻¹).](image)

Two different profiles were found for the C-H stretching absorption region (2824-3000 cm⁻¹) allowing the identification of two distinct situations: a profile that closely matches the infrared spectra of a proteinaceous component such as egg white (Figure 79b, grey), and the situations where a low-intense band at 2850 cm⁻¹ accompanied by an higher intense broad band at 2923 cm⁻¹ (of which intensity increases as the 2850 cm⁻¹ intensity band increases) is present (Figure 79b, red). An intermediate profile is also identified (Figure 79b, black) for the infrared spectra of red paints.

⁹⁸ Identified through its characteristic strong absorption bands at 1432 cm⁻¹and 878 cm⁻¹ [Sagín et al. 2012].
a) Principal Component Analysis

Principal Component Analysis (PCA) was applied to the C-H absorption region\textsuperscript{99} (3000-2840 cm\textsuperscript{-1}) of a set of 78 infrared spectra of red paints from the Lorvão, Sta. Cruz and Alcobaça manuscripts\textsuperscript{100} (please see representative infrared spectra of red paints for each manuscript in Appendix VII.2). Two approaches were followed: for the first, the PCA model was calibrated with infrared spectra of red paints (non-calibrated model), whereas for the second the infrared spectra of red paints were projected on a PCA model calibrated with pure binders\textsuperscript{101} (calibrated model), Figure 80.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure80.png}
\caption{\textbf{a)} Scores plot of a PCA model calibrated with infrared spectra of red paints from the Lorvão (grey squares), Sta. Cruz (red circles) and Alcobaça (black triangles) manuscripts; \textbf{b)} Scores of the projection of the infrared spectra of red paints from the Lorvão (grey squares), Sta. Cruz (red circles) and Alcobaça (black triangles) manuscripts on a PCA model calibrated with pure binders. Both PCA models were applied to the C-H absorption region (3000-2840 cm\textsuperscript{-1}). The yellow circles highlight the PCA scores the three infrared spectra displayed in Figure 79 \textit{b}).}
\end{figure}

\textit{Figure 80a} displays the scores of the PCA model applied to the infrared spectra of the red paints from the Lorvão, Sta. Cruz and Alcobaça manuscripts restricted to the C-H

\textsuperscript{99} The C-H absorption region was selected based on [Miguel et al. 2012b].

\textsuperscript{100} PCA was applied to infrared spectra of red paints from 6 manuscripts (10 micro-samples; 18 infrared spectra) from the Lorvão collection, 5 manuscripts (15 micro-samples; 42 infrared spectra) from the Sta. Cruz collection and 7 manuscripts (8 micro-samples; 18 infrared spectra) from the Alcobaça collection. All infrared spectra were pre-processed for baseline slope correction, followed by standard normal variate (SNV) and positivity correction by adding each spectrum to its minimum value. Afterwards, spectra were processed with a Savitzky-Golay filter with 15-points window size, 2\textsuperscript{nd} order polynomial and 1\textsuperscript{st} derivative, followed by mean centering (please see Appendix IV).

\textsuperscript{101} For the calibration it was used a set of infrared spectra of parchment glue, egg white and egg yolk, the most common proteinaceous binders for medieval illuminations’ production [Muñoz-Vinás 1999]. Please see Appendix X.1.1 for representative infrared spectra of parchment glue, egg white and egg yolk.
absorption region. It was verified that the first principal component (PC1) includes circa 88% of the variability of the infrared spectra restricted to this wavenumber region. The scores’ analysis was based on the analysis of the loadings for PC1 and PC2 and of each infrared spectrum. PC1 concerns the variability on the infrared spectra related to the absorption bands at 2923 cm\(^{-1}\) and 2850 cm\(^{-1}\) (\(\nu_{\text{asym}}(\text{CH}_2)\) and \(\nu_{\text{sym}}(\text{CH}_2)\), respectively\(^{102}\)): for negative PC1 values, the infrared spectra do not present these absorption bands, whereas for positive PC1 values, they are present. The second principal component (PC2) includes circa 4% of the variability in the infrared spectra restricted to the same region. PC2 concerns the variability on the absorption bands of the \(\nu_{\text{asym}}(\text{CH}_3)\) at 2965 cm\(^{-1}\) and the \(\nu_{\text{asym}}(\text{CH}_2)\) at 2936 cm\(^{-1}\): for positive PC2 values these two bands are better resolved than for negative PC2 values. PCA of the infrared spectra restricted to this wavenumber region showed three main clusters concerning\(^{103}:\) A) the infrared spectra where the characteristic absorption bands of \(\nu_{\text{asym}}(\text{CH}_3)\) at 2965 cm\(^{-1}\) and \(\nu_{\text{asym}}(\text{CH}_2)\) at 2936 cm\(^{-1}\) are well resolved; B) infrared spectra were these two bands are not well resolved; and C) infrared spectra presenting the absorption bands of \(\nu_{\text{asym}}(\text{CH}_2)\) and \(\nu_{\text{sym}}(\text{CH}_2)\) (2923 cm\(^{-1}\) and 2850 cm\(^{-1}\), respectively), Figure 80a.

Alcobaça infrared spectra did not evidence the characteristic absorption bands attributed to the presence of fatty acids in the paints formulation (at 2923 and 2850 cm\(^{-1}\)). Scores plot analysis evidenced that these two bands are only present in the infrared spectra of one manuscript from the Lorvão collection (Lorvão 6), and four manuscripts from the Sta. Cruz collection (Sta. Cruz 20, 21, 27 and 34), Figure 80a – cluster C. Moreover, concerning the infrared spectra of red paints from Alcobaça, within the eight manuscripts concerning this collection, only two (Alcobaça 358 and 421)\(^{104}\) present the two absorption bands at 2965 and 2936 cm\(^{-1}\) (\(\nu_{\text{asym}}(\text{CH}_3)\) and \(\nu_{\text{asym}}(\text{CH}_2)\), respectively) though not well resolved, Figure 80a – cluster B. From these results it is shown that these two manuscripts from Alcobaça present a different binding media formulation when compared with the Lorvão and Sta. Cruz collections. In fact, only the manuscripts from the Lorvão and Sta. Cruz collections presents indications for the characteristic absorption bands attributed to the

\(^{102}\) These two absorption vibrations are characteristic of fatty acids [Meilunas et al. 1990].

\(^{103}\) The scores’ analysis was based on the analysis of the loadings for PC1 and PC2 and of each infrared spectrum.

\(^{104}\) Alcobaça 358 is represented by one microsample (3 infrared spectra), whereas Alcobaça 419 is represented by 2 micro-samples (6 infrared spectra).
presence of fatty acids in the paints formulation (at 2923 and 2850 cm\(^{-1}\)).

Figure 80a – cluster C: from the Lorvão collection, the Lorvão 6 (De Avibus) appears to be distinct from the remaining manuscripts; whereas Sta. Cruz 20, 21, 27 and 34 stands out from the set of manuscripts from the Sta. Cruz collection considered in this study. However, it would be necessary to analyse a larger number of infrared spectra from each manuscript to validate these results.

In the calibrated approach, the model will be more sensitive to the discrimination among the three binders (that were used as calibration set), and not to the discrimination among the red paints’ infrared spectra. The analysis of the scores plot of the infrared spectra projected on a PCA model calibrated with parchment glue, egg white and egg yolk evidenced a slight worsening on the ability for discriminating the information, when compared with PCA following a non-calibrated model, Figure 80b. This slight reduction in the discrimination ability demonstrated that a small part of the information accountable for discrimination following a non-calibrated model, is not being covered by the three binders selected as calibrated set. It is however important to have present that a contemporaneous set of reproductions of proteinaceous binders is being compared with circa 850 years old micro-samples. Nevertheless, the results following both approaches revealed consistency and allowed to establish important considerations.

b) Partial Least Squares Regression

The PLSR model was used to predict the binding media composition of red paints based on the infrared spectrum. The model was calibrated using 180 infrared spectra of 20 vermilion paints’ reconstructions using known compositions (pure binders and binder mixtures) (please see Table AP X.1 in Appendix X). As a different model was calibrated for each binder (\(y_i, i=1,\ldots,3\)), three independent models were developed.

The PLSR predictions are shown in Table AP X.2 (see Appendix X). It was not expected that the sum of the weight ratio compositions predicted by each model would match 1 (as each model was applied to the infrared spectra independently). However, it was interesting to find that invariably this sum was circa 1 for all infrared spectra, demonstrating that the samples space was adequately covered in the calibration data set (please see Table AP X.2 in Appendix X). PLSR predictions identified the uniform use of a mixture of parchment glue and egg white on the infrared spectra of red paints from the Lorvão, Sta. Cruz and
Alcobaça manuscripts. It was not found that there was a characteristic formulation for each scriptorium, although accordance was found with the predictions of the compositions for each micro-samples’ replica, demonstrating the robustness of the method as well as the homogeneity of the paint’s formulation. It was not found that there was a use of different binding media formulations for the letterings and for the illuminations. Similarly to what was found in the PCA of the red samples, PLSR also demonstrated the exceptions found for the Lorvão 6, Sta. Cruz 20, 21, 27 and 34, predicting the highest egg yolk ratios (of which fatty acids will contribute with its characteristic ν_{asym}(CH₂) and the ν_{sym}(CH₂) at 2923 cm⁻¹ and 2850 cm⁻¹, respectively, for the infrared spectra of these red paints).

In an attempt to validate the PLSR predictions a microsample was selected from each collection to be analysed by ELISA antigen-antibody assay, Table 6.

**Table 6.** ELISA quantifications and PLSR predictions for the binding media formulations of red samples from the Lorvão, Sta. Cruz and Alcobaça manuscripts.

<table>
<thead>
<tr>
<th>sample</th>
<th>ELISA</th>
<th>PLSR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>egg white (ng/µL)</td>
<td>parchment glue (%wt)</td>
</tr>
<tr>
<td>Lorvão 43, f.200</td>
<td>0.24±0.05</td>
<td>65±21</td>
</tr>
<tr>
<td>Sta. Cruz 27, f.15</td>
<td>0.56±0.12</td>
<td>37±10</td>
</tr>
<tr>
<td>Alcobaça 238, f.206v</td>
<td>0.36±0.18</td>
<td>23±4</td>
</tr>
</tbody>
</table>

*Note: The negative PLSR predictions were removed from this table.*

Due to the reduced size of the samples, it was not possible to determine its weight (<0.1µg), Figure 81. For this reason the concentrations of the samples were determined in terms of ng_{binder} : µL_{extract solution}.

**Figure 81.** Red paint micro-samples from the Lorvão, Sta. Cruz and Alcobaça collections analysed with ELISA antigen-antibody assay. The grey circle marks the microsample from Sta. Cruz used in the assay.
The concentrations were determined based on calibration curves for parchment glue, egg white and egg yolk (please see Appendix X.3). It was only possible to detect the presence of egg white, although the fact of not being detected parchment glue nor egg yolk does not indicate its absence on the binding media formulation. The non-detection may be due to the differences on the detection limits for each binder (for parchment glue it was 0.15 ng/µL; for egg white was 0.01 ng/µL; and for egg yolk 6.0 ng/µL), or to a different ability for extracting these proteinaceous binders from circa 850-year aged samples (the optimization of their extractions was performed in non-aged red paint samples that might well present a different reticulation and, thus, ability to be extracted, please see Appendix X.3). Nevertheless, considering the differences on the samples’ size, it was verified that the results obtained by ELISA and predicted by the PLSR model succeed in detecting the lowest amount of egg white for the microsample from the Lorvão manuscript, Table 6. It is possible that ELISA is detecting a lesser amount of egg white, most probably due to a low efficiency of the binding media extraction process. Although ELISA assay allows for very low detection limits of proteins, the success of the method revealed to be extremely dependent on the effectiveness of the extraction procedure. In fact, the extraction procedure optimized in this work demonstrated higher effectiveness for egg white and parchment glue when compared with its efficacy in the extraction of egg yolk from unaged samples, most probably due to the interference of the fatty acids on the protein extraction. ELISA assay allowed for promising results on the analysis of illuminations, please see Appendix X.3.

For the first time, it was possible to quantify proteinaceous binders in artworks based on an ELISA antigen-antibody assay. It was also possible to identify, for the first time, the presence of egg white in medieval paints’ illumination. PLSR demonstrated high ability for predicting the binding media formulations based on infrared spectra of medieval paints’ illuminations. Additionally, it allowed identifying for the first time the use of proteinaceous mixtures in medieval paints’ illumination, namely the mixture of egg white with parchment glue. Finally, the PLSR predictions for formulations with a small amount of egg yolk in egg white-based paints corroborates some medieval recipes, such as

105 The fact that these formulations were characterized in red paints’ illuminations, red writing inks and in the letterings suggest that egg white was used mixed with parchment glue, and not applied as a varnish over a parchment glue-based paint.
the *Montpellier Manuscript*, that suggest tempering cinnabar by adding “glair and a little egg yolk” as a formulation “very suitable for miniating with a pen” [Clarke 2011b, p.107].

### 3.3.2. Medieval textual sources for producing vermilion

It is currently accepted that the know-how for vermilion production was brought into Europe by the Arabs who had already mentioned the reaction of sulphur with mercury to produce a red compound in the 8-9th century [Ball 2001, p.86]. The recipes for producing vermilion are ubiquitously present in medieval treatises [Gettens *et al.* 1972, Clarke 2001b]. Its production is referred in important treatises such as the *Mappae Clavicula* (9th-12th century) [Smith and Hawthorne 1974, p.26, 42, 61], *De diversis artibus* by Theophilus (12th century) [Hawthorne and Smith 1963, p.40], *De Arte Illuminandi* (14th century) [Brunello 1992, p.49], the *Montpellier Manuscript* (14th century) [Clarke 2011b], the *Bolognese Manuscript* (15th century) [Merrifield 1999, p.478, 480] or the *Libro de como si facem as cores* (13th-14th century) [Strolovitch 2010, p.229]. The vermilion synthesis following a *dry method* has long been characterized as a sublimation process by several authors [Eastaugh *et al.* 2008, Gettens *et al.* 1972, Rinse 1928], please see Appendix IX. Nevertheless, the historical accurate reconstruction of the recipe described in *Libro de como si facem as cores* has shown that this is a solid-state reaction that does not involve the sublimation of mercury sulphide, in either of its black or red forms [Miguel *et al.* 2012].

### a) Specificities of the vermilion recipe from the Portuguese medieval treatise the “*Libro de como si facem as cores*”

The recipe for producing vermilion described in the *Libro de como si facem as cores* has several particularities that distinguish it from other medieval treatises on materials for illumination (please see the full recipe in Appendix IX) [Strolovitch 2010, p.229]. The accuracy and detail of the instructions presented by the author may well indicate that the synthesis of vermilion that was brought to Europe by the Arabs was already known in Portugal at the time. Furthermore, the presence of a realistic depiction of vermilion synthesis in a Portuguese book written in Hebrew characters suggests that Jewish and Muslim cultures were sharing a common scientific and technological background in the Peninsula. On the other hand, when comparing the recipe for producing vermilion from the Portuguese medieval treatise the *Libro de como si facem as cores* with those present in other treatises such as the *Mappae Clavicula*, *De diversis artibus* by Theophilus, *De Arte
**Illuminandi, the Montpellier Manuscript or the Bolognese Manuscript**, it becomes apparent that the best detailed instructions for the synthesis of vermilion are those present in the Portuguese medieval treatise, please see *Appendix IX*. Also, it is possible to say that these instructions are in great part straightforward to follow and an almost stoichiometric ratio Hg and S is used (1:5 sulphur to mercury, wt:wt) - taking into account that the reaction stoichiometry is one part sulphur to six parts mercury (wt:wt) - whereas for the other treatises the quantity of mercury used is between 6 to 12 times lower than what would be required (please see *Table AP IX.1* provided in *Appendix IX*) [Melo et al. 2010b].

**b) Rationalization of the recipe for vermilion production described in the “Libro de como si facem as cores”**

The recipe consists of two main steps. In the first step, mercury and sulphur are ground to produce metacinnabar, a silver-black compound with a cubic crystal structure (please see *Appendix IX*), *Figure 82(a)*. In the second step, the pot containing metacinnabar is placed over embers, with the temperature inside the pot achieving 350-370 °C, *Figure 82(b)*.

*Figure 82*. Schematic representation of the process described to produce vermilion in the *Libro de como si facem as cores*: a) grinding mercury and sulphur to produce metacinnabar; b) placing the clay pots containing metacinnabar over the embers to produce vermilion; and c) opening the clay pot after let to cool to room temperature.

In a successful experiment, after two and a half hours, the pot was taken from the embers, cooled to room temperature, and then opened, *Figure 82(c)*. The process proved to be complex and reproducibility was difficult to achieve, mainly due to the difficulty in controlling the temperature to which the pot was exposed. When sublimation occurs, at temperatures higher than 580 °C, a black amorphous product, not yet characterized, is formed. Grinding also revealed to be a crucial step. In fact, whenever the grinding of liquid mercury with solid sulphur was not completely effective, the reaction was unsuccessful.
- metacinnabar production

Grinding solid sulphur with liquid mercury proved to be a laborious and patient work. The suggestion of using a “dog’s foot with its hair and wool” mentioned in the *Libro de como si facem as cores* was imitated by using a bone with wool; with this tool, grinding became less laborious as it became possible to control the mercury droplets during the grinding process (with an agate pestle the mercury tends to escape from the mortar). It is expected that for quantities closer to those mentioned in the recipe (circa 2.7 kg of metacinnabar, whereas in this work it was never ground more than 0.5 g of metacinnabar per batch), this improvement would be even more noticeable. The friction of grinding mercury with sulphur results first in a reduction of the size of the mercury drops, giving rise to the formation of mercury microspheres. Consequently the surface tension is reduced, allowing sulphur grains to become adhered at the reaction interface [López et al. 2010]. Despite the value for ΔG° (kJ/mol) of −47.73 [Weast 1971] suggesting the spontaneity of metacinnabar formation from its elemental constituents, the fact is that metacinnabar formation is not achieved by simply placing liquid mercury together with powdered sulphur. Sufficient heat must be provided throughout grinding to reach the activation energy necessary for the reaction to take place, suggesting the kinetic influence over the production of black mercury sulphide.

- vermilion production

The conversion of ground metacinnabar in cinnabar was studied by following the heating of a pellet of ground metacinnabar\(^\text{106}\) and its transition into vermilion by XRD. *Figure 83* shows the characteristic X-ray diffractograms for metacinnabar (cubic α'-HgS) and cinnabar\(^\text{107}\) (hexagonal α-HgS). For metacinnabar the peak at 30.5° was chosen (black curve; black arrow), and for cinnabar the peak at 45.6° (red curve, red arrow), *Figure 83*. These were the most promising peaks to follow the phase transition, once the remained peaks present or a very low intensity, or reflect an overlapping of both metacinnabar and cinnabar peaks.

\(^{106}\) Metacinnabar pellets were used as a way of controlling some volatilization processes that could occur inside the XRD chamber during the heating procedure.

\(^{107}\) In crystallography, the red hexagonal form of α-HgS is commonly named as cinnabar (independently of having a mineral source or a synthetic origin).
A pellet of ground metacinnabar was placed on a platinum filament that was afterwards heated with a heating step of 5°C/minute from 35°C to 325 °C (for more details about the experimental conditions, please see Appendix IV). Figure 84 displays four X-ray diffractograms corresponding to four different steps of the heating of a pellet of ground metacinnabar: 35°C, 195°C, 235°C and 275°C.

**Figure 83.** Representative X-ray diffractograms of black cubic metacinnabar (the black curve is a mixture of cinnabar and metacinnabar) and red hexagonal cinnabar. The arrows indicate the peaks used on the study of the phase transition of metacinnabar (30.5°) into cinnabar (45.6°).

**Figure 84.** X-ray diffractograms of black cubic metacinnabar at 35°C (black), 195°C (grey), 235°C (carmine) and 275°C (red). The inset, a detail evidencing the peaks used on the study of the phase transition of metacinnabar (30.5°, black arrow) into cinnabar (45.6°, red arrow).
At 35 °C the peaks of ground metacinnabar are broadened, a characteristic of nanocrystalline materials, *Figure 84* (*black line*). With heating, the crystallites become larger and the broad peaks becomes sharpened [Patel *et al.* 2007], please see the *inset* of *Figure 84*. At 275 °C a complete conversion of black cubic metacinnabar in red hexagonal cinnabar was achieved (please see the *inset* of *Figure 84*, where it is evident the disappearance of the peak at 30.5° that characterizes black cubic metacinnabar).

The phase transition profile of the conversion of metacinnabar in cinnabar was studied by following the area variation for each peak at each heating step, *Figure 85*.

*Figure 85*. Phase transition profile of cubic metacinnabar (*black*) conversion into the hexagonal cinnabar (*red*) followed by XRD. Metacinnabar transition was followed using the peak at 30.5°, whereas vermilion conversion was followed using the peak at 45.6°.

The temperature of transition was set at 235 °C. At this temperature, metacinnabar rearranges from the cubic form into the hexagonal form, cinnabar. At 275 °C the cinnabar composition ceases to increase. Between 275 °C and 325 °C the pellets broke.

The conversion of cubic metacinnabar in to hexagonal cinnabar, followed by X-Ray diffraction, demonstrated the importance of kinetics over thermodynamics in the

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108 The two last temperature steps of analysis, not shown in *Figure 84*. 

120
reaction$^{109}$. Moreover, the fact that black metacinnabar is formed more rapidly than red cinnabar confirms the existence of a kinetic barrier. Temperature becomes thus fundamental to overcome the kinetic barrier and to convert metacinnabar into cinnabar. Considering that metacinnabar becomes the stable product at higher temperatures, the reaction yield becomes dependent on the optimization of two factors: 1) ensuring that a temperature high enough is achieved to overcome the kinetics barrier (contributing to more rapidly take place the conversion of metacinnabar into cinnabar); 2) ensuring that this high temperature will not exceed the conversion temperature of cinnabar into metacinnabar$^{110}$, avoiding the recently formed red cinnabar being transformed in black metacinnabar, which at this point is the thermodynamic stable species.

With this approach it was also possible to verify that mercury-sulphur compounds exist in a complex solid-state phase system. Two parameters revealed crucial for the success of vermilion’s production following the recipe described in the *Libro de como si facem as cores*: the effectiveness of the grinding process and the temperature control. The first would be very dependent on the patience and rigor of the worker, whereas the second was much dependent on the control of the temperature of the embers and on the design of the clay pot, namely of thickness of its walls$^{111}$. Finally it is demonstrated the importance of reproducing medieval recipes as accurate as possible for know more and understand more on the alchemical medieval knowledge and on the specificities of the materials used to produce medieval illuminations.

### 3.3.3. Reproducing red paints

Red paints were reproduced$^{112}$ using vermilion synthesised following the recipe from the *Libro de como si facem as cores*, and using a ground crystal$^{113}$ extracted from a mineral of Almadén mines, Spain.

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$^{109}$ Cinnabar is the thermodynamically stable product at room temperature, whereas black metacinnabar turns to be the thermodynamically stable product at higher temperatures [Rodic et al. 1996].

$^{110}$ According to Rinse, 386 °C [Rinse 1928].

$^{111}$ Serendipity showed that the best clay pots used in our reproductions had to have both thick walls and thick bases enabling them to avoid close contact with the fire (i.e., high temperatures) as well as to maintain a more constant temperature (thermal inertia). In Appendix IX is displayed an image and a schematic representation of the clay pot used in this approach.

$^{112}$ To prepare the paints, please see Appendix IV.

$^{113}$ The crystal was first ground dry on an agate mortar with an agate pestle for half an hour, and then ground for another half an hour with water to improve the homogeneity of the particle sizes.
The vermilion synthesised following the medieval recipe enabled us to reproduce a red paint comparable to the historical red paints, Table 7.

**Table 7.** CIEXYZ colour coordinates\(^5\) for two vermilion paint reconstructions using vermilion produced following the *Libro de como si facem as cores* a cinnabar, and for a red paint from *Lorvão 43, f.200.*

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Libro de como si facem as cores</em></td>
<td>46.64±0.11</td>
<td>36.18±0.06</td>
<td>26.30±0.52</td>
</tr>
<tr>
<td>Cinnabar from Almadén</td>
<td>45.24±0.06</td>
<td>47.64±0.05</td>
<td>24.43±0.05</td>
</tr>
<tr>
<td><em>Lorvão 5, f.25</em></td>
<td>47.00±0.09</td>
<td>37.25±0.21</td>
<td>29.52±0.21</td>
</tr>
<tr>
<td><em>Sta. Cruz 34, f.94v</em></td>
<td>51.78±0.69</td>
<td>41.76±0.52</td>
<td>39.87±0.19</td>
</tr>
<tr>
<td><em>Alcobaça 238, f.210</em></td>
<td>49.17±0.08</td>
<td>38.35±0.23</td>
<td>34.48±0.10</td>
</tr>
</tbody>
</table>

\(^5\)The L* coordinate represents the *lightness*, a* coordinate the *redness* and b* coordinate the *yellowness*.

Considering the morphology of the samples’ surfaces, the differences between the vermilion-red paint (*Figure 86, left*) and the cinnabar-red paint (*Figure 86, right*) become evident.

**Figure 86.** SEM backscattered images of red paints’ reproduction with: a) *left*, vermilion following the recipe described in the *Libro de como si facem as cores*; b) *right*, with cinnabar from Almadén mines.
In vermilion paint’s reproduction the surface is wrinkled and after grinding the particles get a rounded shape (sizes vary from \textit{circa} 0.2 \mu m to 1.9 \mu m), Figure 86, left. It displays a sinterization effect, resulting from the high temperature achieved during the heating process\textsuperscript{114}. This phenomenon was consistent for other vermilions produced by the \textit{dry synthesis} and seems to be a characteristic of this procedure. For the other hand, the cinnabar paint reproduction presents well-shaped angular particles, (sizes vary from \textit{circa} 0.3 \mu m to 1.4 \mu m) of which morphology is closer to the one found for the red micro-samples from the Lorvão, Sta. Cruz and Alcobaça manuscripts.

3.3.4. Final remarks on \textit{Le rouge} in Portuguese Medieval illuminations

The study of red paints in Portuguese medieval illuminations demonstrated the importance of accurate reconstructions based on medieval texts as well as on the evidence of analytical results. As expected from the very good conservation condition evidenced by the red paints, high quality materials were used as well as very stable binding media formulations. Again, chemometrics proved to be a powerful tool for studying the specificities behind medieval illumination paint production. The extensive use of binding media formulations based on mixtures of parchment glue and egg white revealed a surprise. To the best of our knowledge, it was the first time that this formulation was identified in medieval illuminations, as for the best of our knowledge this is not a common formulation suggested in medieval recipe books for illuminations. Likewise the study of colour suggested the high fingerprint of Christian and Islamic cultures in Portuguese Romanesque illuminations, the approach to the \textit{Libro de como si facem as cores} suggested the sharing of knowledge that co-existed between Christians and Jews.

\textsuperscript{114} It is still possible to identify regions where the fusing of the particles still remains due to an untidy grinding of the pigment in the backscattered image, Figure 86, left.
4. Dissemination

Besides the dissemination of the results achieved during this research among the scientific community in the form of scientific papers and oral and panel communications in national and international meetings, it was a main concern to share this knowledge among the general public. For this, several hands-on workshops were organized on Portuguese Romanesque illumination, Figure 87.

*Figure 87. Workshops on Portuguese Romanesque illuminations.*
In these workshops, besides presenting the main findings for the study of the materials and painting techniques of Portuguese Romanesque illuminations, participants were offered the opportunity of reproducing an illumination following the same procedures as the monks might have used in the 12th-13th century. The workshops were organized for the general public, for young or elderly people, or for a more specialized public such as archivists, librarians, art historians or experts on medieval illuminations. It followed the worksheets of the “À descoberta da Iluminura Medieval” web book produced in the framework of the research project [Iluminuras 2]. The workshops were considered a great success by all who attended it.

Furthermore, a new critical translation was produced of the Libro de como si facem as cores. It was the aim of this work to reveal the science behind the documentary evidence, focused on establishing the chemical and technical rationale of the recipes. This rationale was based on laboratory reconstructions of the processes for making pigments, colourants and binders, that were afterwards compared with what was found in Portuguese Romanesque illuminations. The final products were fully characterized by XRD, μ-FTIR, μ-Raman spectroscopy and other relevant analytical techniques, and colorimetry, Figure 8. This edition is organized as worksheets, and had the contribution of many students of History and Art Production Techniques of the Masters in Conservation and Restoration, New University of Lisbon, who attempted to reproduce many of the recipes present in the Libro de como si facem as cores. The worksheets may be downloaded from http://www.dcr.fct.unl.pt/LivComoFazemCores.

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Figure 88. Worksheet for the making of vermilion following the instructions of the Libro de como si facem as cores, Chapter 15 [Strolovitch 2010, p.229].
Voici mon secret. Il est très simple: on ne voit bien qu'avec le cœur. 
L'essentiel est invisible pour les yeux

Antoine de Saint-Exupéry in Le petit Prince, Chp.21

5. Conclusions
The approach followed in this work for studying the materials and paint formulations in medieval illuminations proved to be an effective modus operandi for a deep understanding of the specificities behind the production of medieval manuscripts. The colour mapping of the *Hagiographic readings* from the Lorvão, Sta. Cruz and Alcobaça collections suggested the importance of Islamic culture for the Portuguese Romanesque period, as shown by the extensive use of green in these manuscripts (as this deep saturated green colour has a strong spiritual significance for the Islamic culture). Moreover, the importance became apparent of studying the history and culture that contextualize the manuscript at the time of its production whenever one aims to establish a meaning for the use of a colour. The use of a chemometric approach on the analysis of μ–FTIR data revealed a crucial tool for determining important paint specificities that by a direct analysis of the infrared spectra would be difficult to achieve. Concerning the bottle-green paints it was possible, for the first time, to establish a relation between the copper-proteinate band, the molecular changes in the protein and the macroscopic alterations evidenced by these bottle-green paints. Concerning red paints, chemometrics allowed characterization, for the first time, of the use of proteinaceous binding media formulations (such as the mixture of parchment glue and egg white) in medieval illuminations. For both coloured paints it was possible to infer the relation between manuscripts and *scriptoria*. Such important achievements for the characterization of the binding media formulations were only possible because micro-sampling was performed. This is a very controversial subject that has been much debated among conservation scientists and conservators. And yet, much has to be debated. If micro-sampling might be considered as an intervention on the manuscript, the fact is that much important information might result from the analysis of a single micro-sample (as demonstrated by the work presented here). If well planned, micro-sampling is a one time operation, involving much less handling of the manuscript than *in situ* analysis. More important, by analysing the micro-sample instead of the entire manuscript, the manuscript

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116 Here is my secret. It is very simple: It is only with the heart that one can see rightly; what is essential is invisible to the eye.
will not be subjected to the energy radiation required by some analytical techniques, as Raman microscopy. It is a fact that many analytical techniques are described as non-destructive techniques, however there are no references for its long-term destructiveness. In this sense, it would be extremely important to monitor the illuminated paints that were analysed by *in situ* techniques over a period of 10, 20 or even 50 years to see if any damage had appeared due to these analysis to insure on the non-destructiveness of these techniques and on the advantages of micro-sampling. Furthermore there is some molecular information that is not (yet) possible to obtain by *in situ* analysis alone. The characterization of the binding media formulation (that displays a crucial role on paint stability) is perhaps the most important example of this limitation.

The study of the materials and paint formulations of the Alcobaça collection emphasized its specificities in the Portuguese context. Of the three Portuguese collections so far analysed by this research team (Lorvão, Sta. Cruz and Alcobaça), it was in Alcobaça that was first identified the use of gypsum as an extender on a paint formulation. This use suggests the relation of this *scriptorium* with its *Mother Abbey* of Clairvaux in France; a relation that might well have exceeded the influence on the ornamentation and on the iconographic systems, to influence also the use of the materials and paints formulations in Alcobaça. Moreover, comparing the paint formulations used to produce the *Lorvão 15* (*Gradual*, 1201-1250) and the *Alcobaça 427* (*Bible*, 12th-13th century) demonstrated the similarities between these two manuscripts. These results support the possibility of these two manuscripts have been produced in the same *scriptorium*, most probably in the Alcobaça *scriptorium*, as already highlighted by some art historians. Finally, the use of the most important and expensive colour sources used in medieval illumination production was demonstrated. In this sense, the Alcobaça collection occupies an important place among the European context as one of the most consistent and high quality Romanesque collections of illuminated manuscripts.

Finally, likewise the study of colour suggested the high fingerprint of Christian and Islamic cultures in Portuguese Romanesque illuminations, the approach to the *Libro de como si facem as cores* suggested the sharing of knowledge that co-existed between Christians and Jews.
5.1. Future work

There are some considerations that shall be drawn concerning the future work that might be developed based on the work here presented. The first consideration relates to the mapping of colour, as it proved to be a powerful tool for establishing possible relations between manuscripts. In this sense, it would be important to extend this approach to the remaining Romanesque manuscripts from the Lorvão, Sta. Cruz and Alcobaça collections to determine the consistency of the results achieved for the *Hagiographic readings*. Additionally, it would be very interesting to extend this study to contemporaneous manuscripts from Clairvaux (namely to contemporaneous *Hagiographic readings* from Clairvaux) to determine if, besides the influence on the drawing and painting techniques, Clairvaux was also influencing the use of colour in Alcobaça. The second consideration relates to the study of binding media formulations. It would be important to follow the same methodology used for the study of red paints (the analysis of infrared spectra following a chemometric approach) to the remaining colours that comprise the Lorvão, Sta. Cruz and Alcobaça colour palettes to find out if a similar binding media formulation was consistently used, or if there was specific formulations for specific colour paints. The third consideration relates to ELISA antibody-antigen assay. It would be very interesting to test ELISA on artificially aged paint reconstructions to ascertain on the effectiveness of this methodology for quantifying proteinaceous binding media formulations. The forth consideration concerns some preliminary studies that were performed on the suitability of using ELISA for determining the animal source used to produce medieval parchments. The results were very promising, thus it would be very interesting to explore this new applicability of the ELISA antibody-antigen assay. Finally, it is of extreme importance to be able to develop a systematic study of Iberian 12th-13th century Muslim and Jewish manuscripts to validate the importance and extent of use of bottle-green paints in Muslim and Jewish illuminations and its relation with the Portuguese Romanesque manuscripts.
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