Universidade de Évora - Instituto de Investigação e Formação Avançada
Università degli Studi di Roma "La Sapienza" Aristotle University of Thessaloniki

Mestrado em Ciência dos Materiais Arqueológicos (ARCHMAT)

Dissertação

Fonte de cor verde em scriptoria portuguese - uma abordagem arqueométrica

Urmila Hasnat
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Orientador(es) | Catarina Miguel
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Green colour sources in Portuguese *Scriptoria*-an archaeometric approach

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Abstract

Green colour sources in Portuguese *Scriptoria*-an archaeometric approach

This thesis presents the holistic analysis of a set of eight manuscripts produced at the Portuguese *scriptorium* of Alcobaça monastery during the 12^{th}-16^{th} century: Alc. 433, Alc. 260, Alc. 166, Ms 17, Alc. 167, Alc. 255, Alc. 341, and Alc. 26, currently preserved at the Biblioteca Nacional de Portugal and National Archive of Torre do Tombo, Lisbon-Portugal.

The work aimed to study the chronological use of green pigments in the Portuguese *scriptorium* of Alcobaça and outline the history of the green paint colour sources over three centuries of activity with a chronological timeline. The study also contributes fresh input into the discussion about the possible presence of verdigris in copper-proteinate paints. The representative folia of the above-mentioned manuscripts were characterized following a holistic approach based on liturgical analysis and material characterization, making use of in-situ non-invasive analysis (h-EDXRF and UV-Vis-NIR-SWIR FORS).

The Principal Component Analysis (PCA) of reflectance spectra of historical green paints indicates that the manuscripts produced in the last quarter of the 12^{th} century might have used copper proteinate as a green colour source. The years 1191-early 13^{th} century saw a transitional phase between copper-proteinate to malachite, for a brief return to copper-proteinate close to the 15^{th}-16^{th} century. From the first half of the 13^{th} century to the first half of the 14^{th} century, malachite was used fully. But again, they shifted to copper proteinate around the 15^{th} -16^{th} century. h-EDXRF data also substantiated the PCA analysis results. Based on these findings, a timeline of the use of green pigments in the Portuguese *scriptorium* of Alcobaça during the 12^{th}-16^{th} century was proposed.

Keywords: Portuguese Mediaeval Manuscript; Alcobaça scriptorium; FORS; h-EDXRF; malachite; verdigris; copper proteinate; green pigments

Resumo

Fonte de cor verde em scriptoria portuguese- uma abordagem arquemétrica

A presente tese apresenta a análise holística de um conjunto de oito manuscritos produzidos no scriptorium português do Mosteiro de Alcobaça durante os séculos XII-XVI: Alc. 433, Alc. 260, Alc. 166, Ms 17, Alc. 167, Alc. 255, Alc. 341 e Alc. 26, que atualmente se conservam à guarda da Biblioteca Nacional de Portugal e do Arquivo Nacional da Torre do Tombo, Lisboa-Portugal.

O trabalho teve como objetivo estudar o uso de pigmentos verdes no scriptorium português de Alcobaça, e de estabelecer a história do uso de pigmentos verdes, numa abordagem cronológica, ao longo de três séculos de atividade do scriptorium. O estudo também contribui com novas informações para a discussão sobre a possível presença de verdigris nas tintas à base de proteinatos de cobre. Os folios representativos dos manuscritos mencionados foram caracterizados seguindo uma abordagem holística, baseada na análise litúrgica e caracterização material, fazendo uso de análise não invasiva in situ (h-EDXRF e UV-Vis-NIR-SWIR FORS). A análise de componentes principais (PCA) dos espectros de refletância das tintas verdes históricas indica que os manuscritos produzidos no último quartel do século XII podem ter usado proteinato de cobre como fonte de cor verde. As tintas verdes produzidas nos primórdios da atividade do scriptorium, isto é, de 1175 a 1191, apresentam uma formulação à base de proteinatos de cobre. O período de 1191 até o início do século XIII revelou-se um período de transição do proteinatos de cobre para a malaquite, para um breve retorno ao proteinatos de cobre no período mais próximo do séculos XV-XVI. Da primeira metade do século XIII à primeira metade do século XIV, a malaquita foi plenamente utilizada. Estes resultados foram corroborados pela análise elementar das tintas por h-EDXRF. Com estes resultados, propõem-se, assim, nesta dissertação um cronograma para o uso de pigmentos verdes na produção de manuscritos iluminados no scriptorium de Alcobaça entre os séculos XII e XVI.

Palavras-chave: Manuscritos iluminados portugueses; *scriptorium* de Alcobaça; FORS; h-EDXRF; malaquite; verdigris; proteinato de cobre; pigmentos verdes.

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List of abbreviations

δ	bending mode
ν	stretching mode
ν_a	asymmetric stretching mode
ν_s	symmetric stretching mode
2ν	first overtone (stretching mode)
3ν	second overtone (stretching mode)
4ν	third overtone (stretching mode)
$(\nu + \delta)$	combination band (stretching + bending mode)
BNP	Biblioteca Nacional de Portugal
ANTT	Arquivo Nacional Torre do Tombo
FORS	Fiber optic reflectance spectra
h-EDXRF	Handheld Energy Dispersive X-ray fluorescence spectroscopy
UV-Vis-NIR-SWIR	Ultraviolet-visible-near infrared-short wave infrared

IN-TEXT REFERENCES OF ILLUMINATED MANUSCRIPT COLLECTIONS

In-text Reference	Title of the Manuscript	Location	Online Access
Alc. 433	*Leccionário*	Biblioteca Nacional Portugal	https://purl.pt/25154
Alc. 260	*Colectário*	Biblioteca Nacional Portugal	https://purl.pt/29651
Alc. 166	*Colectário*	Biblioteca Nacional Portugal	https://purl.pt/33143
Alc. 167	*Evangeliário*	Biblioteca Nacional Portugal	https://purl.pt/28819
Alc. 255	*Missal*	Biblioteca Nacional Portugal	https://purl.pt/27035
Alc. 26	*Missal*	Biblioteca Nacional Portugal	https://purl.pt/24863
Ms 17	*Calendas e regra de São Bento*	Arquivo Nacional Torre do Tombo	https://digitarq.arquivos.pt/details?id=4484151

NOTES TO THE IMAGES

All images from the Mss Alc. 433, Alc. 260, Alc. 166, Alc. 167, Alc. 255, and Alc. 26 used in this thesis are intellectual property of the National Library of Portugal, which is acknowledged with the notation "© BNP".

Similarly, all images from MS 17 are intellectual property of the National Archive of Portugal, being acknowledged under the notation "© DGLAB - ANTT".

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INTRODUCTION

Preamble

Every society associates colours with spiritual, religious, or cultural significance. Modern-day graphic designers appraise the observer's psychological and perceptual response to colours, so they choose each tint strategically. For instance, they classify red, oranges, and yellows as *warm* tones capable of rendering positive feelings (Debner, et al., 2010, p. 99): red achieves passion or strong emotions, whereas yellow is the hue of cheerfulness. On the other side of the spectrum, blue, purple, and green, and their variations are *cool* colours, thus having connotations of calmness and reservedness (Ballast, 2002; Wexner, 1982).

Despite these general principles, the personal and cultural response to colour does not adhere to a clear standard, some contemporary scholarship shows (Kaya & Epps, 2004; Kwallek & Lewis, 1988; Mahnke & Mahnke, 1993). This fact holds not only for our days, as cultural and political views on certain colours have polarised chromatic appreciation in the past as well. The scholar Maribel Fierro refers to a powerful instance in this regard: 11th-century Northern Arabs (Qays) wore red as their primary colour, while Southern Arabs (Yemen) acquired yellow as their symbol (Fierro, 1993; 1998). Through that, mediaeval Islam provided one case of intentional use of colours for political legitimacy. Not only early times, but also the modern and contemporary periods set more instances of symbolistic uses of colour. Ever since the Revolution of 1848, red has been used to embody socialistic and communistic political views; slightly before, a plain red flag has been the symbol of the revolutionary movements of Robespierre of the French Revolution (1789-1799). Thus, colours do not only stimulate a perceptual or instinctive response but entangle with the cultural, social, or political fabric of societies and individuals.

Going further in the past, the European Middle Ages developed a specific view on colour as well. In some cases, colour was seen in relation to radiance, so that its view fused with the divine significance of light ever since the beginning of Christianity (Huxtable, 2008; Saint Basil, 1995). Early Christian writers and thinkers elaborated some theories on the latter, interpreting light neither as a physical nor a physiological phenomenon; instead, they considered it as the direct manifestation of God. In fact, St Basil the Great (c. 329-379) deemed light an emanation of the divine or an intrinsic property of objects, while St. Augustine of Hippo (354-430) wrote that terrestrial light derived primarily from God's light. These views are grounded in some Biblical pericopes that established associations between the notions of God and light, characterising Him as luminosity. One of these descriptions is of "Father of Lights", from the Book of James (1.17);

another, less direct, is from Psalm 36, which reads: "in thy light shall we see light". Later theories understood light as an entity *received* by the eye; by extension, being illuminated signified receiving God himself. Belonging to the *illuminist* school were Peter of Limoges (fl. 1199-1237)[1], partly the Franciscan philosophers Thomas Aquinas (1225-1274)[2], and Roger Bacon (c.1214-c.1292)[3]. More specifically, the last two thinkers interpreted vision as an intellectual act.

Speaking of colour, the medieval view of the chromatic system and perception derived its fundamentals from the Aristotelian conception of colour, namely that colour is a physical property embedded into matter itself (Dinkova-Bruun, et al., 2013, p. 25). Original views on colour were theorised much later, in the 11th-13th century. In this period, the thinkers Avicenna (980-1037) and Robert Grosseteste (c. 1175-1253) developed a scientific theory regarding colour and its perception: for them, colour arises from the purity of transparent media as light passes through them (Sparavigna, 2014).

Aside from them, other medieval thinkers were not as much interested in the physical effects of colour as their moral implications. One of the prominent figures of the Cistercian order, St Bernard of Clairvaux (1090-1153), was one of these individuals; he expressed a rather severe position apropos, perhaps one of the most negative. St Bernard patently abhorred all forms of coloured objects as sinful precipitation: colour is beautification, thus celebration of vanity[4]. These ideas found a place in his *Apologia ad Guillelmum* (1124-1125), a document written at the request of his friend and fellow monastic reformer William of St-Thierry to elaborate a clear statement within the early 12th-century controversy over art. Chapters 28 and 29 of the *Apologia* seal St Bernard's view, illustrating how artworks induces spiritual distraction in the observer: "painstaking representations [...] deflect the attention while they are in them of those who pray and thus hinder their devotion", he declared (Rudolph, 1987, p. 17).

[1] Peter of Limoges was the author of *Tractatus Moralis de Oculo* (=A Moral Treatise on the Eye or On the Moral Eye), an ethical guide for Catholic priests.

[2] In his *Summa Theologiae*. On this point, see also (Gaine, 2016).

[3] In his *Opus maius*. On it, see also (Mantovani, 2021).

[4] Eccleston, Florence (2019). *Light and Colour in Medieval Christianity*, from "Introducing Medieval Christianity". Online at: https://introducingmedievalchristianity.wordpress.com/2019/05/09/light-and-colour-in-medieval-christianity/#:~:text=Early%20Christianity%20conceived%20of%20light,to%20direct%20knowledge%20of%20God. (Accessed on: November 30, 2023).

In all of that, manuscript illumination took some time to align with the Bernardin prohibition. As a matter of fact, the first Cistercian manuscripts made by the order reveal lavish illumination. Earliest manuscripts such as Gregory the Great's *Moralia in Job* (c. 1111, Cîteaux)[5] or the *Bible d'Etienne Harding* (c. 1109-1111, Cîteaux) (Figure 1)[6] are extensively decorated.

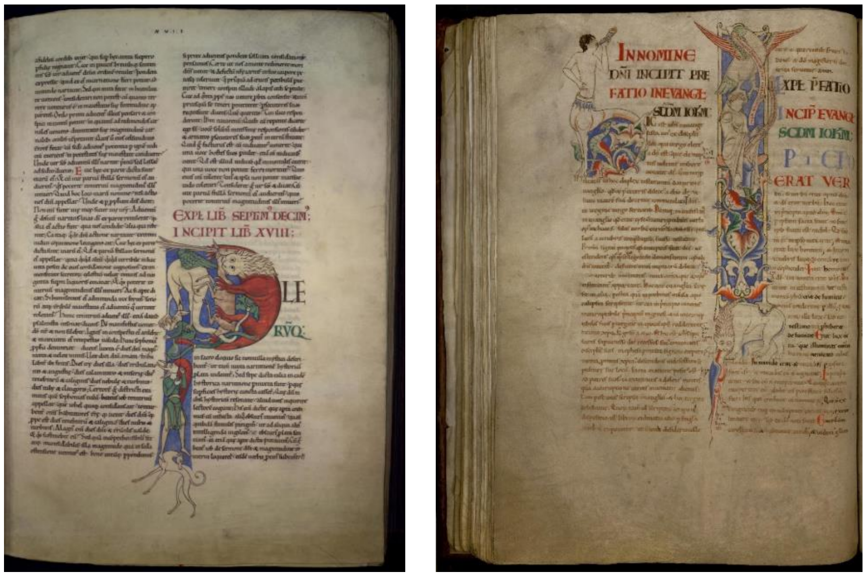

Figure 1. Full-page view of two Cistercian illuminated manuscripts: left (a), Dijon, BM, Ms 173, f. 17^{r}; right (b) Dijon, BM, Ms 15, f. 56^{v}. © Bibliothèque municipale de Dijion (a,b).

Aside from the so-called *Grande Bible de Clairvaux* (c. 1150-1160, Cîteaux)[7], those from a few decades later, like Dijon, BM Ms 77 (c. 1145-1155, Cîteaux)[8] (Figure 2) already mirror the hostility of Bernard of Clairvaux concerning exuberant illuminations. They relinquish figurative representations, their graphic articulation becoming diminished.

[5] St. Gregory the Great, *Moralia in Job*, c. 1111, Cîteaux (Burgundy, France). In Dijon, Public Library (France), Ms 173.

[6] *Bible d'Etienne Harding*, c. 1109-1111, Cîteaux (Burgundy, France). In Dijon, Public Library, Ms 15.

[7] *Grande Bible de Clairvaux*, c. 1150-1160, Cîteaux (Burgundy, France). In Troyes, Public Library (France), Ms 27.

[8] Beda Venerabilis, *Expositio in Evangelium Lucae*, c. 1145-1155, Cîteaux (Burgundy, France). In Dijon, Public Library (France), Ms 77.

Figure 2. Details of monochromatic illuminations from: left (a) the so-called *Grande Bible de Clairvaux* (Troyes, BM, Ms 27, f. 4r); right (b) Dijon, BM, Ms 77, f. 4r. © Bibliothèque municipale de Troyes (a) and Dijion (b).

Outside France, a similar trend arises. In England, such manuscripts as Harley Ms 3641 (c. 1180-1200)[9] display mostly non-figurative initials (Figure 2c), and only two manuscripts from this Cistercian monastery (BL, Harley Ms 2807[10]; York, Minster Library, MS XVI.I.7[11]) have limited figurative decoration[12] (Figure 2d). Through this argument, the scholars Lawrence-Mathers and Charles were able to determine a non-Cistercian origin of English manuscripts of the Rievaulx abbey dating this period (1150-1250) in local Cistercian monasteries, such as BL, Royal MS 8 E IV (Charles, 2020, p. 10; Lawrence-Mathers, 1986, pp. 284-289; Lawrence-Mathers, 1995, pp. 33-34; Lawrence-Mathers, 2002, pp. 208-210).

[9] William of Malmesbury, *Gesta Pontificum*, c. 1180-1200, Byland Abbey (England). In British Library, London (United Kingdom), Harley Ms 3641.

[10] Bible, c. 1225-1250, Byland Abbey (England). In British Library, London (United Kingdom), Harley Ms 2807.

[11] Psalter, c. 1280-1300, Byland Abbey (England). In Monster Library, York (United Kingdom), Ms XVI.I.7.

[12] Drieshen, Clarck (2021). *A newly discovered manuscript from Byland Abbey*, in "Medieval manuscripts blog. Blog of the British Library." Available at: https://blogs.bl.uk/digitisedmanuscripts/2021/04/newly-discovered-ms-from-byland-abbey.html (Accessed on: December 2, 2023).

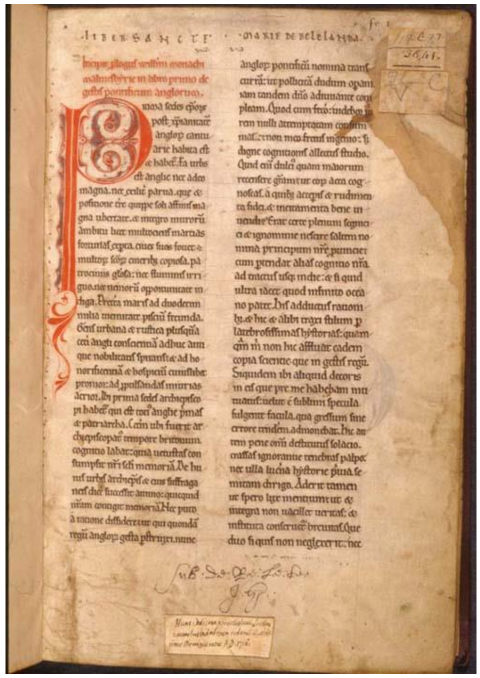

Figure 2(c). Full-page view of BL, Harley Ms 3641, f. 1r © The British Library.

Figure 2(d). Full-page view of BL, Harley Ms 2807, f. 3r © The British Library.

At the roots of the increasing depletion and graphic simplification of Cistercian manuscripts is a specific rule of the Cistercian statute (ca. 1139-1147) that prohibited the use of colours and figures in books[13]. This rule dates later than the Bernardin *Apologia* (1145-1451)

[13] Cistercian *statute* 80 of 1134, see (Rudolph, 1987) and the references here mentioned.

(Thompson J. A., 2000, p. 23), which explains why the Cistercian *scriptoria* adhered to St. Bernard's hostility toward artistic excesses only after his death (1153).

In Portugal, one of the most prolific Cistercian *scriptoria* was in the Alcobaça monastery. Several of its manuscripts are still extant: 467 books from the period between the end of the 12th century to the 18th century (Barreira, 2016c, 2017, pp. 33-34; Jamroziak, 2013, pp. 210-211; Nascimento, 1979; 1992; 2018, pp. 283-284). The great majority of these items might have been produced locally (Casanova, et al., 2022). These surviving items show generous illumination in the shape of decorated initials, *litterae florissae*, or pen flourished initials, each occurring in an equally plentiful chromatic palette. The reasons behind augmenting books with such decoration were diversified, ranging from the need to establish a textual hierarchy via visual means (Rudy, 2016, pp. 15-50) to the desire to express artistic identity.

Speaking of colour hues, previous studies on the materials of illumination in use among early mediaeval Portuguese *scriptoria* of Cistercian, Benedictine and Augustinian monasteries (Alcobaça, Lorvão, and Santa Cruz de Coimbra) revealed the use of white and black materials, yellow, red, blue, and green (Melo, et al., 2011; Miguel, et al., 2018). Considering the importance of colour and coloured mixtures, this thesis focuses on the production of illuminated manuscripts by the Alcobaça monastery from the end of the 12th century (the start of the *scriptorium* activity) to the 15th-16th century, and in a particular type of mixture, i.e., those green.

Research context

Located in central Portugal, the Alcobaça monastery was founded around 1153 (Gomes, 2000; 2013). It was established by the first Portuguese King Afonso Henriques (1112-1185) following the conquest of Santarém from the Moors a few years before, in 1147. Ever since its foundation the Alcobaça monastery would place itself in a prominent position within the contemporary political framework, thanks to its vocation to open itself to outward connections. By the year 1300, this Cistercian monastery had become the wealthiest, most influential, and among the greatest in Portugal. With a large monastic community, the Alcobaça monastery engaged in diversified economic exchanges in their whereabouts and had frequent contacts with the other Cistercian monasteries of the Portuguese kingdom and beyond (Miranda A. , 1984; Miguel C. , 2012)[14].

A few decades after its foundation, the Cistercian monks of Alcobaça formed a library and an independent workshop for book production or *scriptorium* (Barreira, 2016a; 2017, p. 33). Regarding the latter case, a part of the books made in the local workshop circulated in other monasteries: notable instances are some manuscripts made in Alcobaça for the libraries of São Mamede do Lorvão and others. (Nascimento, 2012, pp. 295,402; 2016, p. 34; Cavero, et al., 2016). The largest part of the Alcobaça corpus is represented by autochthonous books and a few university manuscripts brought by their monks who went to study at the universities (in France, Theology; and in Italy, Canon Law) (Barreira, 2016a). Each Cistercian monastery received a set of books from the mother monastery after its foundation; unfortunately, the composition of the donated *corpus* is unknown to date (Barreira, 2017, p. 36; Bell, 2013, p. 140). These books, mostly liturgical, were intended to ensure that the monastic community had all the necessary books for the celebration of the Divine Office and Mass, as well as to guide the spiritual development of its monks. Despite this general situation, the Alcobaça fund bears no trace of these founding volumes, and its number counts mostly items made by its *scriptorium*.

The Alcobaça *scriptorium* was exceptionally prolific in the production of illuminated manuscripts between the 12th and the 16th centuries (Casanova, et al., 2022), and the last few decades have seen a considerable increase in academic attention to its scriptorium, its library and the monastic community in general.

Numerous studies delved into several aspects of the materiality of these books, ranging from the codicological aspects and characteristics of the *scriptorium* (Barreira, et al., 2022; Casanova, et al., 2022; Tourais, 2020; Tourais, et al., 2022), to the illumination techniques (Miguel C. , 2012; Cavero, et al., 2016) and the manuscripts' content, namely around liturgical issues (Miguel C. , 2012; Barreira, et al., 2016; Cavero, et al., 2016; Casanova, et al., 2022). Equally important knowledge was gained through the R&D project "*Cistercian Horizons*. Studying and characterizing a medieval scriptorium and its production: Alcobaça, local identities and liturgical

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[14] It was evident that the monastery was economically independent from royal donation during the early 13th century (Barreira, Melo, Araújo, & Casanova, 2016; Barreira, 2021). Moreover, Barreira (2016a) confirmed a direct cultural connection between the University of Paris and the Alcobaça monastery. Her research supported Nascimento's (1995) observations about a possible movement of Cistercian monks from Alcobaça to the College of St. Bernard in Paris to pursue theological education, providing proof of actuality for the period following the second half of the 13th century.

uniformity in dialogue" (PTDC/ART-HIS/29522/2017), which sought to clarify as much the material aspects of the Alcobaça fund as their liturgical content. The first side of the project, intimately connected to this thesis, aimed at elucidating the illuminating techniques specific to the Alcobaça *scriptorium* through a scientific approach, using the information from the liturgical studies to establish a chronology of production. Thus, the vocation of the *Cistercian Horizons*' project was not only to produce new gainful details regarding the Cistercian community of Alcobaça but also on the history of its *scriptorium*, over several centuries of its production. To target this need for knowledge, the research team of the *Cistercian Horizons*' project considered as many books from the *Fundo Alcobacensis* as possible for detailed inspection and analysis.

Following this goal, one M.Sc. thesis was realised as a collaboration between the ARCHMAT Erasmus Mundus program and the *Cistercian Horizons* project (Fitri, 2020). The work employed the above research approach, i.e., it merged liturgical information with material studies to determine a chronology of production for one manuscript, the Alc. 433. As a long-lived item within the Cistercian religious routine, it qualified as a good candidate, and it was possible to determine the material specificity for each chronological layer of the manuscript.

A recent study addressed the composition of blue paints of a large group of illuminated manuscripts by the Alcobaça *scriptorium* (Miguel & Bottura-Scardina, 2024). The latter study arose from the perception that the *scriptorium* gave only ultramarine, blue-based paints to their manuscripts at the beginning of its activity and that starting from the middle 13th century, azurite was adopted instead. Through a larger pool of manuscripts and more detailed liturgical-chronological data, material studies were able to narrow this period down to the decades 1197-1255 and to elucidate the transition as neither direct nor immediate. In fact, the analysis of a set of manuscripts (Alc. 167, 255, 252, 410, and 231) was able to define this fascinating situation and to elaborate a new hypothesis on the use of these two pigments. The previous hypothesis on the replacement of ultramarine blue with azurite insisted previously on a scarcity of economic availability of the local atelier. Showing that the two pigments co-existed in the same manuscript (Alc. 167 and 255) or alternated among the manuscripts (Alc. 252, 410, and 231) opened again the debate about the socio-economic history of the two pigments.

Blue mixtures seem not to be the most widely used among the books by the Alcobaça *scriptorium*. As to (Melo, et al., 2011), other coloured paints occurred more widely. In fact, a comparative analysis of the colour abundance of the Alcobaça fund showed a large use of green for the monastery of Alcobaça (20-25%) from the end of the 12th century until the 14th century (Melo, et al., 2011; Cavero, et al., 2016). This fact qualifies green as one of the most relevant pigments of the monastic production of early age of the *scriptorium*. Considering the abundance of the green and the scientific maturity reached by the research teams involved in the *Cistercian Horizon* project, this thesis targets the green mixtures of the Alcobaça production, aiming at establishing (I) trends of use in and (II) understanding the use of green mixtures across different typologies of illuminations using the data produced during the Cistercian Horizon *in situ* field surveys.

As to green mixture, previous studies appointed at the use of two possible materials, namely copper proteinate and malachite (Miguel C. , 2012); moreover, important concern arose as to whether copper proteinate was intentionally used as a colouring agent. These concerns arise from the observation that the spectral fingerprint of in-situ spectra of mixtures within some Alcobaça manuscripts have intermediate features between verdigris and protein-based materials (Miguel C. , 2012, pp. 86-90), and oxalates may as well occur here. In truth oxalate patinas form as degradation products of a wide range of artistic artifacts (Rampazzi, 2019) including paints (Poli, et al., 2014). Within this process copper may indirectly play a role–oxalates seem to include calcium rather than copper as the coordinating ion (Miguel C. , 2012, p. 88).

With novel data from the *Cistercian Horizon* project, this master's thesis has the objective of (I) contributing fresh input into the discussion about the possible presence of verdigris in copper-proteinate paints, (II) determining the exact period of transition as to the green mixtures in the colour palette of Alcobaça *scriptorium*, and (III) outlining the history of the green pigment in the Alcobaça *scriptorium* over three centuries of activity.

Research design

The goals of the thesis, previously presented, adopt an interdisciplinary approach based on two scientific methods: one from the social sciences and humanities (centred on contextualised liturgical analysis), and the other from the so-called "hard" sciences (archaeometric analysis) (Figure 3). The first intends to determine the chronology of production for the liturgical books of the Alcobaça fund based on existing studies; the second consists in the use of scientific methods of elemental and molecular analysis for a material characterisation of the materials of illumination, all through an in-situ, non-invasive approach.

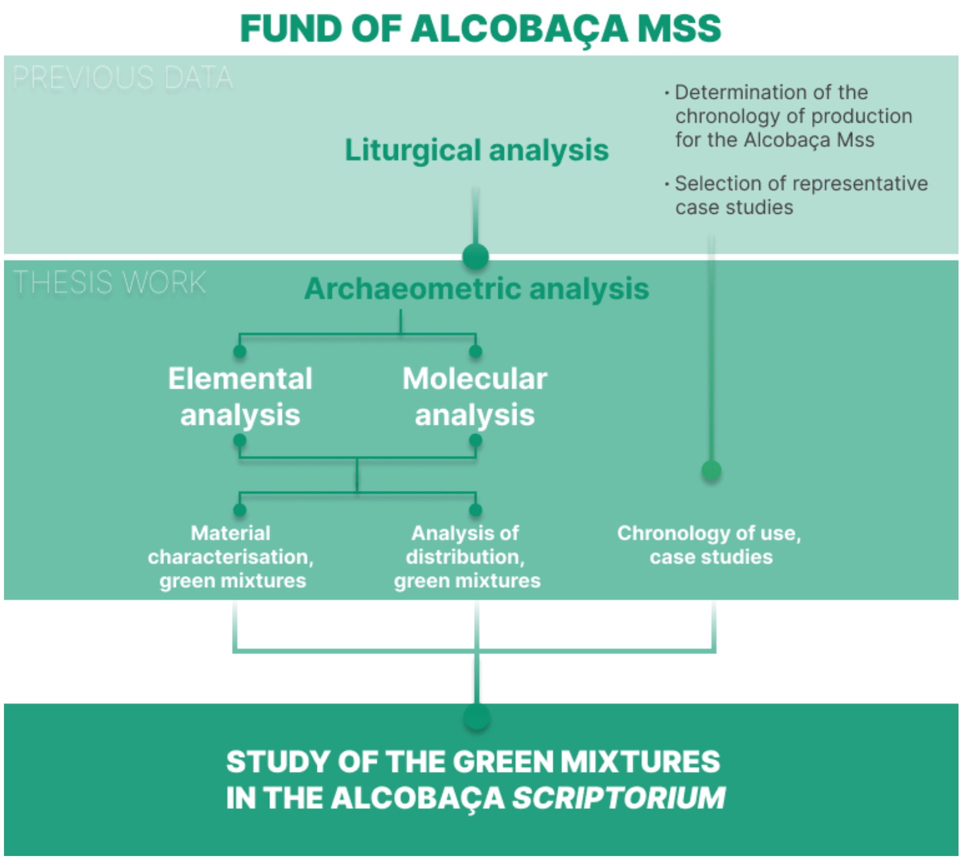

Figure 3. Scheme of the research approach adopted for the work.

The Cistercians celebrated many feasts, each dedicated to a particular saint. The number of these celebrations was so great that attempts were made to reduce the Cistercian liturgy (King, 1956, p. 73). Despite these efforts, the standard Cistercian liturgy was able to accommodate more feasts over the years, some being elevated in rank and others being downgraded. In any case, each feast had to be authorised by discussion at the General Chapter–the annual periodic assembly of the order's monasteries (Citeaux). Once sanctioned, a feast could officially become part of the Cistercian liturgies. Written records were drawn up at the end of these annual meetings in the form of statutes, i.e. *Statuta Capitulorum*, to record the decisions made, including the new festivities and how they were to be celebrated. From the information obtained via the *Statuta*, concerning the new festivities, it is possible to establish a chronology of production for a large number of items within the Alcobaça fund (Barreira, 2016; 2017; Barreira, et al., 2022) and create a detailed picture of many chronological layers for those manuscripts that saw continuous additions (Fitri, 2020).

Such need for determining the date of production for the Alcobaça manuscripts arises from the absence of written records and documental accounts, as Navala reminds (2019, p. 39). Through the shortage, their dating must rely on other information, such as stylistic and formal analysis of the artistic decoration, analysis of material aspects of the manuscripts, paleographical analysis, or simultaneously with the liturgical analysis as to above (Barreira, 2017; Barreira, et al., 2022). About the Alcobaça manuscripts, all this data was used to select a set of representative pieces for archaeometric inspection, namely those produced between the 12th and 14th centuries. The manuscripts from this period were chosen as the most representative because previous research in the area has been pointing to these centuries as the possible transition from one mixture to another (copper proteinate to malachite).

The archaeometric analysis acts as the core of this research work. It has been carried out through analytical techniques of elemental analysis and molecular analysis, each for a specific purpose. The former two have been used to determine the elemental and molecular palette of the spots of analysis, respectively to study the presence of accessory elements which have been typically found in association with copper proteinate, verdigris, or malachite; the second to study the presence of functional groups that can elucidate the structural features of the materials at issue.

Gathering the chronological data from the liturgical studies based on existing studies (Barreira, 2024), the material characterisation and analysis of distribution, it has been possible to establish the use of different mixtures within the given period, if they were used in the same book and their use for illuminations in different hierarchical levels.

State of the art

The Alcobaça collection has attracted considerable attention from the scientific community, particularly in the last half-century. Before the recent interest, a starting point in this field could be the catalogue of the original nucleus of the library or the so-called *Index Alcobatiae*[15]: written by Francisco de Sá and printed in 1775, it was intended to detail the entire collection of manuscript books of the monastery of Alcobaça, in other words, it was a working tool for the library itself and its librarian.

This *Index Alcobatiae* has rendered great service in understanding the collection structure preceding the suppression of the religious orders in Portugal (1834)[16], although there are more index before and after, considering the subsequent events. Following that time, all possessions of the institute (including the Alcobaça *corpus*) passed through several hands: initially, to the Portuguese Ministry of Finance (1838)[17]; then, to the Royal Treasury Department (1839)[18]; finally, it was divided among the newly formed National Library of Portugal (*Biblioteca Nacional de Portugal*, hereafter BNP) and the National Archives (*Arquivo Nacional Torre do Tombo*, hereafter ANTT) around 1887[19].

One of the most notable was Aires Nascimento: he personally identified some manuscripts in the ANTT as originally part of the dismantled *corpus* (Nascimento, 1979, pp. 205-206; 1985, p. 107; 2012, pp. 205-214,237) and added a few more–the so-called *Alcobaça Legendary*[20] (Nascimento, 1978, p. 523) and a Bible in 5 volumes (Nascimento, 1978, p. 523; Nascimento & Diogo, 1984, p. 15). Castro et al. similarly contributed to this extent, as they assigned the BNP copy of the *De Avibus* (Alc. 238) to the Alcobaça *scriptorium* (Castro, et al., 2014). Through those studies, the original composition of the Alcobaça fund could be understood.

Other scholars got involved in other branches of Cistercian research. They traced the origins of volumes from outside Portugal or incorporated from other abbeys (Barreira, 2015; 2016c; Sousa, 2015), studied the Cistercian rule of Alcobaça (Bouton & Van Damme, 1974; Barreira, et al., 2019; Waddell, 1999; 2002) or the local liturgy (Barreira, 2016c; 2016d, Barreira, et al., 2022b).

[15] Full name: *Index Codicum Bibliothecae Alcobatiae*, published by the Portuguese royal typography.

[16] Following the Royal Decree of May 28, 1834–issued on May 30, 1834.

[17] The Alcobaça fund was a possession of the previous monastery; with the subsequent law, it was regarded as the so-called *Próprios da Fazenda Nacional* ("Own by the National Treasury"), so it fell under the public policy remit as well.

[18] The Ministry of Finance handed the collection to an appointed officer of the Royal Treasury Accounting department (December 7, 1838), sanctioned slightly later via Ordinance of the Ministry of the Kingdom (January 11, 1839).

[19] Decree of December 29, 1887. See also (Barata, 2011).

[20] A *legendary* is a collection of lives of saints.

Another line of research in the field was interested in the material aspects of the Cistercian production, especially in their codicology (Nascimento & Diogo, 1984; Casanova, et al., 2022; Tourais, 2020; Tourais, et al., 2022), and composition of inks (Faustino, 2020). However, the richest contribution was about the materials of illumination in the Alcobaça *scriptorium*.

Regarding this aspect, a group of Portuguese scientists invested considerable effort in understanding the technical features of Romanesque illuminating through two projects– POCTI/EAT/33782/2000 and PTDC/EAT/65445/2006, respectively "An interdisciplinary approach to the study of colour in Portuguese manuscript illuminations" and "The identity of Portuguese medieval manuscript illumination in the European context". This scientific investigation gained knowledge into the illuminating practises of early Portuguese miniaturists, including those active in the Alcobaça *scriptorium* (Claro, 2009; Cavero, et al., 2016; Mas, et al., 2014; Melo, et al., 2011; 2016; Miranda, et al., 2008; Miranda & Melo, 2014). Years late, the *Cistercian Horizons* project (PTDC/ART-HIS/29522/2017) returned to devote special attention to the Alcobaça fund, this time limiting its efforts solely to this particular collection to study both its historical course and involvement in the spiritual edification of the Alcobaça monastic community[21]. The project approached the manuscripts in their liturgical as well as material aspects; speaking of the latter, it contributed to the field of material studies of the Alcobaça *scriptorium*. A selected group was examined holistically, namely with a view to studying the historical significance of the materials of production, including those of illuminating (Casanova, et al., 2022; Barreira, et al., 2022; Fitri, 2020). So deep was the project's understanding of the material aspects of the manuscripts that its research teams could draw hypotheses around the actual period of transition for one particular mixture, i.e., blue paints (Miguel & Bottura-Scardina, 2024).

Green paints have also been studied, although to a lesser degree. One doctoral thesis has been studying the red and green mixtures of Romanesque paintings, including those of the Alcobaça *scriptorium* (Miguel C. , 2012). Despite the scientific rigour of the work, the scope of that work was narrowed to a limited period, not being interested in the exact transition of execution.

[21] See Section *Research Goals*.

CHAPTER 1

The Alcobaça fund and the case studies

Chapter 1. The Alcobaça fund and the case studies

Reading historical materials presupposes reading them in connection with their historical context. The Alcobaça fund, a collection of manuscripts crafted for spiritual and moral upliftment, provides significant information about the Cistercian community of Alcobaça (Barreira, 2016; 2017; 2019). Therefore, understanding the context of these manuscripts is crucial, especially considering their location split between the National Library and the National Archive of Portugal.

For this purpose, this thesis further delves into the historical journey of these manuscripts in Section 1.1, explaining why the case studies are sourced from these two institutions. Section 1.2 clarifies the classification of manuscripts within the Alcobaça collection, shedding light on their intended audience and origins.

The unique relationship between the Alcobaça community and its manuscripts resulted in irregular material aspects within individual items. This irregularity stems from the monks' approach to manuscripts as evolving items, accommodating changes in liturgical patterns over time. Understanding this complexity is essential for any research into the chronological evolution of green mixtures among the Alcobaça corpus. Thus, Section 1.3 outlines the codicological succession of selected case studies, emphasizing the necessity of considering their individual histories.

1.1. The history of the Alcobaça fund

The history of the Alcobaça collection is closely linked to the fortunes of the monastery *Santa Maria de Alcobaça*. Its monastic community was founded (Barreira, 2017; Gomes, 2000; Gomes, 2013) in a process that ended in 1153, but it was not until centuries later that the monastery was completed (Barreira, 2017, p. 33). During this long period, the monastic community engaged in practical and spiritual activities, including a systematic production of books. Historical and material traces of operation for a local *scriptorium* date back to before the close of the 12th century, and a group of extant manuscripts from these decades indeed survived (Barreira, 2016a, p. 100; 2017; Nascimento & Diogo, 1984; Nascimento, 1992, p. 154). Most of them are represented by autochthonous books with a few codices for university use brought by its monks who went to study at the universities in France and Italy. The monastery *scriptorium* played a pivotal role in copying manuscripts provided by the mother abbey during the establishment of the monastery (Barreira, 2017; Navala, 2019). A small number of books circulated in other Cistercian monasteries (Cavero, et al., 2016; Nascimento, 2012, pp. 295,402; 2016, p. 34).

After the abolition of religious organizations in 1834, all possessions of the abbey (including the Alcobaça *corpus*) passed through several hands. At first, to the Portuguese Ministry of Finance in 1838. The collection was known as the so-called *Próprios da Fazenda Nacional* ("Own by the National Treasury"). So, from then, it became under the proposition of public policy. On December 7th, 1838, the Ministry of Finance handed the collection to an appointed officer of the Royal Treasury Accounting Department, though sanctioned slightly later via the Ordinance of the Ministry of the Kingdom on January 11, 1839. Finally, it was divided among the newly formed National Library of Portugal (BNP) and the National Archives (ANTT) around 1887 according to a Decree of December 29, 1887, issued by the Portuguese Government (Barata, 2011).

The National Library of Portugal (BNP) preserves around 160 manuscripts from the 12th to the early 13th centuries within the broader context of the BNP collection of 456 mediaeval manuscripts, whereas the National Archives (ANTT) preserves a few manuscripts. In fact, 3 manuscripts of this collection are found in the catalogue of the British Library, but how they reached there is unknown to Nascimento (1992).

1.2. Composition of the Alcobaça fund

The liturgical manuscripts of the Alcobaça fund are collectars, psalters, missals, breviaries, lectionaries, a processional, an evangeliary, a pontifical and a Book of Hours. Based on their origin and inclusion in the library collection, Barreira (2021) classified these manuscripts into four distinct groups, which are presented below.

The **first class** is of codices made in the local *scriptorium*. Being the largest group, the magnitude of this cluster mirrors the importance that the Cistercian communities gave to book production. Crafting manuscripts was regarded as a spiritually constructive activity, so a *scriptorium* not only a space of transcription but also a laboratory of ideas (Barreira, 2021).

The **second class** includes manuscripts added to the Alcobaça fund through acquisition. The most notable of these are the so-called *Parisian codices*. These are books that the monks from Alcobaça used for study purposes while attending a period of education in Paris, which were imported to Portugal afterwards (Barreira, 2021). As such, these books testify to the cultural movement specifically aimed to the intellectual edification of these monks in theological matters as well as an international engagement of the Alcobaça monastery. Most of these books are from the period 1250-1300, with a second period of import seen in the years 1400-1450 under the direction of abbot D. Estevão de Aguiar.

The **third class** includes codices produced in from external *scriptoria*. Some manuscripts, borrowed for copying, found their way to the Alcobaça monastery, and remained for reasons unknown. Examples include Alc. codex 143, housing the Life and Miracles of St. Thomas of Canterbury, previously belonging to the Monastery of Lorvão (Nascimento, 2016). The presence of others, like Alc. 162, a Pontifical for the use of Braga, raises intriguing questions about the circumstances that led to their integration into the Alcobaça Manuscript Collection (Barreira, 2021).

The **fourth** and last **class** is of books that circulated between the Alcobaça monastery and other monasteries. Some of these items were loaned to other monasteries; while a part of these was returned such as Alc. 62[22], others like the Ritual of Salzedas, could not find their way back. Eventually, this mechanism of loan and trade resulted in many losses for the Alcobaça monastery. Part of these small stories left some trace in the inventories of Alcobaça, which kept some records of book loans, but others were not recorded at all. The story further entangled with the dissolution of the Orders in 1834 first, and the incorporation to National Library afterwards. The continuous displacement and change in ownership depleted the historical records of the collection, thus reducing its number. Therefore, the dynamic nature of manuscript circulation and preservation has become considerably more challenging (Barreira, 2021).

1.3. Presentation of the case studies

The examination of the Alcobaça Manuscript Collection offers valuable insights into the historical processes that shaped this remarkable corpus of illuminated manuscripts. The journey of the manuscript, from its origins in the *scriptorium* to its use and circulation, sheds light on the evolutionary dynamics of medieval monastic book culture and the legacy of the monastery of Alcobaça in the preservation and dissemination of knowledge.

[22] It is an Ordinary of the Divine Office.

Seven manuscripts were chosen based on a chronological criterion, for further research as the case studies of this thesis. Six of these items belong to the BNP, whereas the last one is part of the ANTT collection. All of them but one were copied in the 12th and 13th centuries; that remaining book is Alc. 26, which dates to the 14th century. Although these manuscripts are from the Middle Ages, some folia and even entire quires were added to them over the following periods and until the 18th century (Barreira, 2017; Barreira, et al., 2022; Fitri, 2020). The purpose of these additions was to update the books from a liturgical point of view, namely by adding new texts and prayers and the new feasts which were added to the Cistercian Calendar over time. The incremental nature of these items posed considerable challenges to the researchers who intended to understand the history of use and production of these books. Nonetheless, a holistic approach was recently used to combine the history of the introduction of these festivities with the liturgical contents of the manuscripts of the Alcobaça funds. These studies provided a date of production and date of every addition for the case studies.

Based on this data, the case studies could be arranged by chronological order (Figure 4). A part of these manuscripts was made in the early year of the Alcobaça *scriptorium* and other from the latest phases. The full list of the case studies, organised chronologically, which is as follows: BNP, Alc. 433, Alc. 260, Alc. 166, Alc. 167, ANTT Ms 17 and BNP, Alc. 255, and Alc. 26. As far as the ANTT Ms 17 codex is concerned, according to Barreira (2024), it was copied in the *scriptorium* in Alcobaça, and in the middle of the 13th century, it went to Lorvão. Follows a description of the manuscript organised by chronological order and a succinct explanation behind their choice.

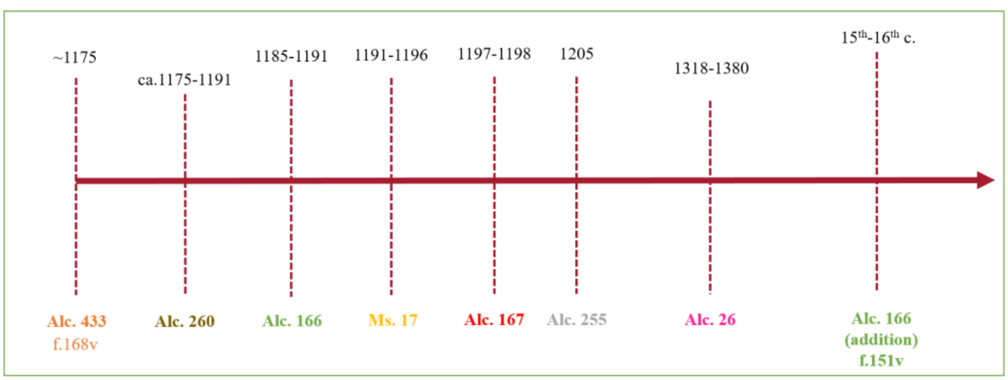

Figure 4. Timeline of the chosen case studies based on the previous research, only relative to the period of activity of the Alcobaça *scriptorium*(late 12th-16th c.). The timeline included the addition of Alc. 166 in 15th-16th century.

Case study 1: ca. 1175 (Alc. 433) Alc. 433 is the second volume of a Lectionary for the Office[23], and it is part of a set of three volumes (Barreira, 2024, p. 107). A single portion of Alc. 433 only was chosen for this research, i.e., the original textual core (f. 18^{v}-227^{v}). Previous research of this item showed that this particular section was written and illuminated at the beginning of the Alcobaça *scriptorium*'s activity[24], around 1175. Additional folia and quires were added to this codex afterwards, specifically after 1175, 1292, 1318, and in the 17th century. Thus, the textual core only (ca. 1175) was chosen as a case study because it corresponds to the first chronological layer of the manuscript.

Case study 2: ca. 1175-1191 (Alc. 260) Second in line for this thesis' research is Alc. 260, a Sacramentary-collectar[25] dating 1175-1191 (Barreira, 2022; Barreira, 2024, p. 108). Several folia were throughout the manuscript were chosen for closer inspection for the purposes of this thesis' work.

Case study 3: 1185-1191 and 15th-16th c. (Alc. 166) Alc. 166 is a Collectar-ritual. The earliest portion of the Alc. 166 (f. 7^{r}-147^{r}) was made between 1185 and 1191, based on Barreira's analysis of this item (Barreira, 2017, pp. 33-62; 2022, pp. 154-182; 2024, p. 108). A first addition to this core was made in 1202 (f. 147^{v}-149^{r}); a second addition dates ca. 1260, and it is the manuscript calendar (f. 1^{r}-6^{v}); the last addition dates back to the 15th-16th centuries (Barreira, 2024). Only the portions of the original textual core (1185-1191) and the last addition (15th-16th c.) were chosen as the case studies of this thesis.

Case study 4: 1191-1196 (ANTT, Ms 17) ANTT, Ms 17 is a Martyrology[26] and Rule of Benedict (Barreira, 2024, pp. 112-113). Originally produced in the *scriptorium* of Alcobaça between 1191 and 1196, it was continuously used in the second half of the 13th century.

[23] A *Lectionary for the Office* is a liturgical book containing readings in use in the liturgy (Brown, 2018, p. 63).

[24] It corresponds to the *Temporal* or *Proper of Time*. Although this group of folia is highly likely to be the core if the manuscript, its position within the manuscript is not the initial, and the start of this section is indeed f. 18^{v} of the current foliation. On the structure of the manuscript and a detailed explanation of its codicology, see (Fitri, 2020; Barreira, 2024; Miguel, Fitri, Bottura-Scardina, Casanova, & Barreira, 2024).

[25] A *Sacramentary* is the part of the Missal which contains the prayers and directives for public service according to the Roman Mass rite; a *Collectar* is a book containing the collects (prayer) used for the celebration of the canonical hours of the Divine Office (Brown, 2018, p. 30).

[26] A *Martyrology* is a collection of martyrs, beati, and other saints arranged by calendar order, or the celebration of their feast in the calendar year.

Folia had been included sequentially to the core text in the indicated period, and some were trimmed after the 13th century. This book contains multiple historical records relative to the monastery of Alcobaça as well as its next location or the Convent of Lorvão (16th century), recently discovered by Barreira (2024, p. 112). She refers indeed several instances of marginal notes indicating notations about the death of abbots of Alcobaça[27], thus showing a journey of this book from the Alcobaça monastery to the feminine Convent of Lorvão. The process of marginal note addition and trimming provides a nuanced understanding of the manuscript use over time. While in Alcobaça, extensive marginal notes were possibly added, attested by the severe trimming, indicative of removal after becoming irrelevant for the monastic community of Lorvão. Later notes, added during the relocation of the manuscript in Lorvão, kept being added in the margins of the folia. Their very presence shows a continuing engagement with the text even after its moving (Barreira, 2024). Several folia from this manuscript were chosen for purposes of research as per this thesis' work.

Case study 5: 1197-1198 (Alc. 167) Alc. 167 is an Evangeliar[28] (Barreira, 2024, p. 113; Miranda A. , 1997, pp. 239-240) copied between 1197 and 1198[29]. Several folia from this manuscript were chosen for purposes of research as per this thesis' work.

Case study 6: 1205 (Alc. 255) Alc. 255 is a Missal copied between 1203 and 1205, based on the analysis of the Sanctorale by Barreira (2024, pp. 114-115). Several folia from this manuscript were chosen for purposes of research as per this thesis' work.

Case study 7: 1318-1380 (Alc. 26) The last case study is the Alc. 26, a Missal copied in the Alcobaça *scriptorium* between 1318 and 1329. This date was proposed through a close inspection of both its *Temporale* and *Sanctorale* by Barreira (2018; 2024). Although the date of production is the 14th century, some addition in form of marginal notes were

[27] She mentions the marginal notes on indicating the death of the first abbot of Alcobaça, D. Randulfo (fl. 1152-1664, f. 42r) and abbot D. Martinho (fl. 1170-1191, f. 124v) as well as the Abbes of Lorvão Catarina de Albuquerque (fl. 1574-1604, f. 3v), Catarina de Eça (fl. 1471-1521) and Margarida de Eça (fl. 1522-1537, f. 20r). See Antunes, 2013, p. 179; Barreira, 2024, p. 112.

[28] An *Evangeliary* is a liturgical book which includes only biblical readings from the Gospels.

[29] Barreira (2024, p. 113) proposes this date based on the presence of the presence in the Sanctorale of the Feast of St. Peter of Tarentaise, which was moved to May 23 (*8 idus maii*) by the General Chapter of 1196. She rejects the possibility of a later dating because of the absence in the Sanctorale of the Feasts of St. Anthony and St. Nicholas, which the General Chapter approved in 1198 and 1199 respectively.

added afterwards. One case in point is a note concerning the shortage of olive oil in the monastery in 1565, placed at the beginning of the volume; another, an addition appears concerning the ritual of monastic profession from the late fifteenth century (Barreira, 2018; 2024). Only one folio from the Alc. 26 was considered for closer inspection for this thesis.

Instances of the folia selected as the case studies are presented in Figure 5.

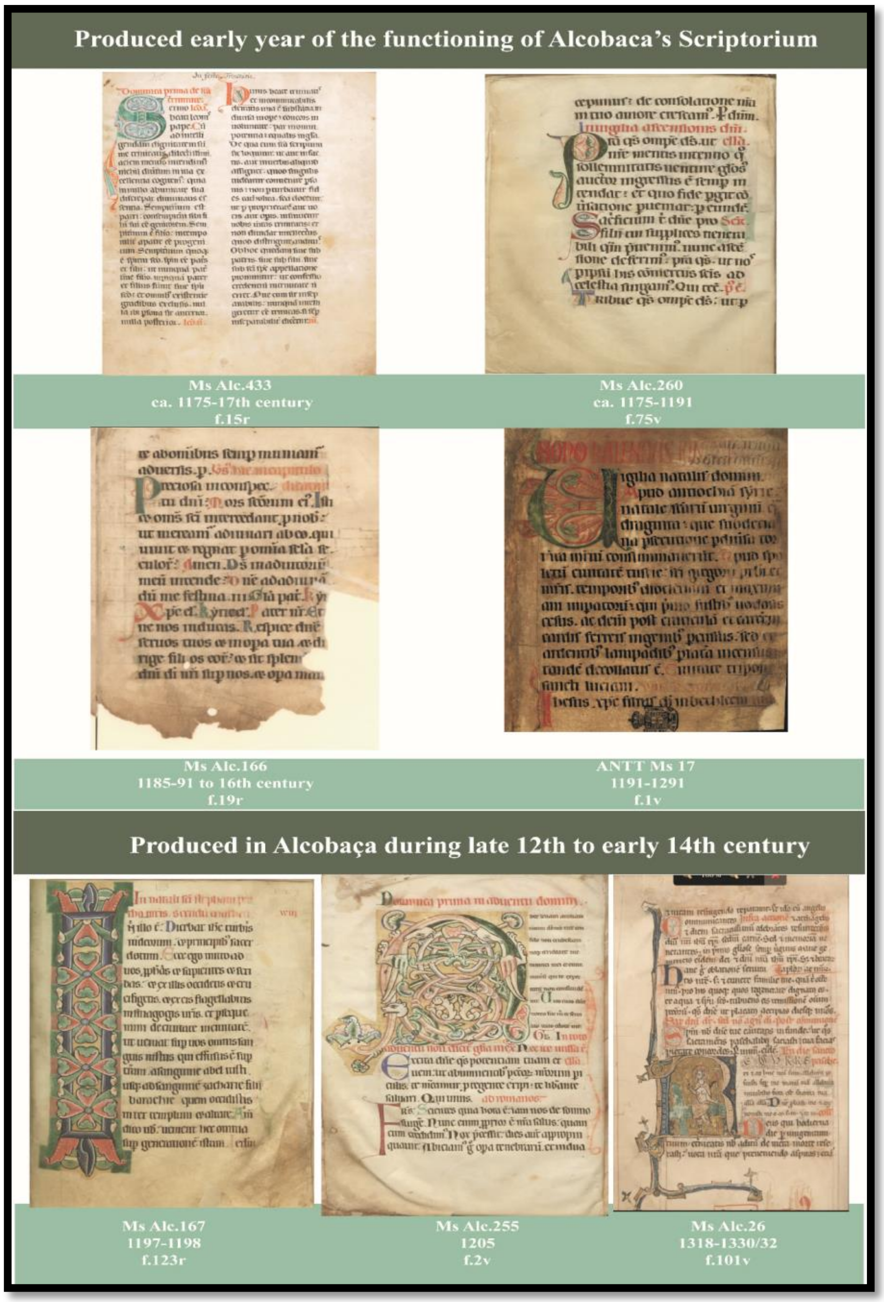

Figure 5. Representative digital reproduction of the selected case studies, arranged by chronological order. The dates indicated in the labels are from either the initial nucleus or the dates of their liturgical additions © BNP and DGLAB – ANTT.

CHAPTER 2

Illuminations of the Alcobaça fund and its materials

Chapter 2. Illuminations of the Alcobaça fund and its materials

Exploring the origins of green colour sources in Medieval Portuguese illuminated manuscripts requires a clear understanding of the intricate hierarchical principles that governed the embellishment of these precious artefacts. These principles, although tacitly understood by scholars, often remain unarticulated in contemporary scholarship (Rudy, 2016). The essence of this hierarchical framework lies in its capacity to discreetly guide the choices made in pairing text and image during manuscript creation (Rudy, 2016). This concept, elucidated by Rudy (2016), posits that the decorative elements within a manuscript play a crucial role in reinforcing its textual structure, resulting in a visually harmonious and internally consistent design logic.

The hierarchical decoration facilitates the navigation of its contents for the user. The use of vibrant colours on certain pages serves as visual cues, indicating the commencement of significant texts. Simultaneously, smaller initials, accompanied by marginal decorations, aid users in pinpointing specific passages within the manuscript. It is imperative to recognize that the evolution of this hierarchical structure has undergone changes throughout codex production, and a thorough exploration of this evolution can provide valuable insights into the study of manuscripts (Rudy, 2016; Barreira, 2017).

This chapter examines the hierarchical nuances of illumination within the selected case studies to shed light into the way in which these principles were put in practice. By doing so, this section seeks a deeper understanding of the intricate relationship between hierarchical decoration and the use of green pigments in the medieval Portuguese illuminated manuscripts from the Alcobaça *scriptorium*.

2.1. Hierarchy of illuminations

Understanding the hierarchical principles governing the illumination of medieval Portuguese illuminated manuscripts is crucial to comprehend the relationship between various elements. Richter & Stegmann (2019) recommended approaches for encoding illuminations, particularly major and minor initials, provides a systematic framework that enhances the utility of digital transcriptions for scholars across disciplines[30]. Rudy (2016) also suggests some rules to understand the hierarchy of illumination in manuscripts. Based on their perspectives hierarchy, diverse form of illumination used in medieval manuscripts has been highlighted in the next two sections.

2.1.1. Hierarchy of Decoration: A Material Perspective

Rudy (2016) outlines two fundamental rules dictating the hierarchy of decoration in manuscripts. Her first rule associates specific border decoration levels with each kind of initial, emphasizing the grandeur of border decoration based on materials such as gold, painted figures, abstract designs, paint alone, or penwork. The second rule involves the emanation of border decoration from an initial, further influencing the visual hierarchy.

All medieval manuscripts adhere to a structured page layout, regardless of their level of adornment. Rudy's second rule allows understanding how textual arrangement was achieved in mediaeval manuscripts, namely with a strategic use of visual augmentation. Illuminated initials are an ideal candidate for the purpose: for instance, placing the largest and more lavishly decorated initials at the top left corner marked their greater importance over the other, especially smaller initials placed elsewhere. A comparison of these factors can allow building up an hypothesis of hierarchical order of the illumination, thus of the same text they complement (Rudy, 2016). A first step to understand the textual sequence of a manuscript is to identify the major and minor initials as well as other types of illumination, as also stated by Richter and Stegmann (2019).

The latter scholars put special stress on the importance of observing the formal features of illuminated initials like size, colours, forms, ornamentation, and artistic execution. Only via a thorough inspection of all aspects of visual supplements, a scholar can hope to achieve a full understanding of the text they complement and the service of decoration also as active textual tools rather than mere form of embellishment. Taking this perspective into account can help looking major initials, encompassing opening, text, or chapter initials and their features under another light, namely of devices capable of organising textual portions and sections. Similarly, minor initials occur rather frequently to mark paragraph or divide sentences.

[30] A Guidelines for the electronic encoding of Medieval Nordic primary sources published by Medieval Nordic text Archive in their website (menota.org) where Friederike Richter and Beeke Stegmann suggested an encoding system to better describe and analyze the illumination. They also introduced new terminology to specify the initials.

2.1.2. Diverse Forms and Decorations: Cultural Significance

Richter and Stegmann (2019) suggest various forms and decorations characterize initials, contributing to the richness of the manuscript. Their encoding process involves identifying and describing these elements, including historiated initials[31], foliate initials[32], pen-flourished initials[33], pen-work initials[34], inhabited initials[35], versals[36], colour-stroked initials[37], and incipits[38]. These forms and decorations provide valuable insights into the cultural and artistic choices made during manuscript creation, enhancing the overall understanding of the visual elements within the manuscript (Richter & Stegmann, 2019). Apart from initials, various other illuminations contribute to the manuscript's visual richness. Understanding and recording types such as full-page illumination, miniature, marginal drawing, bas-de-page[39], border, incipit page, display page, line fillers, frieze, cartouche[40], vignette[41], and *maniculae*[42] offer insights into the manuscript's layout and highlight the emphasis placed on specific passages.

Motifs within illuminations, whether representational or abstract, are described using basic keywords, providing a cultural context for the depicted objects, beings, or scenes. Representational motifs are identified in free text, while abstract motifs are described by their form, type, and potentially involved motifs. This adds depth to the cultural interpretation of the manuscript

[31] The initial comprises identifiable representational motifs with an illustrative function (i.e. referring to the content of the text).

[32] According to the Menota Handbook 3.0 foliate initial is the initial is decorated with botanical decoration as creeping branches with leaves, buds and flowers or spiral vines.

[33] Fragile embellishment of both geometrical and foliate motifs executed as very fine hair-lines solely in (coloured) ink.

[34] Initial solely drawn with a pen (not a brush) with a subdued degree of decoration as loops and curlicues.

[35] Human, animal or fantasy creatures are placed within the letter or its foliage, often playfully climbing in it with a solely decorative function.

[36] the first letter of a line is clearly out-dented into the left margin, frequently with no or only little decoration and using the same ink as the text.

[37] Sentence initials that are highlighted by an additional stroke of ink, usually in red.

[38] The incipit of a text written in display script, i.e. enlarged, colored, decorated or written in another script.

[39] Elaborate drawing that usually covers most of the lower margins and that is connected to a bar attached to an initial.

[40] Frame comprising a short caption, usually emulating three-dimensional organic forms.

[41]Small ornamental element at the end of a text, as often found in early modern manuscripts. They often co-occur with half-diamond indention of the explicit of a text.

[42] A small hand in the margin pointing at a word or phrase of the written text.

(Richter & Stegmann, 2019). The use of different shades of ink and colours in illuminations is crucial for understanding the indented structure of a text.

The contents of illuminated manuscripts vary based on factors such as production period, scriptorium, social environment (e.g. politics, religion, trade), and type of manuscript. Liturgical manuscripts may include these topics to illuminate readers with God's words during the ritual. Cistercian illuminated manuscripts were heavily influenced by the Order's rules in terms of contents.

2.2.Analysis of the illuminations of the Alcobaça manuscripts

Because of the diverse timeframes of creation, the illumination of the Alcobaça manuscripts includes a wide range of decorations, colours, characters, and styles to portray the spirit and meaning of the text. Even within the same document, many decorative schemes have been detected. These manuscripts have a variety of decorations, including miniature illuminations, incipits, explicit, small motifs, and so on. The most noticeable variation in artwork is their initials. Illustrative ornamentation ranging from historiated initials to basic pen stroke initials may be seen here. The *palmette*[43] and the *rinceaux*[44] drawing style had been followed in most of the cases (Miguel C. , 2012). A significant colour palate has been chosen to decorate these initials, including red, blue and deep glassy green colour. Oppositely placed colour scheme red and green has been used frequently to brighten and intensify those initials (Miguel C. , 2012, p. 79).[45] All of these elements give the illuminated manuscript of Alcobaça a unique and distinct appearance.

To achieve the research goal, in-depth observation for illumination of case studies has been avoided. This section only attempt to observe what type of illumination can be seen in the manuscripts. The selected manuscripts from the Alcobaça *scriptorium*, including the Mss Alc. 433, 260, 166, 167, 255, 26, and ANTT Ms 17, will be discussed individually to highlight their characteristics, historical context, and artistic features.

[43] The palmette, which mimics fan-shaped palm tree leaves, has been used as artistic embellishment since ancient Egypt. (Miguel C. , 2012)

[44] The rinceaux ornament is a pattern of interlaced foliate branches that creates a movement and labyrinth effect in lighting. (Miguel C. , 2012)

[45] Hagiographic readings in the Ph.D desertation of Catarina Miguel's revealed that the red-green colour scheme was only found in the Legendaria from Sta. Cruz and Alcobaça collections, which very unique of variety. (Miguel C. , 2012)

2.2.1. Illuminations of the initial stage of Alcobaça *scriptorium* (Alc. 433, Alc. 260, Alc. 166 and Ms 17)

The manuscript Alc. 433 is a lectionary produced in the Alcobaça *scriptorium* during its initial establishment, around 1175 (Barreira, 2017; Fitri, 2020). Previous research on the liturgical contents of the several quired showed that the Alc. 433 has a stratigraphic nature made of multiple additions over centuries, from this initial stage up to the beginning of the 17th century (Fitri, 2020)[46]. The Alc. 433 has only decorated initials, which display abstract or phytomorphic decoration (Figure 6). Painted in red, green, and blue, the major initials at the heading or *incipit* is often in red, and so are the following letters which open a textual sequence. Each incipit is either to mark the beginning of each chapter or to highlight the importance of the next textual portion. Along with these visual features, some folia show a so-called *explicit*, namely a coloured dash indicating the end of a chapter.

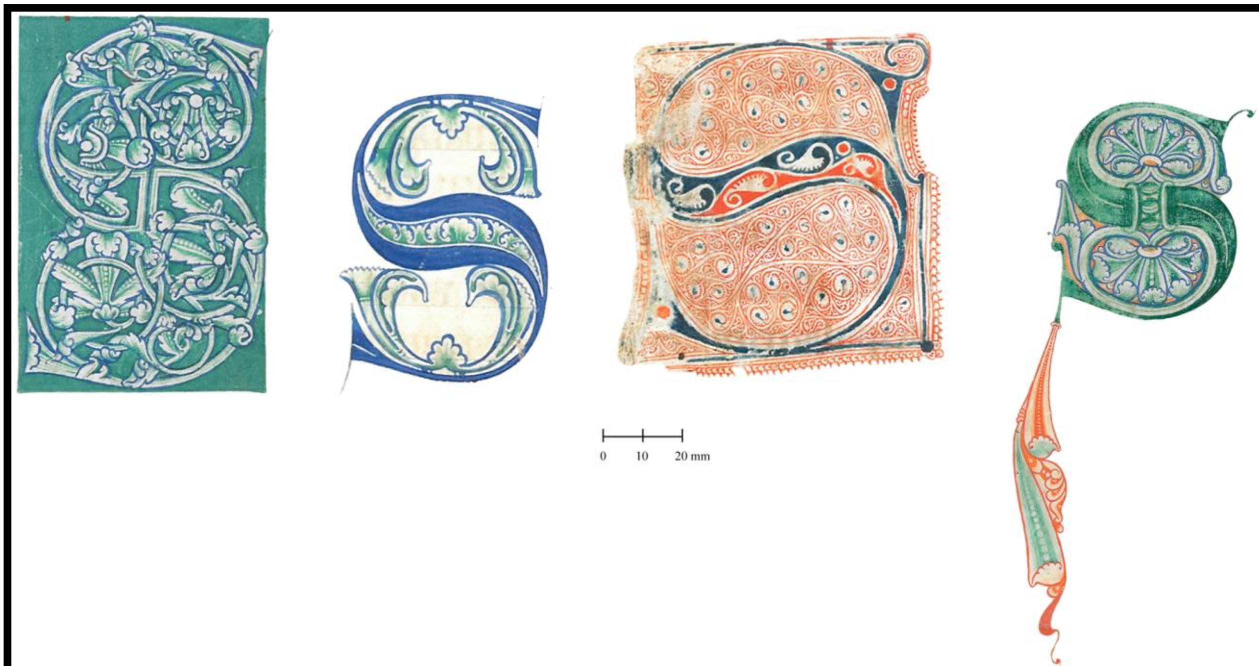

Figure 6. Decorative initials with floral and geometric motifs painted with green, blue and red colours in Alc. 433, from left to right; f.56^r, 18^v, 1^r and 15^r © BNP. (All initials are according to the scale)

[46] A timeline of production was proposed for the Alc. 433 in 2020, with the M.Sc's thesis of Shatila Fitri (2020). In that occasion, the manuscript was analysed with a multidisciplinary approach, until establishing the period of production for the core and all additions of the item.

The Alc. 260 is a Sacramentary copied in the Alcobaça *scriptorium*. As such, it offers a glimpse into the liturgical practices of the 12^{th} century, combining elements from earlier materials (Barreira, 2022). The manuscript features initials in red, blue, green, and purple. Unfortunately, the manuscript is in poor condition with missing folia at the end. The damaged state may affect the overall understanding of the manuscript full content and intended artistic expression[47]. Illumination of the Alc. 260 presents only pen-flourished chapter initials, pen-flourished paragraph initials, colour stroke sentence initials and some folia ornamented with music notation (Richter & Stegmann, 2019)[48]. The manuscript displays no historiated initials, foliated initials, nor any other form of illumination (Figure 7).

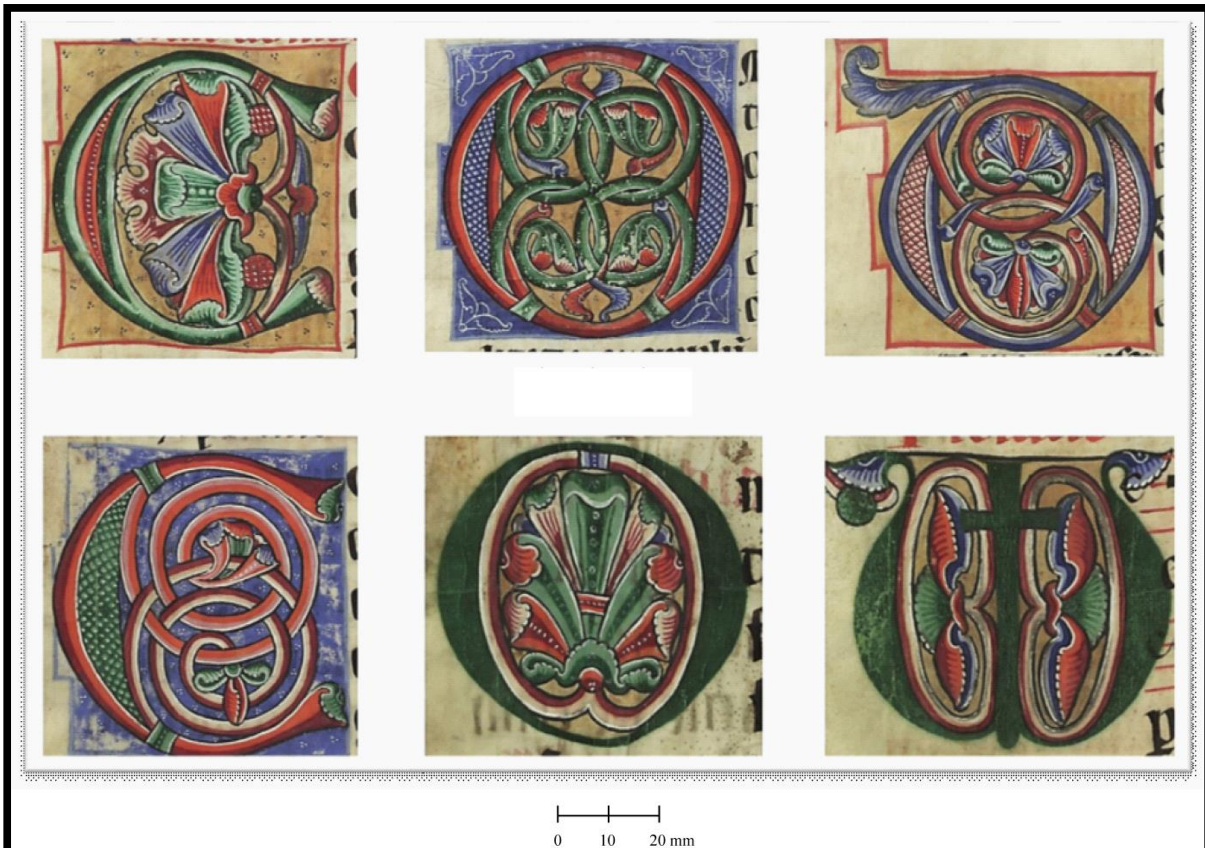

Figure 7. Pen flourished chapter opening initials with floral motifs painted with green, blue and red colour in Alc. 260. Top: from left to right, f. 22^{v}, 54^{v}, 68^{v}. Bottom: from left to right, f. 75^{r}, 83^{r} and 99^{v} © BNP. (All initials are according to the scale)

[47] In the website of BNP catalogue for each manuscripts has been provided where current status and the details were inscribed though the information should be confirmed with other sources.

[48] See Section previous section for the type of initials.

Alc. 260 stands as a testament to the evolving liturgical practices and the continuous adaptation of manuscripts over centuries (Figure 8, Figure 9). The combination of various prayers, hymns, and liturgical elements from different periods provides valuable insights into the religious traditions of the time. Despite its poor condition, this manuscript contributes to our understanding of medieval manuscript production and the rich cultural and artistic heritage of the Alcobaça *scriptorium* (Barreira, 2022).

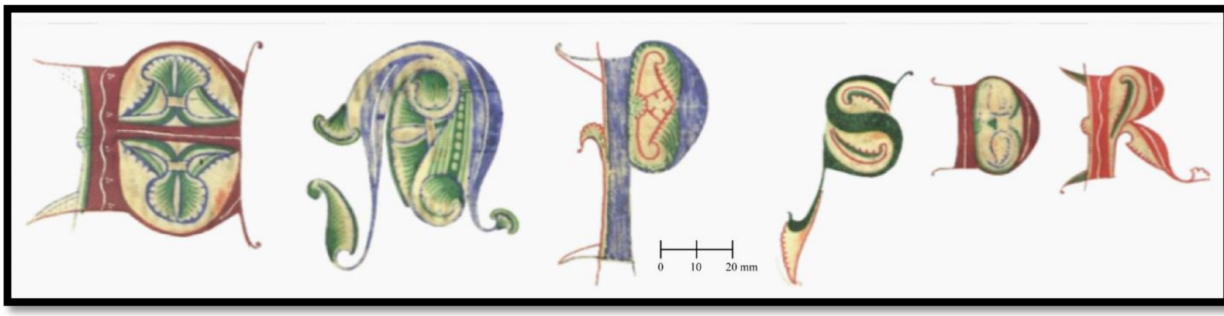

Figure 8. Different sizes of pen-flourished paragraph initials in Alc. 260 © BNP. (All initials are according to the scale)

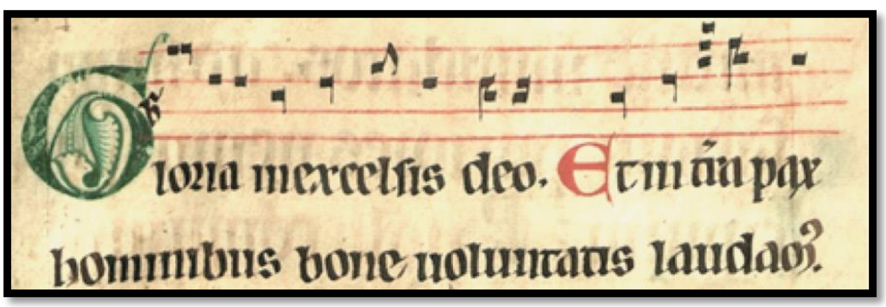

Figure 9. Music notation with pen flourished initials in Alc. 260 from f. 14^r © BNP.

The illumination of the Alc. 166, a collectar-ritual, could be design as a visual tool of textual arrangement for its liturgical contents. In other terms, illuminated decorations helped to attract the reader’s attention on certain passages, to visually discriminate a textual portion, or establish a correlation between lines of text by simply using a standardised colour palette. In this way, illuminated applications were not a mere a device of aesthetic embellishment but rather an active device of reading, which improved accessibility to the textual contents of the decorated manuscript. As to Alc. 166, alternating bright red, dark red, and green were to mark feasts and the twelve lessons throughout the Calendar, thus suggesting an intentional scheme, perhaps to indicate the hierarchical importance of these celebrations (Figure 10).

Figure 10. Different patterns of illumination of Calendar in Alc. 166. From left to right: f. 3^v, 3^r, 4^r and 6^v (the Calendar was copied and added to the manuscript around 1260) © BNP.

Aside from the mentioned decoration, there is no historiated initials or full-page illumination in any part of this item. Chapter initials, paragraph initials and sentence opening initials are decorated with floral, geometrical, and other foliated motifs. The opening of the Calendar is decorated with KL (kalendes), foliated and floral motifs that are stylistically dissimilar from the rest of the manuscript decoration.

Starting from the initial at the highest hierarchy (chapter opening), they are generally decorated in green, blue, and orange-red and generally curvy, undulated features in the Alc. 166. We can see the undulated ornaments within the E curves (Figure-11, centre) and the style of decoration typical of the Romanesque period. The initial letter S in f. 65^r (Figure-11, right) is decorated by green, blue and orange-red colour with undulated ornament.

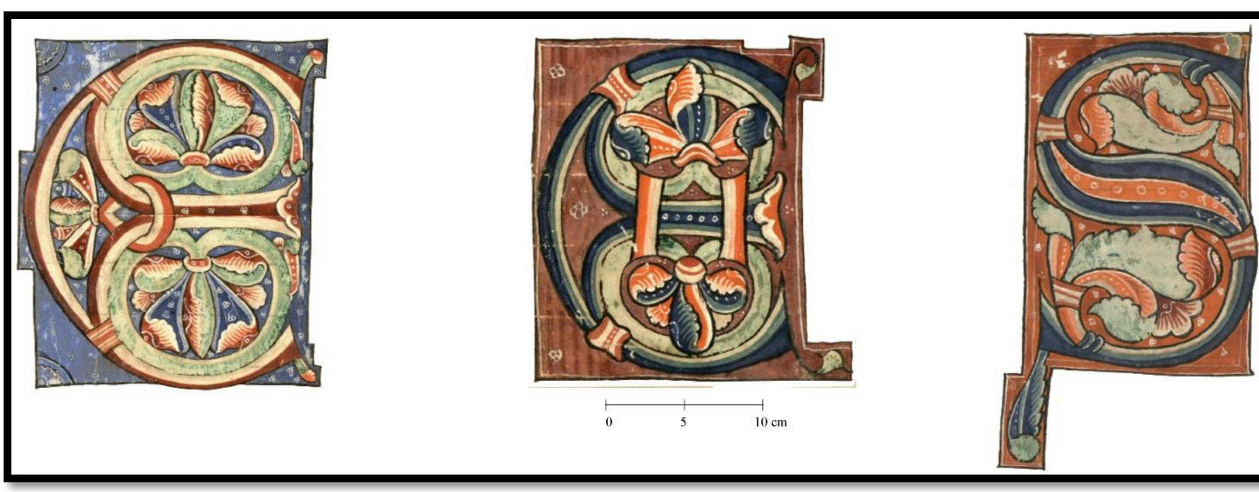

Figure 11. The pen flourished chapter initial letters E and S present in Alc. 166. From left to right: f.8^v, 43^v, 65^r, all painted in green, blue and orange-red with undulate ornament © BNP. (All initials are according to the scale)

Proceeding down to paragraph initials and sentence initials are decorated with calligraphic floral decoration, undulated floral ornamentation, cadels, and so forth. Orange-red, blue and green colours have been used to ornament them. In f. 15^{r}, the paragraph opening initials O, F and A (Figure 12) are painted in green, blue, and orange-red and supplemented with cadels and calligraphic, undulated floral motifs. Instances of this type of illumination are found in f. 15^{v} and 16^{v} (Figure 12), all sentence initials showing the mentioned features.

Figure 12. Types of cadel in floral style as seen in the initial letters O, F and A of f. 56^{v}, 95^{v}, 80^{r}, respectively. Follow the initial letters P, F and E present from f. 15^{r} and D, A and S present from f. 80^{r} in green, blue and orange-red decoration. All decorated letters are from Alc. 166 © BNP. (All initials are according to the scale)

ANTT Ms 17 manuscript was produced after 1191 but before 1197, and it was further augmented with later marginal notes and trimming. As such, it serves service as a valuable artefact offering liturgical information as well as details of the evolution of illumination techniques and the historical context of Alcobaça (Barreira, 2024). Liturgically speaking, the integration of the Martyrology and Rule of Benedict in a single codex emphasizes their joint significance in the daily rituals of the Chapterhouse after the morning Mass. The Martyrology provided readings commemorating saints, while the Rule of Benedict offered guidance for the monastic community.

Speaking of the manuscript illumination, no historiated initials in this codex. This fact is similar to what was seen before in Alc. 166, so the chapter and paragraph initials of this item are decorated with sole foliation and phytomorphic motifs and red, blue, green, and yellow penwork (Figure 13).

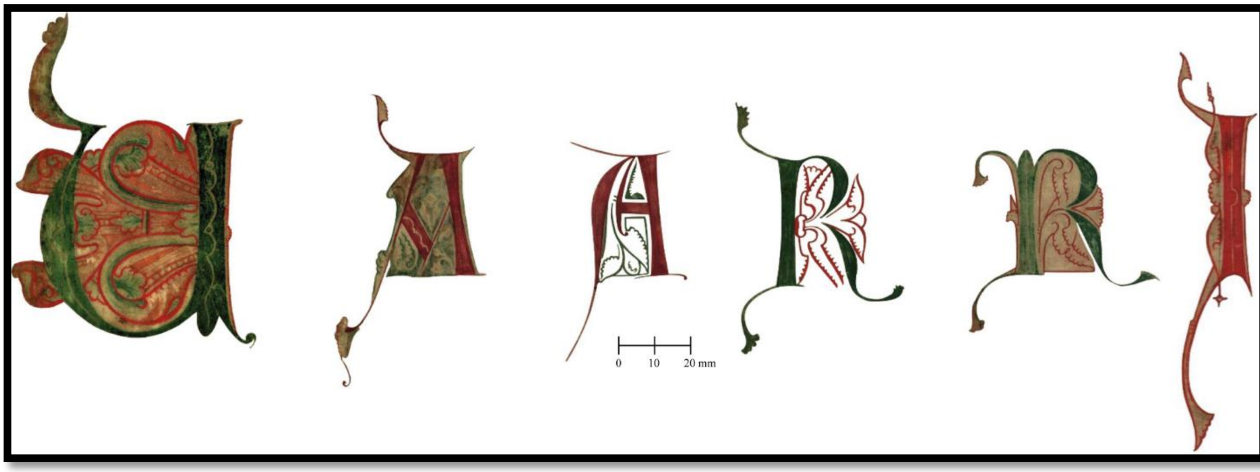

Figure 13. Pen flourished chapter opening initials from different folia with phytomorphic motif and foliation in ANTT Ms 17. © DGLAB – ANTT. (All initials are according to the scale)

2.2.2. Changes in decoration and colour palette for late 12th-century illumination (Alc. 167 and Alc. 255)

The illumination of Alc. 167, an Evangeliary dated from the end of the 12th century, holds great significance not only for its historical and religious use but also for the artistic decoration and material used in its creation.

This item include Gospels for the use in the monastic Mass, organised by liturgical year. As a matter of fact, the Gospel lessons are not presented in the regular biblical order but accordingly to the Proper of Time and the Sanctorale. Moreover, the item includes some musical notation and other votive masses (Barreira, 2024).

The most striking aspect of the manuscript's illumination lies in its use of vibrant colours and motifs. Initials adorned in red, blue, green, and purple and decorated initials featuring phytomorphic and zoomorphic motifs[49] enhance its visual appeal (Figure 14). Materially speaking, this codex already offer substantial historical insights for the fact of being painted with two types of blue pigments–ultramarine and azurite–in several illuminated initials (Barata, 2011; Barreira, 2024).

[49] Phytomorphic motif indicate the motif with floral decoration and zoomprphic motif means it has animal figurine. (Barreira, 2024)

Figure 14. Pen flourished chapter openings initials featuring phytomorphic and zoomorphic motif from Alc. 167. From left to right: f 2^{v}, 50^{v}, 120^{v}, 87^{r}, 99^{v}, 123^{r}, 129^{r}, 180^{r} © BNP. (All initials are according to the scale)

Pen flourished chapter opening initials of this manuscript are decorated with green, dark blue and red colour with undulated ornament. Undulation and floral ornamentation are also present along the chapter openings (Figure 14).

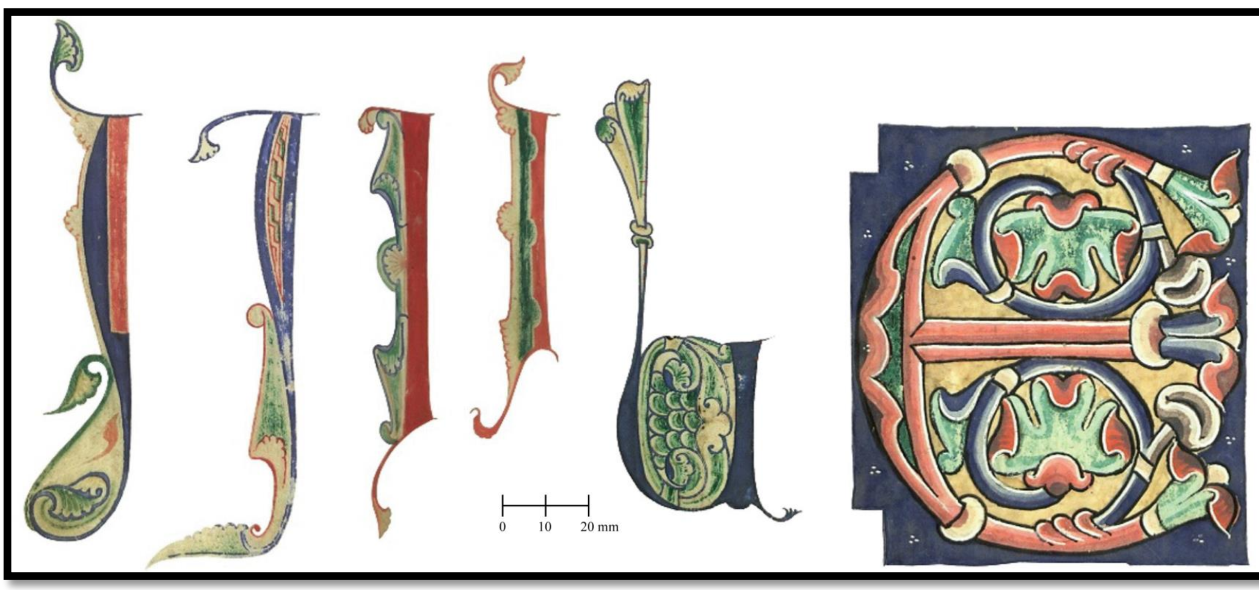

Figure 15. Pen flourished paragraph openings in f. 91^{v}, 94^{v}, 94^{r}, 91^{r}. Music notation with pen flourished initials from f. 82^{r} and 83^{r} in Alc. 167 © BNP. (All initials are according to the scale)

Pen-flourished paragraph opening initials are decorated with green, dark blue and red colours with undulate ornamentation and foliation (Figure 15).

Figure 16. Instance of *incipit* made with several coloured paints, Alc. 167, f. 2^v © BNP.

The heading or incipit can be found in this manuscript, painted in red, green, and blue, most of them are written next to the initial letters. The incipit marks the beginning of each chapter or highlights the importance of the sentence(s) (Figure 16). At the end of some chapters, explicit also found painted red, blue and green. Sentences opening initials are painted with different colour strokes.

The illumination of the Alc. 255 manuscript, a Missal produced after ca. 1202/3 in the Alcobaça *scriptorium*, holds significant importance not only for its artistic features but also for the insights it provides into the historical and material context of the scriptorium during the early 13th century.

Figure 17. In Alc. 255 chapter opening zoomorphic initial "n"f. 3v, Puzzle or phytomorphic initial "R" f. 6r, and "P" f. 11v, using red, blue, green and yellow colour © BNP. (All initials are according to the scale)

The content of the manuscript comprises sections such as the Proper Time, Prefaces, prayers, Canon of the Mass, Proper Time of the Saints and Votive Masses. The choice of pigments, including red, blue, green, and purple for initials, adds a vibrant visual dimension to the text (Figure

17, Figure 18). Notably, some initials are adorned with figures of fantastic animals. To contribute to the manuscript's aesthetic richness, initials are decorated with various decorative patterns: foliate initials, puzzle initials, phytomorphic initials, and zoomorphic initials[50] (Figure 17).

Figure 18. Foliate chapter initial "E" from f. 108^{v}, and Puzzle initial "u" with cross, from f. 102^{r}, Alc. 255 © BNP. (All initials are according to the scale)

The most intriguing aspect of the illumination is the experimental use of azurite pigment. Azurite is employed for only one initial at f. 153v, suggesting a cautious exploration of this new material by the scriptorium of Alcobaça. This choice could be seen as an attempt to assess the capabilities of azurite and its potential applications in manuscript illumination, or an intervention in a later period as a restoration procedure.

Figure 19. Different kind of paragraph opening initials in Alc. 255 painted with red and green. From left to right: $f.8^{v}$, 5^{r}, 9^{v} and 14^{v} © BNP. (All initials are according to the scale)

[50] Please see pages 20, 21 and 28 for more details on decorative patterns of initials.

2.2.3. Illumination of early 14th century Alcobaça *scriptorium* (Alc. 26)

The manuscript Alc. 26 from the Alcobaça *scriptorium* is a "Missal", with various sections, including the Nicene Creed, *Ordo professionis monachorum*, Proper of Time~~,~~ Canon of the Mass, and Proper of Saints[51].

Figure 20. Historiated initials and hybrid decoration in Alc. 26. From left to right: f.1^{r}, 98^{v} and 135^{v} © BNP (All initials are according to the scale)

It contains 20 historiated initials in gold and is decorated with flowers, foliage, and real/fantastic animals. The incarnation of Jesus Christ has been represented by the historiated initials at folio 199 and folio 237 (Barreira, 2014). It has hybrid and dog hare pair decorations which are very common (Barreira, 2014)(Figure 20).

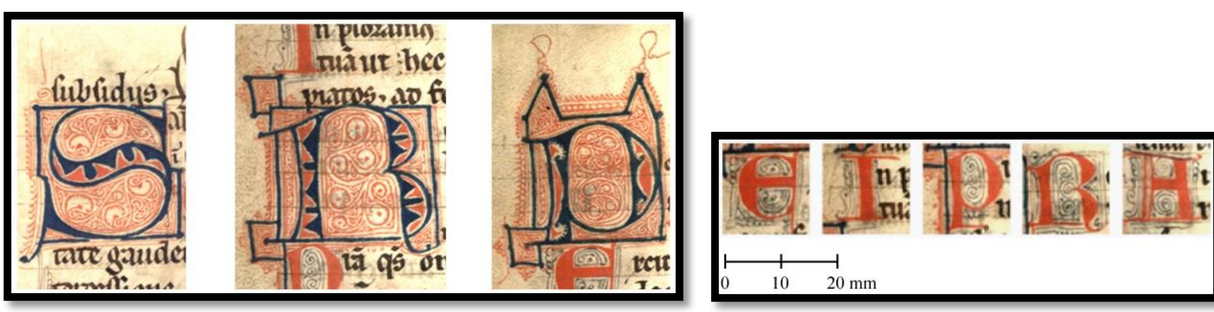

Figure 21. Filigree Chapter initials in Alc. 26, from left to right: f.308r, 8r, 6r and paragraph initials in different folia follows a simpler style © BNP. (All initials are according to the scale)

[51] Digital images of Alc. 26 available on the website of Biblioteca Nacional de Portugal (https://purl.pt/24863).

The chapters and paragraphs start with filigree initials in red and blue colours (Cavero, et al., 2016). Some chapter initials have ascender and descender (ascender means foliation that goes up in a page and descender goes down) (Richter & Stegmann, 2019) (Figure 21). All the initials have ground and infilling[52] decoration; the background of every letter is filled and decorated with geometrical patterns and foliations with very fine lines mostly in red ink (Richter & Stegmann, 2019).

[52] In the Menota handbook 3.0 by Richter & Stegmann, 2019, initials are characterized by several type like historiated initials, floiate initials, pen flourished initial, penwork initial, interlaced initial etc. In the examined manuscripts of Alcobaca we have seen pen flourished initials. It has fragile embellishment of both geomatrical and foliate motifs draw with very fine line in ink.

2.2.4. Illumination of Alcobaça Monastery from the early 12th century to the 14th century

In conclusion, the study of the illumination of selected case studies from the Alcobaça fund provides insights into the artistic expression and cultural context over several centuries of activity for the monastery *scriptorium*. Through a close inspection, we observe distinct trends and innovations in illumination techniques, reflecting not only the changing tastes and preferences but also the religious and historical dynamics of the time. Through time more features had been incorporated, and new colour palettes had been introduced to the illumination of these manuscripts.

During the initial stages of the Alcobaça scriptorium's establishment, illuminations were primarily confined to decorative initials, commonly referred to as pen-flourished initials (Cavero, et al., 2016). However, as time progressed, notable changes in the style and intricacy of these decorations became apparent. Particularly, manuscripts such as Alc. 433, Alc. 260, Alc. 166, and Ms 17 initially featured predominantly pen-flourished initials. Yet, even within this category, variations existed, as seen in Alc. 433, where the pen-flourished initials exhibit either whip flourishes or simpler designs compared to counterparts in other manuscripts.

The manuscripts dating back to the end of the 12th and early 13th century provide insights into transitional phases of illumination, showcasing a blend of traditional techniques and emerging trends. For instance, Alc. 255 demonstrates the use of diverse illumination patterns, including puzzle initials and foliate initials, alongside zoomorphic motifs, a feature also present in Alc. 167. Notably, the chapter initials in Alc. 167 exhibit a higher degree of complexity compared to contemporaneous manuscripts.

Significant shifts in illumination techniques occurred in the early 14th century, as evidenced by manuscripts like Alc. 26, which introduced historiated initials and filigree initials. Contemporary manuscripts corroborate this transformation, suggesting a discernible French influence during this period (Barreira et al, 2016).

Furthermore, manuscripts from the end of the 12th century and early 13th century such as Alc. 167 and 255, demonstrate deliberate colour coding and experimentation with pigments, indicative of a concerted effort to enhance visual comprehension and explore artistic possibilities. Notably, the introduction of azurite alongside lapis lazuli for blue pigments marks a significant development during this period (Miguel & Bottura-Scardina, 2024). These pigments serve as exemplars of colour-coding practices within these manuscripts. For instance, in Alc. 167, azurite is used to mark the most prominent initials and key parts of the manuscript, while ultramarine (Barreira, 2024) is utilised to decorate smaller capital letters throughout the text (Barreira, 2024). These observations suggest a strategic use of pigments, underscoring the sophistication and intentionality behind its production. However, the most substantial changes in pigment usage occurred in the first years of the 14th century, with the absence of green pigment from the palette of earlier periods. Instead, red, blue, and green formed the basic colour scheme of the early *scriptorium* (Cavero, et al., 2016). However, in Alc. 26, the green colour was used very little compared to the other manuscripts discussed here. Additionally, new pigment sources were utilized for colours like red and yellow (Cavero, et al., 2016), while metallic-gold and purple colours became prominent, further reflecting the influence of French manuscripts (Barreira, et al., 2016).[53].

These transformations suggest a potential alteration that could have happened in the use of green pigment during this period, warranting further investigation into the evolving trends in manuscript illumination at the Alcobaça Monastery. The modification of the use of this particular shade from the updated colour palette also piques the desire for future investigation.

2.3. Materials of illumination

The study of illuminated manuscripts offers a profound insight into the craftsmanship and artistic expression of medieval illuminators. The final stage of producing these hand-crafted books involved colouring, where illuminators applied various materials to imbue the manuscripts with visual and symbolic significance. This process required technical competence and a systematic approach to formulating paints that were flexible, durable, and capable of producing various visual effects.

Understanding the materials used in manuscript illumination, particularly pigments and binders, is essential for comprehending the techniques employed by illuminators. Pigments, the coloured substances used in paints, were combined with binders to form flexible films that adhered to the manuscript substrate. The selection and combination of pigments, as well as the properties of the binding medium, played a crucial role in achieving desired visual effects, such as opacity, transparency, and colour intensity.

[53] In the article of Catarina Barreira and et al discussed the influence of French university in the transformation of illumination and material on the basis of a manuscripts from Alcobaça scriptorium, Alc. 54 produced during first years of 14th century.

Illuminators' mastery of paint formulation was often passed down through intensive on-the-job training, and some artists documented their knowledge in technical texts and recipe books such as *Liber diversarum arcium (15th century), De Arte Illuminandi* (14th century), (Moura, et al., 2007; Ricciardi, et al., 2013; Ricciardi & Beers, 2016) etc. These historical sources provide valuable insights into the materials and techniques employed by illuminators, shedding light on their artistic practices and methodologies.

By studying these technical texts and analysing the materials used in manuscript illumination, researchers can gain a deeper understanding of the intricate processes involved in creating illuminated manuscripts. For this purpose, the next section will discuss green pigments, used in medieval Portuguese illuminated manuscripts and Alcobaça scriptorium.

2.3.1. Green pigments in Medieval Illuminated Manuscripts

Previous studies on the colour palette of the illumination of manuscripts from the three medieval Portuguese *scriptoria* of *Lorvão, Sta. Cruz,* and *Alcobaça* showed a relatively extensive use of green for the *Alcobaça* collection (Miguel C. , 2012). In the colour palette of the 12th -13th century, green seem to have been a major colour of illumination of the manuscripts from the local *scriptorium*, as stated in the *Introduction* (Cavero, et al., 2016; Melo, et al., 2011).

The use of colours in medieval arts as well as manuscripts did not solely rest on the local availability of a certain coloured material. Panayotova (2016) refers a powerful case in this regard for lapis lazuli, a well-known source of the pigment ultramarine. She illustrates how this pigment, widely used as a blue material in medieval Europe, was included in an international trade network extending beyond the European continent. The main local extraction areas for the rock source was around the Kokcha River valley, Afghanistan; from here, the rock was imported to Europe until the early modern period (Eastaugh, et al., 2004, p. 218). Like ultramarine, other pigments like Iberian verdigris, vermilion (HgS), lead white (hydroxy-cerussite), and various qualities of pigments circulated across Europe. Iberian verdigris was especially exported in large amounts to Antwerp, Belgium in 1553 (Vermeylen, 2010).

The Portuguese Romanesque tradition saw the use of certain green mixtures for illumination, which have served as helpful markers of artistic production, tradition, or school (Miguel C. , 2012). One of the major materials found in this production is *copper proteinate*. This definition is to label copper (II) complexes with proteinaceous materials (Miguel C. , 2012, p. 54). Although the presence of copper-complexes has been long observed and reiterated, a formal structure for this class of materials has not been proposed to date. Bioinorganic studies on copper investigated the function of copper as a metal centre for proteins (Holm, et al., 1996), but no formal study attempted to describe the coordination geometry of the Cu centre, the type of ligands coordinated by the metal, or the possible presence of residual unbound copper in the typical mixture used for pictorial applications. One study suggested that Cu(II) forms several complexes starting from a square planar geometry (Punis & Zoleo, 2024).

Speaking of the use of this green material, it was found in several previous investigations in manuscripts from the Alcobaça monastery, as stated in the *Introduction* (Melo, et al., 2011; Miguel, et al., 2009; Miguel, et al., 2009). The large presence of the material has even led to belief that this mixture could be used deliberately as a *bottle green* pigment (Melo, et al., 2011; Melo, et al., 2016). It is debated whether the Portuguese *scriptoria* from this period used copper proteinate intentionally as a green material of painting. Miguel (2012) suggested that this pigment could be the result of extensive degradation arising from the interaction of verdigris with a protein-based binding medium, as indicated by a severe loss of cohesion and adhesion to the support (Figure 22). This theory was already proposed by Flieder (1968), and further supported in recent studies on French illuminated manuscripts (Ricciardi, et al., 2013).

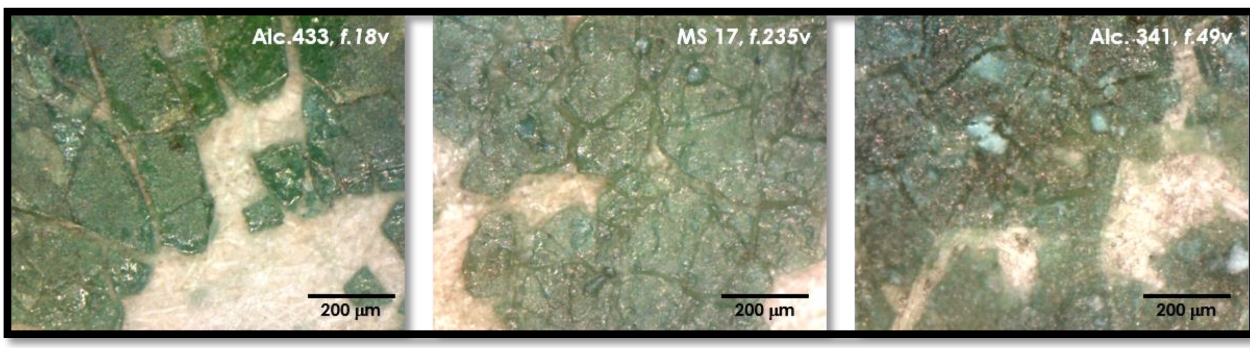

Figure 22. Transparent or glassy appearance of the green paints observed under a digital microscope. From left to right: Alc. 433, f.18[v]; ANTT Ms 17, f. 235[v]; Alc. 341, f. 49[v] © HERCULES Laboratory.

Another common pigment in illumination is *verdigris* [$Cu_{2-3,5}(CH_3COO)_{2-4} \cdot 0\text{-}5H_2O$], a copper-based pigment. *Verdigris* is a collective term to indicate a broad class of blue-green pigments based on copper(II)-acetates, which fall into two main categories: neutral verdigris and basic verdigris.

Neutral verdigris (NV) has chemical formula $Cu(CH_3COO)_2 \cdot H_2O$ and corresponds to the natural mineral *hoganite* (Gregson, et al., 1971; Musumeci & Frost, 2007; Bette, et al., 2017; Brostoff & Ryan, 2020). *Basic verdigris* (BV) is a group of Cu(II)-hydroxide salts with formula $xCu(CH_3COO)_2 \cdot yCu(OH)_2 \cdot zH_2O$, corresponding to several *x-y-z* phases. Rahn-Koltermann et al. (1991) identified multiple BV varieties based on their *x-y-z* notation: 2-1-5 phase (blue-green)[54], 1-1-5 phase (blue)[55], 1-2-0 phase (pale turquoise)[56], 1-4-3 phase (blue)[57], 1-3-2 phase (green to light-green)[58], and 1-3-0 phase[59]. Their differentiation as either NV or BVs has practical implication, because each of them has a specific structural arrangement (Bette, et al., 2017; Švarcová, et al., 2011) and chemical stability (Brostoff & Ryan, 2020). Verdigris pigments were produced by corroding copper with natural acids, generally vinegar, upon exposure to air and moisture. This pigment was often utilized in initial letters to illuminate manuscripts, although there is some historical ambiguity around the terminology.

Despite the modern classification, the definition was used in the past to refer to a variety of copper-containing compounds, not only copper acetates. Copper chlorides, copper carbonates, or other copper(II)-salts underwent the same label, thus generating confusion among the researchers of artistic techniques (Ricciardi, et al., 2013). Verdigris is the only green pigment widely mentioned in 12th and 13th-century technical treatises like the *Liber Diversarum Arcium*[60] (ca. 1300). Despite its aesthetic appeal, it is known for its instability: it tends to darken over time due to oxidation. Its tendency to change in shade posed challenges to the art historians who attempted its identification based on visual inspection (Gilbert, et al., 2003; Ricciardi & Beers, 2016).

To overcome the practical constraints posed by verdigris, medieval artisans explored other alternatives, still copper-based. The goal of producing new materials was to produce more stable as well as optically homogeneous pigments for illumination (Gilbert, et al., 2003). Among these new pigments, copper sulphates, mainly *brochantite* [Cu_4SO_4] and *posnjakite* [$Cu_4(SO_4)(OH)_6$ ·

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[54] Chemical formula: $[Cu(CH_3COO)_2]_2 \cdot Cu(OH)_2 \cdot 5H_2O$.

[55] Chemical formula: $Cu(CH_3COO)_2 \cdot Cu(OH)_2 \cdot 5H_2O$.

[56] Chemical formula: $Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_2$.

[57] Chemical formula: $Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_4 \cdot 3H_2O$.

[58] Chemical formula: $Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$.

[59] Chemical formula: $Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3$.

[60] The anonymous treatise *Liber diversarum arcium* is one of the most extensive and comprehensive medieval handbooks on painting techniques probably composed c. 1300 in Northern Europe (Kroustallis S. , 2022).

(H_2O)], and copper phosphates were a common choice for 15th-16th century Belgium, France, Germany, Holland, and Italy. Each of these pigments was synthetised via a specific process aimed at achieve the desired shade of green (Gilbert, et al., 2003). Some 14th and 15th-century technical treatises like *De Arte Illuminandi*[61] mentioned that *terre-verte* (green earth), malachite, and sap green as green pigments for illumination (Ricciardi, et al., 2013), but not all of them have been observed in the manuscripts by the Alcobaça *scriptorium*. The sole other pigment which was observed is malachite (Miguel C. , 2012).

Malachite is a blueish-green, natural basic copper carbonate [$CuCO_3.Cu(OH)_2$]. It was widely used by the French illuminators in the beginning of the 15th and throughout the 16th century (Ricciardi, et al., 2013). Recent technical-scientific studies on medieval manuscripts suggest that malachite was only seldom used in manuscript illumination until the 15th century (Miguel, et al., 2009; Miguel C. , 2012; Ricciardi, et al., 2013).

Earlier technical literature[62] on European medieval illuminations suggests a scarce use of malachite, perhaps because of its low affinity to oil or oil-resin media, artificial copper greens, such as verdigris and copper resinate were preferred (Gettens & Fitzhugh, 1974). It was identified mostly in the easel paintings of medieval Europe (Ricciardi, et al., 2013) although it had not been used as extensively as azurite (Gettens & Fitzhugh, 1974).

In the context of the Portuguese medieval illuminated manuscripts, the use of malachite has not been explored yet. It was brought to the public attention that copper proteinate and verdigris were in use in the Alcobaça *scriptorium* as major sources of green in the early stages of its activity (Miguel C. , 2012). It is also known that during the 14th century, the abbey started to update their colour palette and sources, most probably under the influence of the French university (Barreira, et al., 2016). Considering the above, it is question when the Alcobaça *scriptorium* started adopting malachite in manuscript illumination.

[61] Technical treaties on illumination from end of the 14th century possibly written by an Italian monk (Moura, Melo, Casanova, & Claro, 2007).

[62] For instance, technical treaties on illumination like *Liber diversarum arcium (ca. 13th century), De Arte Illuminandi (ca. 14th century) etc.*

2.3.2. Binders in Medieval Illumination

Through an accurate choice of pigments and a profound knowledge of their optical and material properties, mediaeval illuminators could achieve a certain aesthetical effect, be it hue vibrance or transparency. Part of their skill encompassed the compatibility of materials, which has ultimately provided illuminated manuscripts with longevity through long centuries of existence (Thompson D. V., 1956). For instance, the illuminators of the Alcobaça *scriptorium* chose a green-red colour scheme where red is considered a warm colour and green a cold colour, and this contrast gave that illumination vibrancy. In this way, despite all the limitations the artist chose the verdigris over other sources because of its perfect deep saturated hue mixing with protein binders. The component may degrade over time, but the colour is still bright and warm.

Numerous proteinaceous binders were employed in medieval illumination, presenting illuminators with a palette of choices, including parchment glue, egg white (glair), egg yolk, and even earwax. Illuminators carefully considered factors such as viscosity, media, transparency, and quantity to achieve a spectrum of hues, glossiness, and colour intensity (Thompson D. V., 1956).

However, the identification of binders presents one of the most formidable challenges in the characterization of medieval illumination Binders are present in the paint as an invisible component. Undesirably, they might react with pigments and create a new component, as in the case of verdigris and copper proteinate.[63]

Follows a description of the types of binders common in medieval illumination.

Parchment Glue Parchment glue[64] served as a versatile binder in medieval Europe, offering not only adhesive properties but also the ability to repair and fill parchment. Parchment glue is made by extracting collagen from animal hides, where collagen molecules are intricately arranged in fibres throughout the dermis. The dermis consists of two layers: the fine-textured, interwoven papillary layer near the epidermis and the coarser, horizontally oriented reticular layer deeper in the skin.

The conversion process of collagen into glue includes protein denaturation, which is achieved by heating the parchment hides in water. The temperature must be set to lower value than the

[63] See the previous section describing colour.

[64] Chemical formula $C_4H_6N_2O_3R_2.(C_7H_9N_2O_2R)n$

melting point and shrinkage temperature for collagen (> 60 ºC). The heating process breaks down the collagen triple helix and forms a gelatinized compound. This transformation can be influenced by factors such as gelatine concentration and the cooling conditions. The collagen susceptibility to degradation, whether by oxidative, hydrolytic, biological, or mechanical means, plays a critical role in the quality and characteristics of the resulting glue. Collagen acted as both a binder and a filling agent, a dual advantage that contributed to its enduring use in manuscript illumination and conservation (Wouters J. , 2000). The main amino acids that make collagen are proline, glycine and hydroxyproline. These amino acids group together to form protein fibrils in a triple helix structure.

Egg White or *Glair* Egg white is the albumen of hen eggs, a fraction rich in proteins and water. Cennino Cennini in his *Il Libro del' Arte,* mentions the use of egg white or *glair* as a binder for pigments and as a varnish (Messier, 1991). Like parchment glue, the preparation process of glair includes denaturation, namely a destruction of the original structure of the protein (secondary-to-quaternary structure), but it involved a mechanical process rather than a thermic one. Glair was prepared by beating vigorously the white of the hen egg until obtaining a cloudy liquid. The liquid was left to settle overnight, and then cleared of the superficial froth. This binder was a highly transparent, water-soluble material which was widely used as a binding agent for medieval illumination (Kroustallis S. , 2011).

Egg Yolk The main components of egg yolk are lipid and protein fractions. The use of egg yolk as a binder is seen already in 11th-century Bavarian Gospels, with notable effects on red lead, imparting warm hues, a yellow glow, and high gloss (Panayotova & Ricciardi, 2016). Widely adopted in medieval Europe, especially for liturgical books, egg yolk offered simplicity and durability (Fitri, 2020).

Additives Medieval colour treatises mention the use of additional additives like honey, sugar, and even earwax to enhance the adhesive qualities of the binding media. Honey and sugar prevented binders from becoming brittle, while earwax addressed issues like bubble formation before painting (Kroustallis S. , 2011).

Extenders Chalk ($CaCO_3$) is a basic calcium carbonate, and it was largely used in the illumination of medieval manuscripts. As an extender in paint compositions, it improved mechanical properties, increased plasticity, and enhanced covering effects when mixed with other pigments (Thompson D. V., 1956). Chalk was also employed in parchment preparation, serving as a surface ground in Alcobaça's manuscripts (Miguel C. , 2012). Gypsum, a dehydrated calcium sulphate ($CaSO_4.2H_2O$) also used as an extender in some of the manuscripts of Alcobaça (Miguel C. , 2012). In Alc. 238, 249 and 419, gypsum was present in deep red organic paints to give it a good texture and hue (Miguel C. , 2012). Lead white is a basic lead carbonate with formula $(PbCO_3)_2 \cdot Pb(OH)_2$. It is mix of anhydrous and hydrated cerussite [$PbCO_3$] (Cucci, et al., 2016), which was used as an extender in paints (Miguel, et al., 2015).

2.3.3. Mixture preparation

There are three or four medieval recipes to produce green colour described in different medieval written sources such as *Mappae Clavicula* (9th-12th century) and *De diversis artibus* (12th century), *Libro de como si facem as cores* (13th-14th centuries) and *Secretum Philosophorum* (14th century) (Miguel C. , 2012, p. 99). Nevertheless, historically accurate reconstructions of these recipes did not lead to the deep-green colour nor the glassy texture of the Portuguese medieval manuscripts[65]. Based on the molecular characterization and experimental analysis it was concluded that to produce this historical bottle green colour copper acetate-based green pigment was ground and then heated with oak-matured homemade vinegar. Within the experimental analysis, gallic acid and sugar, present in the vinegar demonstrate their contribution to the deep green colour production and the final glassy appearance (Miguel C. , 2012, p. 102). As mentioned in *De Arte Illuminandi* malachite with other plant extracts were ground to obtain a very lovely green colour (Ricciardi, et al., 2013). Studies showed that this mineral was extracted from the mines of East Europe, France and Italy (Gettens & Fitzhugh, 1974; Gilbert, et al., 2003). After extraction, it was crushed and cleaned and sometimes for better colour the artist added vinegar (Gilbert, et al., 2003).

[65] Catarina Miguel in her thesis work conducted experimental analysis to reproduce the specific bottle green colour of the Lorvão, Sta. Cruz and Alcobaça manuscripts and identified a different colour recipe had been used to produce this color.

CHAPTER 3

Characterisation of green colour sources in early Alcobaça *scriptorium*

Chapter 3. Characterisation of green colour sources in early Alcobaça *scriptorium*

The research on the chronological usage of green colour sources in the Alcobaça *scriptorium* adopted an analytical approach that included technical-scientific examination. As mentioned in the research design section, the experiment has two sections: one is the inspection and contextualised study of the religious rituals contained in the liturgical books of the Alcobaça fund; the second is to characterise the materials through *in-situ*, non-invasive methods of elemental and molecular analysis. The analysis started with gathering the chronological data from previously done liturgical studies of the collection which is already discussed in the previous section (Barreira, 2017; 2024). The material characterisation focused on the green paints used in illuminated initials. The folios were chosen for analysis based on the chronological order of those manuscripts, for their representativeness and for convenient areas for placing equipment. A total of 37 folia from seven manuscripts were analysed for this purpose (Table 1).

Table 1. Manuscripts analysed from the Alcobaça collection, and the folia were analysed by h-EDXRF, and UV-Vis-NIR-SWIR FORS.

MANUSCRIPT	ANALYSED FOLIA	TOTAL FOLIA
Ms Alc. 433 **~1175-17th century**	1v, 15r, 18v, 42v, 168v	5
Ms Alc. 260 **ca. 1175-1191**	14v, 14r, 21v, 75r, 89v, 98v	6
Ms Alc. 166 **ca. 1185-1191**	19r, 25v, 65r, 151v	4
ANTT Ms 17 **1191-1196**	1v, 1r, 39r, 169r, 235v	5
Ms Alc. 167 **1197-1198**	4r, 20r, 40v, 82r, 83r, 98v, 123r	7
Ms Alc. 255 **1205**	2v, 3v, 36r, 58v, 126r, 148r, 153v, 159v	8
Ms Alc. 26 **1318-1380**	1v, 101v	2

The technical-scientific characterisation of the green paints was carried out in situ, non-invasively, using elemental (h-EDXRF) and molecular analysis (UV-Vis-NIR-SWIR FORS) [66]. PCA analysis[67] was applied to FORS spectra of historical green paints from selected case studies to correlate them with historical perspectives. The results of this analysis are discussed in this section.

3.1. Elemental characterization of green colour sources in early Alcobaça *scriptorium*

The h-EDXRF data for the green paints of the analysed folio indicate the presence of Cu, Ca, and Zn as major elements, with copper being the most intense of all (Figure 23). This fact supports the hypothesis of the presence of a copper-based pigment like verdigris, copper proteinate, or malachite (Gettens & Fitzhugh, 1974; Ricciardi, et al., 2013). Speaking of the other two major elements, zinc is referred as a possible marker of verdigris as a metal source to synthetise this pigment were Cu-Zn alloys (Miguel C. , 2012). The presence of zinc in these spectra could a marker of the presence of verdigris; however, FORS data could be trivial.

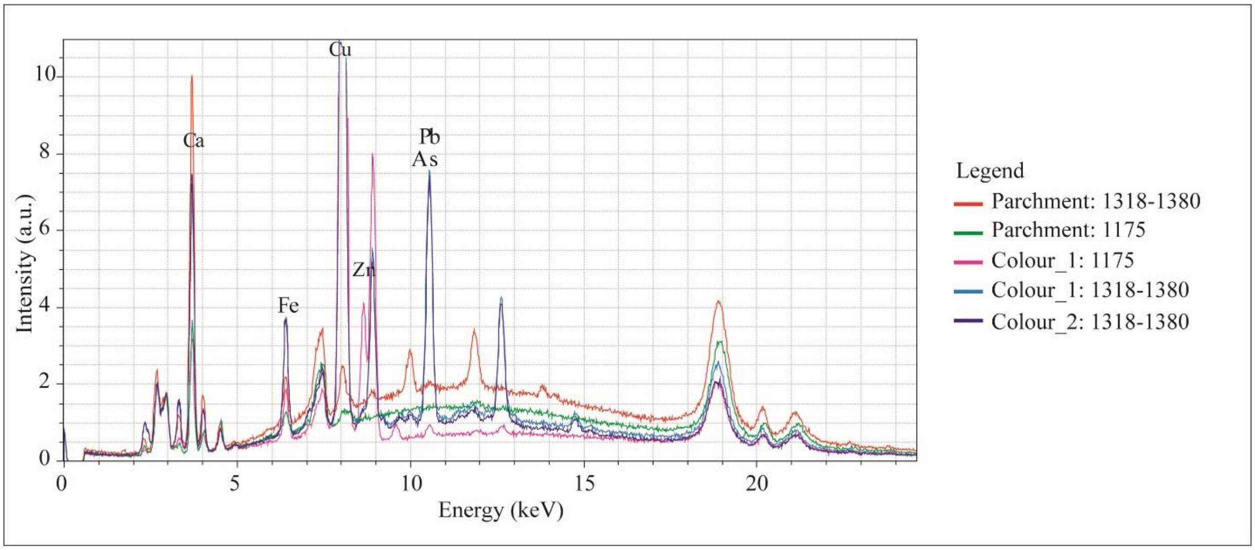


Figure 23. Representative h-EDXRF spectra of green paints and parchment from the folio of 1175 and 1318-1380.

[66] Please see appendix 1 for instrumentation.

[67] Please see appendix 1 for methodology.

The last major element of interest is calcium. It is part of a paint extender (calcium carbonate), but vestigial chalk is also commonly found in parchment. In the latter case, it could either arise from the carbonation of lime, used for the preparation of parchment, or as chalk residual from the surface smoothing–to prepare the parchment to receive the paint mixture (Thompson D. , 1956; Wouters J. , 2000). Other times, calcium carbonate occurred with natural malachite as an accessory phase (Bean, 1968). In brief, calcium could either be part of the paint mixture or the parchment.

To evaluate the use of pigments of studied folios and link them to each period of production, the net counts of Cu, Ca, Zn and Pb were strontium-normalized[68] to get Cu-Ca, Cu-Zn, and Cu-Pb ratios (Figure 24). Three of these elements are those discussed insofar, Pb was chosen as the marker of another common extender, i.e., lead white.

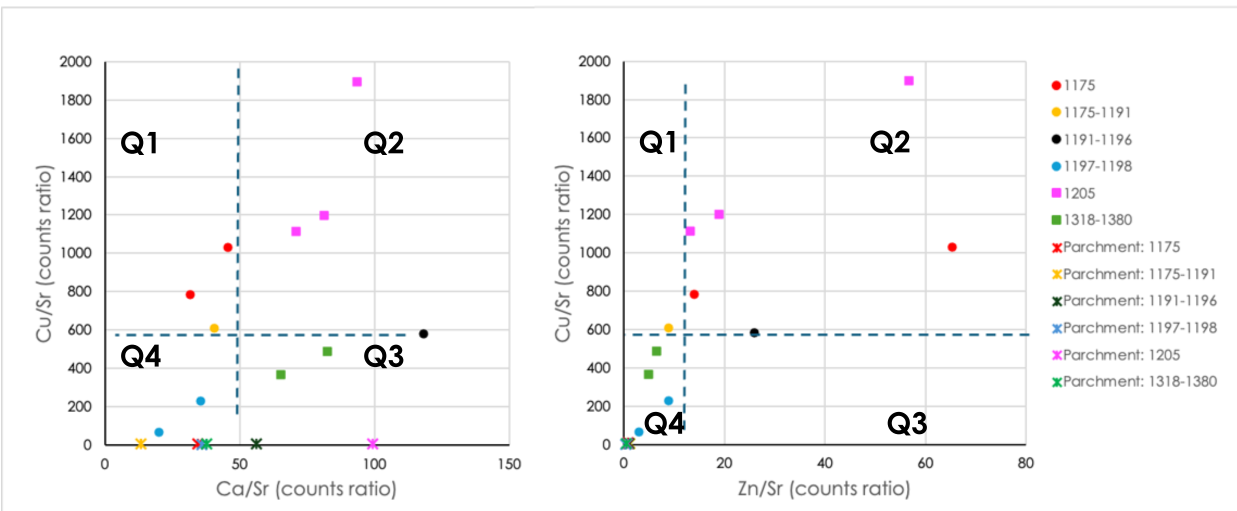


Figure 24. h- EDXRF Strontium normalized Cu:Zn count ratios for 11 green paints of 37 folia in the selected case studies, on left Cu-Ca count ratios and on right Cu-Zn count ratios.

Strontium normalisation allowed drawing four clusters for the Cu-Ca data of the analysed green paints (Figure 24-left). One group (Q4) exhibits lower counts of copper than Q2. This fact reflects on the period of production of the paints, as those from 1197-1198 and 1318-1380 exhibit a lower

[68] For characterization of the green paints strontium normalization were tested to ensure the low influence of the paints thickness over the h-EDXRF results. Strontium is present as a minor element on the calcium carbonate used on the parchment production (Tiburcio, et al., 2019). H-EDXRF spectra were deconvoluted with Artax, To do the analysis MS Excel has been used. Generally to normalize data in excel, the simplest approach is by dividing each value by the maximum value in the dataset. In this case, the value of Cu, Ca, Zn and Pb were divided by the maximum value of Sr.

Cu-counts than the mixtures from all remaining periods. Visual examination of the analysed spot of those paints indicates that the layer of paint is thinner than the others, thus explaining the lower Cu-counts in the Figure 24-left plot. Additionally, green paints from 1205 and the years 1318-1380 showed higher Ca-counts, where the former (1205) may find an explanation in the Cu-Ca values from the parchment. The spots for the parchment from the same period are higher than the other, so the Ca here could be explained as the signal arising from either the parchment ground or some other pictorial material, like an extender. For the paints of 1318-1380, it is possible that the signal for calcium came from the paint itself, either from the pigment or from the extender, because the Cu-Ca count ratio for parchment in this period shows the lower count of the intensity of calcium than others.

The data from the h-EDXRF strontium-normalisation of Cu-Zn counts shows that the spectra for have lower Zn-counts in the green spots from 1175-1191, 1197-1198 and 1318-1380, compared to those from 1175 and 1205 (Figure 24-right). In Alc. 167, f.83 (1997-1198), visual examination showed a thin paint layer with lacunas in analysis, which might be one of the causes for the lower counts of the intensity of Zn in this manuscript (Figure 25). The same trend and visual observation were found for the analysed green paint of Alc. 26, f.101v, produced in 1318-1380. Thus, paint irregularity might be the root for the lower Cu and Zn counts.

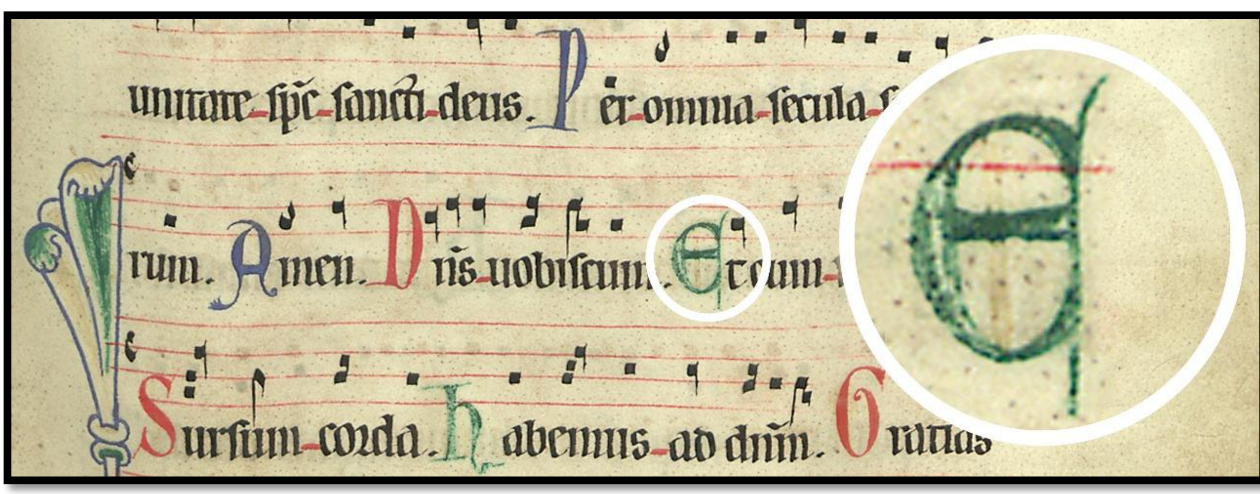


Figure 25. The sentence-initial from the folium of 1197-1198 exhibits a lower count of the intensity of Cu and Zn.

Finally, the h-EDXRF analysis of the green paints of Alc. 260, f. 98^{v} (1175-1191) and Alc. 26, f. 101^{v} (1318-1380) revealed a high counts-ratio of lead (Pb) (Figure 26-left). The detailed observation of the spot of analysis of these paints suggests that these counts of Pb might well come from the thin white layers of lead white paint used as "light" in the decoration of this capital letter (Figure 26-right). Despite this visual observation, the possibility of using lead white as an extender in the green paint formulation shall not be discharged.

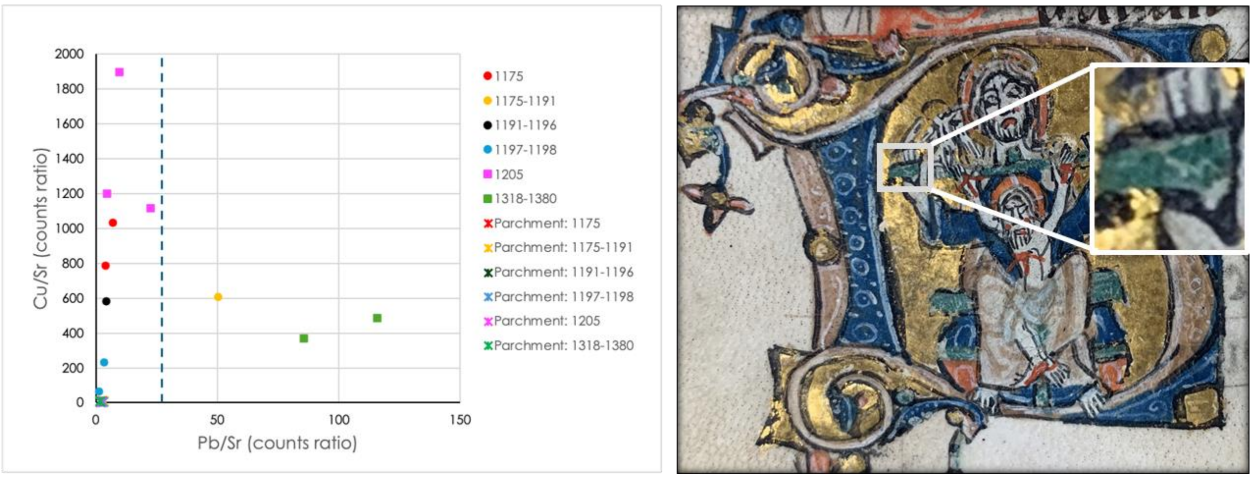


Figure 26. The illumination of 1318-1380 where green paints have the signal of lead might have come from the white paints used in the illumination or from the lead white which could be used as an extender of the paint or from the white area of the paint. On the left is the count ratio of Cu-Pb, and right is the illumination from Alc. 26 f. 101v with the analysis spot.

3.2. Molecular characterisation of green colour sources in early Alcobaça *scriptorium*

The h-EDXRF data suggest a strong presence of copper, thus suggesting that these mixtures might be copper-based. As described in the previous chapter, common copper based green pigments in mediaeval illumination are verdigris, copper proteinate, and malachite. Now this section attempts to identify the type of pigment used.

A typical feature of Cu(II)-based pigments is a characteristics reflectance band falling between 500-550 nm and two absorption bands, one falling at 600-650nm and the other around 800nm arising from the d-d transitions of Cu(II) (Tiburcio, et al., 2019; Reddy & Sarma, 1981). Because this research work aims at identifying the presence of verdigris, malachite, and copper proteinate, an overview of their spectral signature is given.

As per *verdigris*, Section 2.3.1 elucidated that it is a group of copper(II)-acetates, with varying amount of structural water and hydroxyl groups. As such, bands which could be associated with both verdigris groups (NV and BV) are the modes of the CH_2 groups for the acetate, namely a duplet of overtones at 1666 nm and 1682 nm [2ν(C–H)]. For the structural water and the hydroxyl groups, previous research proposed respectively the first overtone of the O–H stretching at 1724 nm and 1785 nm [2ν(O–H), H_2O] (Musumeci & Frost, 2007; Buti, et al., 2013) and the deformation modes of (ν+δ)OH and H_2O at 1948 and 1988 nm.

Malachite is natural basic copper carbonate, so its spectra include modes of the CO_3 group and structural water. Speaking of the former, two bands at 2222 nm and 2272 nm are widely associated to the $2\nu_3$(CO) modes of CO_3; the signature of the structural water is at 1412 nm and at 1921 nm, namely the 2ν(OH) and (ν+δ)OH modes of H_2O (Buti, et al., 2013; Dooley, et al., 2013).

As per *copper proteinate*, its identification relies mostly on the presence of features associated to proteins. Typical modes of several proteinaceous materials are associated to CH_2, N–H, O–H groups and amide modes (table Table ***2***). Vagnini et al. (2009) showed that the combination of anti-symmetric stretching and bending modes of CH_2 and the 2ν(CO) amide I+amide II band are seen in the same position for spectra of both parchment and egg white, respectively 2347 and 2179 nm. The bands of the aminic groups and hydroxyl are more characteristic for a certain type of proteinaceous material, although falling in a similar range. For the aminic groups, the (ν_s+δ), N–H falls in the 2049-2058 nm range and the overtone of the stretching [$2\nu_s$(NH)] is seen between 1497 and 1511 nm. For the hydroxyl group, typical bands are combination modes, and overtones of combination mode of the O–H stretching and bending. The former [(ν+δ)OH] is seen at 1092-1096 nm, the second [2(ν+δ)OH] at 1447-1464 nm. Other modes seen in proteins are various overtones of the CH_2 group: 2ν(CH_2) at 1730-1739 nm, $2\nu_a$(CH_2) at 1698 nm, 3ν(CH_2) at 1182-1190 nm, and 4ν(CH_2) at 878 nm for parchment only.

Table 2. List of the bands associated to proteinaceous materials as per Vagnini et al. *(2009)*. The bands of interest for the present thesis are marked in bold and underlined.

BAND	BINDER		
	Animal glue	**Casein**	**Egg white**
	λ (nm)	***λ (nm)***	***λ (nm)***
(ν_a+δ)CH_2	**<u>2347</u>**		**<u>2347</u>**
(ν_s+δ)CH_2	**<u>2286</u>**	2307	**-**
2ν(CO) amide I+amide II	**<u>2176</u>**	2174	**<u>2179</u>**

$(\nu_s+\delta)$NH	**<u>2049</u>**	2055	**<u>2058</u>**
$(\nu+\delta)$OH	**<u>1946</u>**	1944	**<u>1942</u>**
$2\nu(CH_2)$	**<u>1730</u>**	1736	**<u>1739</u>**
$2\nu_a(CH_2)$	-	1698	**<u>1698</u>**
ν(NH) + 2ν(amide II)	-	1595	-
2ν(NH)	**<u>1506</u>**	1497	**<u>1511</u>**
$2(\nu+\delta)$OH	**<u>1447</u>**	1464	-
$3\nu(CH_2)$	**<u>1182</u>**	1190	**<u>1188</u>**
$4\nu(CH_2)$	**<u>878</u>**		

Representative spectra (in Figure 27) for the mixtures and parchment which are analyzed for this thesis, have been attempted to be interpreted based on the spectral signature indicated above. Spectra from both mixtures exhibit the absorption bands at 605 nm and 650 nm probably arising of the d-d transitions of Cu (II) thus confirming the hypothesis from the h-EDXRF data that those mixtures could be produced from copper-based compound.

Green mixtures from Alc. 26, f.101^v present the characteristic band at 1023 nm. The band falls near the 1092-1096 nm range which might arise from the combination of the overtones and the combination of stretching and bending modes [(+) OH] of the hydroxyl group in hydrated Cu(II) based pigments. Another absorption band has arisen at 2031nm, which could be associated with the aminic groups, the $(\nu_s+\delta)$, N–H as it falls close to the 2049-2058 nm range. At 2270 nm, another band has been observed. This band could be interpreted as associated to the $2\nu_3$(CO) modes of CO_3 at the 2222 nm and 2272 nm range or for the $(\nu_s+\delta)CH_2$ of aminic group (at 2286 nm).

Similarly, the green mixtures from Alc. 167, f.123^r present characteristic absorption band at 1360nm, 1429 nm and 1503nm. The first and the second one could have associated to the hydroxyl group, for the second combination modes, and overtones of combination mode of the O–H stretching and bending [$2(\nu+\delta)$OH], at the 1447-1464 nm range. The second band could also be associated to the signature of the structural water at 1412 nm. The third one could be arise because of the overtone of the stretching [$2\nu_s$(NH)] for the aminic groups which is seen between 1497 and 1511 nm.

Spectra from parchment exhibit characteristic bands at 2045nm, 2169nm and 2292nm. The band at 2045 nm could be associated with the $(\nu_s+\delta)$, N–H of the aminic groups falls in the 2049-2058 nm range. The latter two could have arisen because of the 2ν(CO) of amide I+amide II of protein based compound (at 2176nm) or for the $(\nu_s+\delta)CH_2$ of aminic group (at 2286 nm) which is referring the presence of collagen. But this could be the spectral signature of carbonate group, the $2v_3(CO)$ modes at the 2222 nm and 2272 nm range.

Based on these data it is very difficult to specify the characterization of the mixtures. The green paint from Alc. 26, f.101^v has the features for both copper and carbonate group. It could be said that the mixture was produced from malachite. But it is also showing the spectral signature of aminic group. The paint of Alc. 167, f.123^r exhibit the spectral signature of copper and aminic group. Similarly spectral signature of the parchment also referred the presence of aminic group. Thus these observations identified some possible drawbacks in the interpretation. One is the fact that the spectral feature for collagen group of parchment often overlap with the feature of carbonate group which make the identification difficult. Another one is all of the spectra has signature of aminic group. So it is not possible to say exactly which spectram is from malachite which one is copper proteinate.

Moreover, these analysed spectra are unable to identify the presence of verdigris. Though h-EDXRF suggested the presence of Zn which could be considered a possible presence of verdigris, but in scientific research only this data is not enough for any definite assumption. This unclear identification of the spectral features of verdigris through FORS spectra could lie in its molecular composition. Buti et al (2013) and Frost (2007) have provided some description of verdigris. The first ones used unaged, commercial samples without providing details about the basic or neutral quality of the pigment (BV and NV), while the latter referred details relative to neutral verdigris (a monohydrate acetate). The discrimination between the two types is quite crucial, considering that each of them has a defined crystalline structure, and basic verdigris also sees a wide compositional variety (Bette, Kremer, Eggert, Tangc, & Dinnebier, 2017; Brostoff & Ryan, 2020). The former reports bands associated to the CH_2 of the acetate and the O–H groups of the structural water. Unfortunately, previous studies on laboratory mock-ups in aqueous binders (gum Arabic, egg) have also evidenced the following pathways of degradation for NV, and posed a similar possibility for BVs:

- exchange of the acetate groups of the lattice with local ions with consequent decrease of crystallisation and formation of amorphous forms of verdigris in NV.
- reconfiguration of the acetate groups, formation of new sites capable of H–bonding, formation of amorphous phases of verdigris, and possible formation of CuO (tenorite).

These facts elucidate that verdigris could have degraded make the identification of verdigris challenging. So challenging is its identification, that Buti et al. (2013) lamented the impossibility of detecting this pigment in paintings with vibrational spectroscopy. Unfortunately, most of the bands that could be associated with vestigial verdigris (modes of C=O, CH_3, -OH groups) fall near the pigments mentioned earlier. This fact combined with the sole presence of Zn is insufficient by itself to establish the presence of verdigris in the Alcobaça Mss, so neither the FORS data nor the h-EDXRF data can fully support the presence of this pigment.

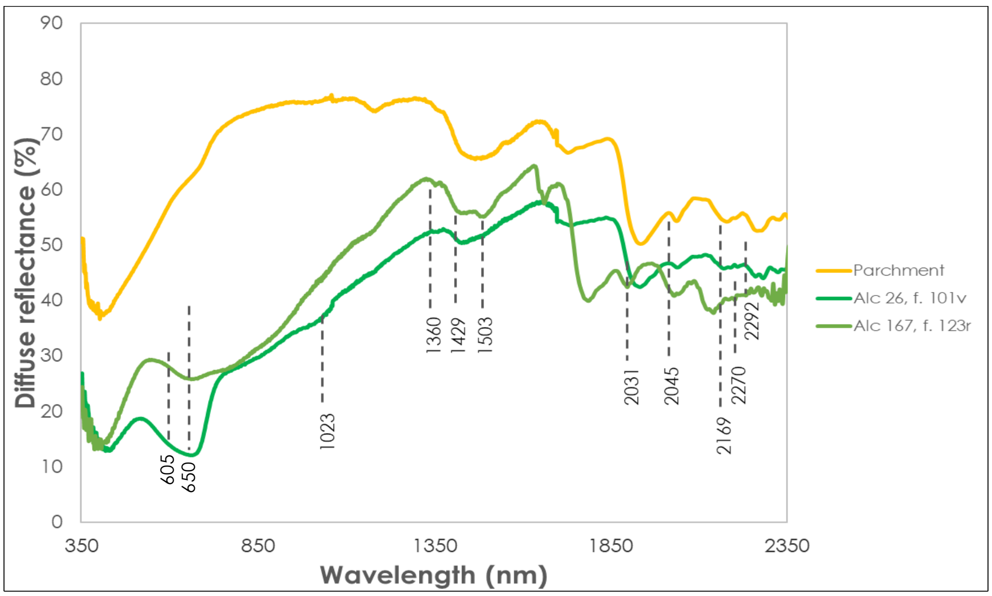


Figure 27. Representative FORS spectra from the parchment and the main green paints detected in the study: represented by Alc. 26, f. 101^{v} and Alc. 167, f.123^{r} respectively.

To minimize the above-mentioned limitations and help the discrimination of the mixture and the creation of compositional clusters, a technique of unsupervised classification was used or *Principal Component Analysis* (PCA). PCA analysis was used on FORS spectra of historical green paints in several modes. The initial dataset for analysis considered the entire wavelength region (350-2500 nm); later, the classification was restricted to the sole SWIR region between 1300 and 1520 nm (Figure 28).

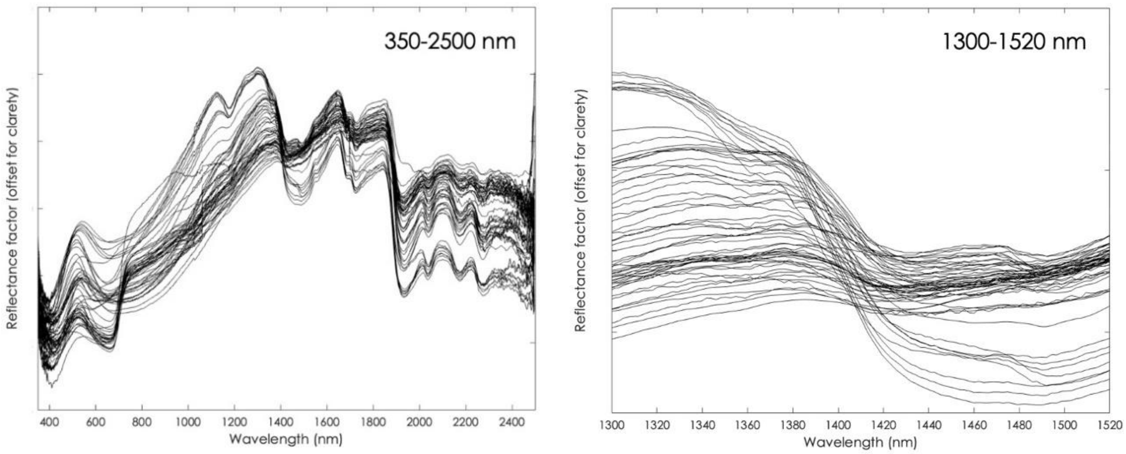


Figure 28. FORS spectra of historical green paints. Left, considering the 350-2500 nm wavelength region; right, restricted to the SWIR region (1300-1520 nm).

The SWIR region (1300-1520 nm) was chosen for integrating two molecular overtones that can be considered as fingerprints for discriminating malachite from copper proteinate: a C–H, CH_3 combination band appears at ~1350 nm (Workman & Weyer, 2008, p. 242) and a second one which could be either the first overtone of O–H stretching at 1493 nm [2ν(OH)] or the first overtone of N–H stretching at 1508 [2ν(NH)] (Badea, et al., 2008; Vagnini, Cartechini, Rocchi, & Sgamellotti, 2009). Regarding the former, the band is observed in aliphatic hydrocarbons, although not specifically in relation to proteins. As per the latter, Badea et al (2008) suggest that a broadening in the region may arise from a strong bond between the water content and the collagen functional groups.

The PCA analysis was applied to the 57 FORS spectra of historical spectra considering the entire wavelength region (350-2500 nm) and restricted to the SWIR region (1320-1500 nm). A first classification for the entire spectral range (350-2500nm) could not afford a satisfactory discrimination, so the analysis was restricted to a limited window of the SWIR wavelength region, i.e., 1320-1500 nm. The latter approach evidenced good discrimination reflected into two clusters of scores–cluster A and cluster B (Figure 29).

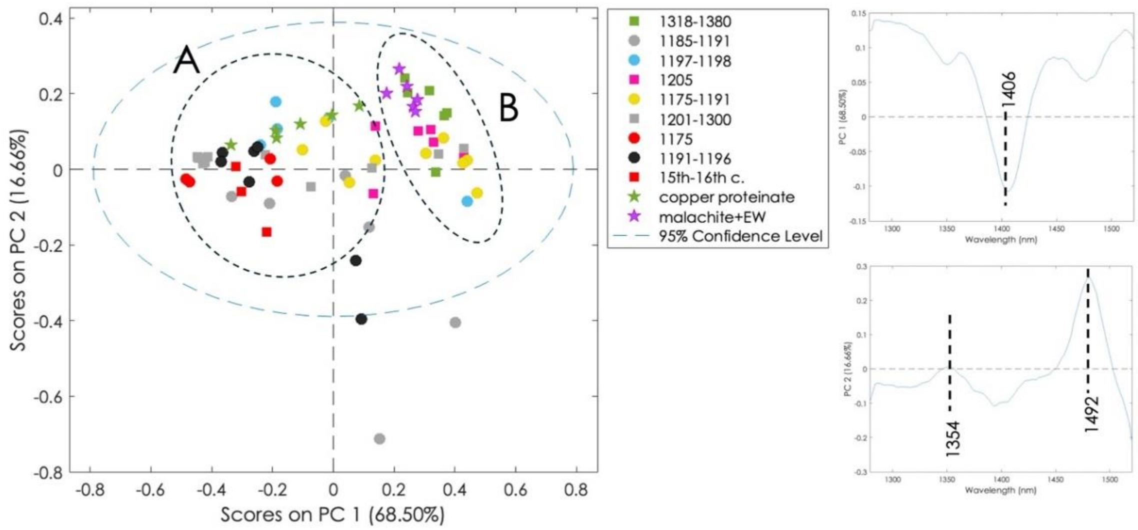


Figure 29. Scores plot of PCA analysis calibrated with 57 FORS spectra restricted to the SWIR region (1320-1500 nm) of historical green paints from manuscripts produced in Alcobaça scriptorium between 1175 and the 15th -16th century, on which was projected 12 FORS spectra of historically accurate reconstructions of copper proteinate and malachite-egg white (EW) paints. On the left, loadings on PC1 and PC2 highlight the absorption bands that most contribute to the discrimination on both principal components.

This discrimination occurs primarily through the first principal component (PC1), which represents 68,50% of the spectral variability: scores of spectra with inflexion at 1404 nm present negative PC1 values (cluster A), whereas the remaining scores of green historical paints present positive PC1 values (cluster B), (Figure 29-left). Regarding the second principal component (PC2), which concerns 16,66% of the spectral variability, the discrimination being mainly due to the presence/absence of the absorption bands at 1354 and 1492 nm, the strongest present for PC2 negative scores (Figure 29-right).

The strong absorption band occurring at 1406 nm for PC1 scores could be assigned to the first overtone of O–H groups of structural water in malachite, which is close to 1412 nm [2ν(OH),H_2O] (Buti, et al., 2013; Dooley, et al., 2013). The other two reflection bands at 1354 and 1492 nm for PC2 scores may feature respectively C–H combination band seen in CH_3 groups at ~1350 nm (Workman & Weyer, 2008, p. 242) and the first overtone of O–H stretching at 1493 nm [2ν(OH)] or the first overtone of N–H stretching [2ν(NH)] (Badea, et al., 2008). As mentioned earlier, the band at 1493 nm could also arise from a strong bond between the water content and the collagen functional groups, which means that this signal could come from the parchment ground. The discrimination through PCA analysis indicates the presence of a functional group, cluster A, which could be proteinate, and cluster B, which could be carbonate. But with these bands, it is not possible to be very conclusive because the signal can come from the parchment too which is also protein-based (collagen).

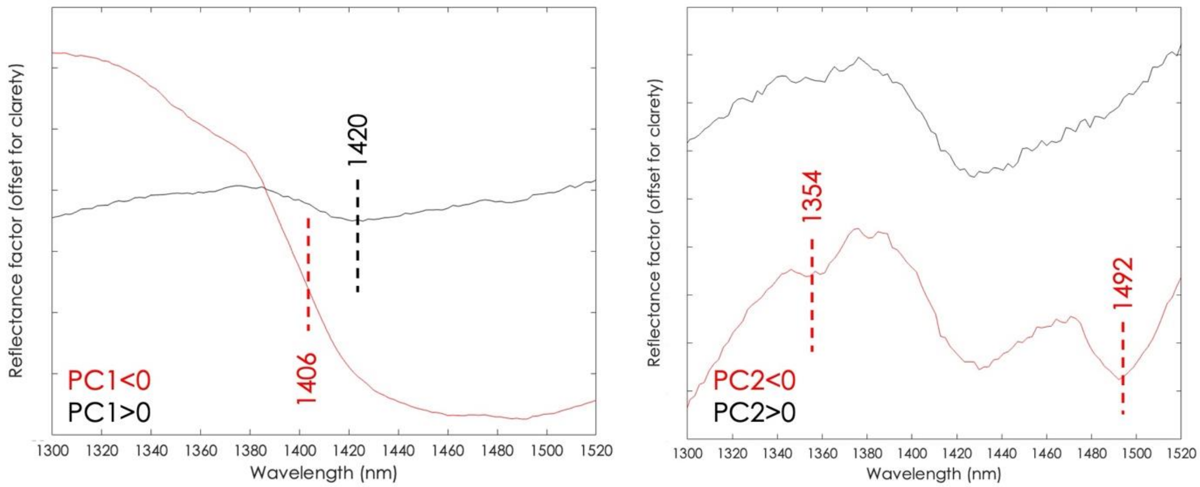


Figure 30. Left, representative spectra of negative (green paint from Alc. 341, f.33r) and positive (green paint from Alc. 255, f.126) PC1 scores restricted to the SWIR region (1320-1500 nm); right, representative spectra of negative (green paint from Alc. 166, f.19) and positive (green paint from Alc. 26, f.101v) PC2 scores restricted to the SWIR region (1320-1500 nm)

To explain the result more specifically 12 FORS spectra of historically accurate reconstructions of copper proteinate and malachite-egg white paints were projected in PCA scores. The projection exhibits that copper proteinate scores FORS spectra were clustered into cluster A, whereas malachite-egg white scores FORS spectra were clustered into cluster B (Figure 30).

Clustered into cluster A (copper proteinate group) are the historical green paints produced in 1175 (Alc. 433), 1185-1191 (Alc166), 1191-1196 (Ms17), some from 1197-1198 (Alc. 167) and 1210-1300 (Alc. 341), all paints from the 15th-16th century (Alc. 166).

Figure 31. Green paints of Chapter initials and paragraph initials from 1175-1191 (Alc. 260) scores in both cluster A and B. On left paragraph initials from f.14 and chapter initials from f. 75 clustered in copper proteinate group (cluster A). On right chapter initial from f. 98^v and paragraph initial from f. 14^v clustered in malachite group (cluster B).

Clustered into cluster B (malachite group) are some green paints produced in 1205 (Alc. 255) and all those from the 1318-1380 (Alc. 26). Special attention must be paid to the Mss Alc. 260 (1175-1191), Alc. 167 (1197-1198) and Alc. 341 (1210-1300), whose scores clustered part into cluster A (green paints from f. 14^r, 21^v and 75^r), and part into cluster B (green paints from f. 14^v, 21^v, 89^v and 98^v). Based on these, it could appear that especially the years 1191-early 13^{th} century saw a transitional phase between malachite and copper-proteinate paints, for a brief return to malachite close to the 15^{th}-16^{th} century (addition to Alc. 166). In this consideration, it is important to observe the appearance of green paints from both clusters. The naked-eye green paints from cluster A have thinner, more transparent, and lighter shades than the paints from cluster B. Paints from both clusters are used to draw chapter initials and paragraph initials (Figure 31). Paints from the 15^{th}-16^{th} century are thicker and darker, like the paints from cluster B (Figure 32).

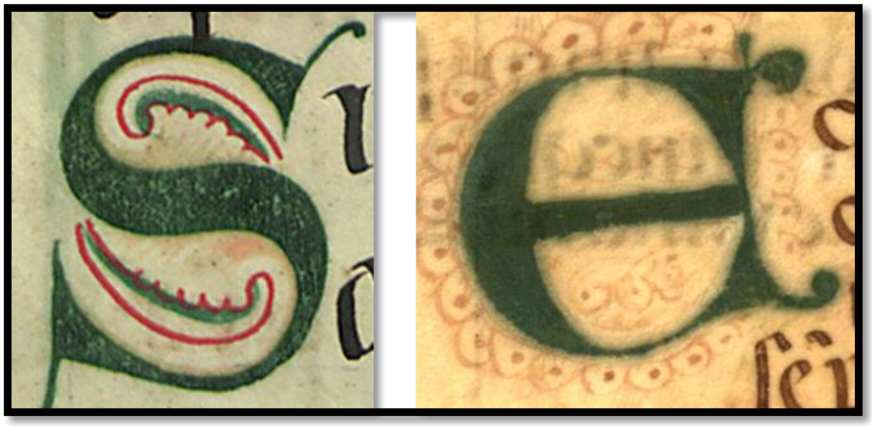


Figure 32. Left: sample initial for the malachite cluster (Alc. 260, f. 14^{v}); right: sample initial for the copper proteinate group (Alc. 166, f.151^{v}) © BNP.

The PCA analysis of FORS spectra could not provide any clear conclusion about whether this copper proteinate paint could have derived from verdigris.

3.3. Final remarks

Going back to the original three objectives of the thesis:

(I) determining the presence of verdigris in copper-proteinate paints

(II) determining the exact period of transition as to the green mixtures in the colour palette of Alcobaça *scriptorium*

(III) outlining the history of the green pigment in the Alcobaça *scriptorium* over three centuries of activity.

The data presented and discussed in this chapter allows providing some answers to each of them. Regarding the presence of verdigris, the data proved insufficient to satisfy the question, so the doubt about the presence of verdigris in copper proteinate require further research. As to the period of introduction of malachite in the production from the Alcobaça *scriptorium* for the period late 12th-late 15th century, the PCA results could offer some indication of time, although not fully conclusive. The data seem to suggest that the transition from copper proteinate to malachite was not sudden; instead, it points at a transitional period for the years 1175-1191, then to a return to copper proteinate, then a full shift in change from 1205 until 1380, to later return to the use of the former mixture in the 15th and 16th century (in the addition of Alc. 166) (Figure 33).

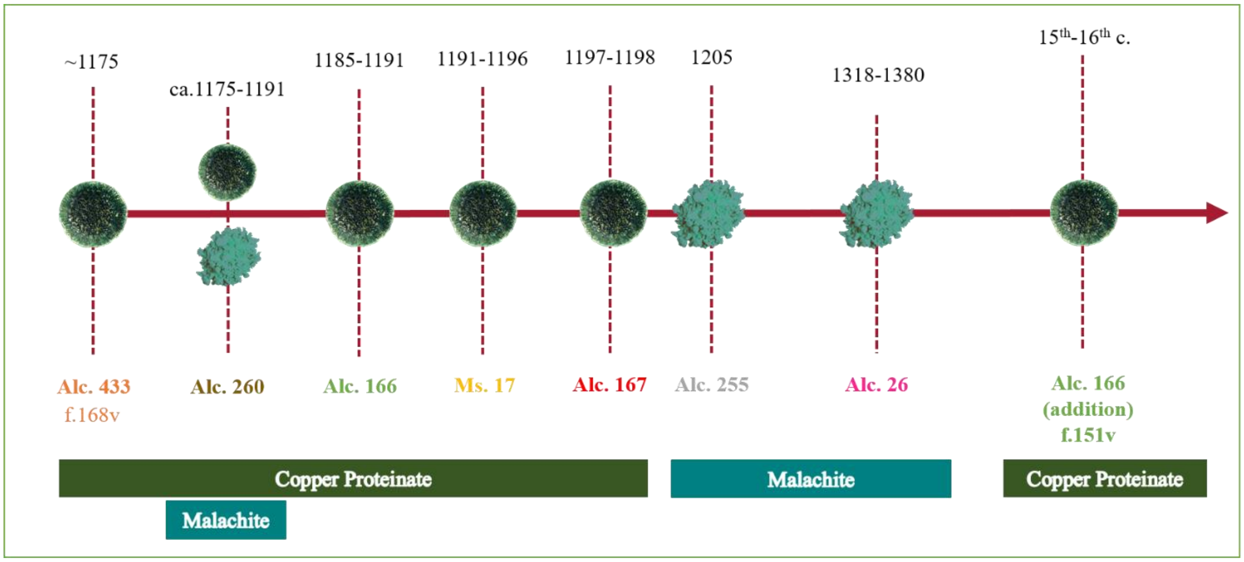
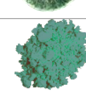
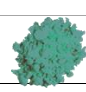
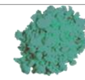
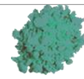
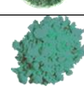
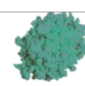
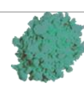
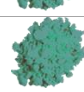
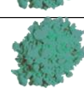
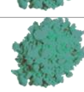
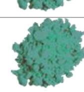


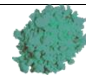
Figure 33. Tentative timeline for the chronological use of green pigments for the period 12th to 16th century for the Alcobaça *scriptorium*.

Analysis of the paint mixtures used in the illuminated decorations (initials) of the case studies based on the results from the PCA-FORS classification also indicates the above-mentioned results (Table 3). Table 3 exhibits that in Alc. 260, copper proteinate and malachite both used in the paints of chapter initials, paragraph initials and sentence initials. Moreover, both mixtures may be used in the same folia 21v to paint chapter initials. This manuscript was produced during the 1175-1191 century.

Table 3. Scheme of the paint mixtures identified for the case studies of this thesis. The illuminated decorations are classified as chapter initials, paragraph initials, and sentence initials (See Chapter 2 for them). Each field shows the results from the PCA-FORS classification, and the number of spectra for that mixture is given between brackets.

PERIOD OF PRODUCTION	CASE STUDY		TYPE OF ILLUMINATION		
	Manuscript	*Folio*	*Chapter initial*	*Paragraph initial*	*Sentence initial*
~1175	Alc. 433	168v		 (2)	
1175-1191	Alc. 260	14r		 (2)	
		14v		 (1)	
		21v	 (1)		

PERIOD OF PRODUCTION	**CASE STUDY**		**TYPE OF ILLUMINATION**		
	Manuscript	***Folio***	***Chapter initial***	***Paragraph initial***	***Sentence initial***
			 (2)		
		75r	 (2)		
		89v		 (1)	
		98v	 (1)		
1185-1191	Alc. 166	25v		 (2)	
		65v		 (2)	
1191-1196	ANTT Ms 17	39v		 (2)	
1197-1198	Alc. 167	4r		 (1)	
		20r		 (2)	
		40v		 (1)	
		82r	 (1)		
		83r		 (1)	 (1)
		123r	 (1)		
1205	Alc. 255	2v	 (2)		
		36r		 (2)	
		58v	 (1)		
		126r	 (1)		
		148r	 (2)		
		153v	 (2)		
		159v	 (1)		

PERIOD OF PRODUCTION	CASE STUDY		TYPE OF ILLUMINATION		
	Manuscript	*Folio*	*Chapter initial*	*Paragraph initial*	*Sentence initial*
1318-1380	Alc. 26	101^{v}	 (2)		
15th-16th century	Alc. 166	151^{v}		 (3)	

A possible reason behind the uncertainty is that all pigments analysed are copper-based mixtures. The h-EDXRF data could confirm this fact; however, it could not provide clues for a more straightforward indication among verdigris, copper proteinate, or malachite. Additionally, the thin paint layers may allow signals from the underlying parchment to interfere with the pigment signals, complicating the interpretation. The spectral region for parchment overlaps with the functional groups of these pigments, making it challenging to distinguish between them.

However, the discriminating band at approximately 1406 nm in the PC1 scores suggests the presence of a basic carbonate compound, which could indicate malachite (cluster B), namely a copper carbonate. Contemporaneously, the h-EDXRF data for the paints in the same cluster also show higher counts of calcium and lower for zinc. This fact is consistent with the presence of malachite. Conversely, the paints in the copper proteinate group (cluster A) show lower calcium and higher zinc counts, suggesting they were likely produced using a Cu-Zn alloy, indicative of copper proteinate.

The analysis of FORS spectra from historically accurate reconstructions of copper proteinate and malachite-egg white paints supports these findings. Therefore, it may be concluded that paints from cluster A were likely produce from copper proteinate, while those from cluster B were likely produce from malachite.

The data from this thesis was observation in the framework of other mixtures whose transition has been already determined. Previous research on blue pigments in use in the Alcobaça *scriptorium* proposed that both lapis lazuli and azurite were used in the same codex from 1197-1198 in the illuminated manuscripts of Alcobaça (Miguel & Bottura-Scardina, 2024), marking these years as their transition point (Figure 34). This indicates that this workshop experienced a transitional phase for both blue and green pigments during the same period. However, while the FORS spectra provided clear discriminative fingerprints for the blue pigments (ultramarine and azurite), it was more challenging to distinguish between the green pigments due to their similar copper-based composition.

Ultramarine and azurite could be distinguished thanks to their different chemical compositions. One (*ultramarine*) owes its blue colour to the mineral *lazurite*, a sodium aluminosilicate isostructural with sodalite containing with trisulfite S_3 ions trapped within[69]. The other (*azurite*) is a hydrated basic copper carbonate (Bicchieri, et al., 2001)[70]. This clear distinction contrasts with the overlapping spectral features of copper-based green pigments, which complicates their identification.

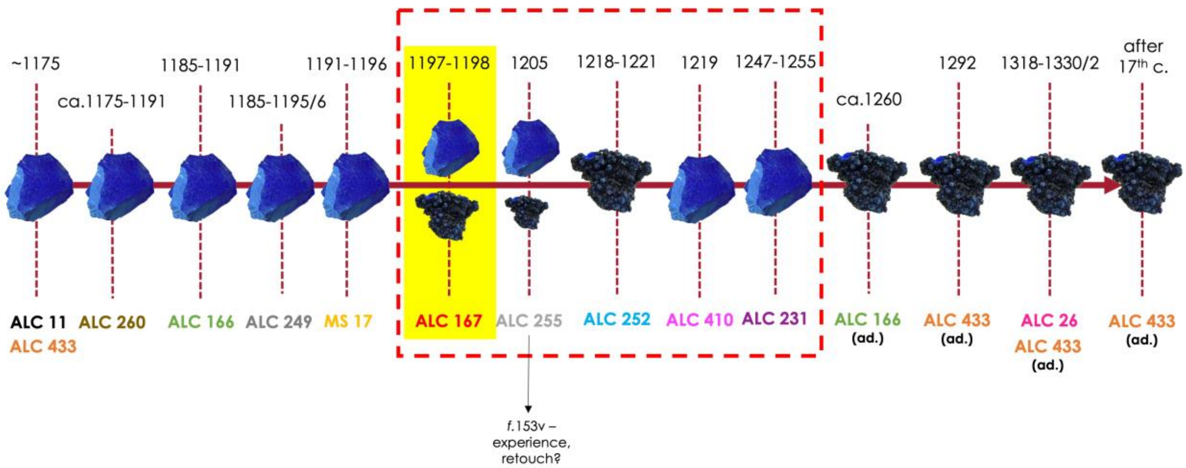


Figure 34. Timeline for the use of inorganic blue pigments in the eleven selected Liturgical manuscripts (core texts and additions) considering the accurate dates determined by the liturgical analysis and the blue pigments' sources identified by the material characterization. From *(Miguel & Bottura-Scardina, 2024)*.

During the transitional period from 1191 to the early 13th century, the Alcobaça *scriptorium* was highly active in the production of illuminated manuscripts and engaged in diverse economic exchanges, including interactions with other Cistercian monasteries within Portugal and beyond (Miranda A. , 1984; Miguel C. , 2012). This period of prolific production and exchange likely influenced the colour palette used in the illuminations. The end of the 12th century and the early 13th century saw significant changes in the illumination practices (see Section 2.2), thus suggesting that illuminators were experimenting technically.

[69] Chemical formula $Na_{6-10}Al_6Si_6O_{24}S_{2-4}$

[70] Chemical formula $2CuCO_3.Cu(OH)_2$

In the early 14th century, significant changes in illumination and colour palettes occurred on a large scale, perhaps under the influence of the French artistic trends (Barreira et al, 2016). Interestingly, while malachite began to be used in French manuscripts around the mid-15th century, traces of malachite are evident in Portuguese manuscripts from the late 12th century, highlighting a divergence in pigment adoption timelines between the regions (Figure 35).

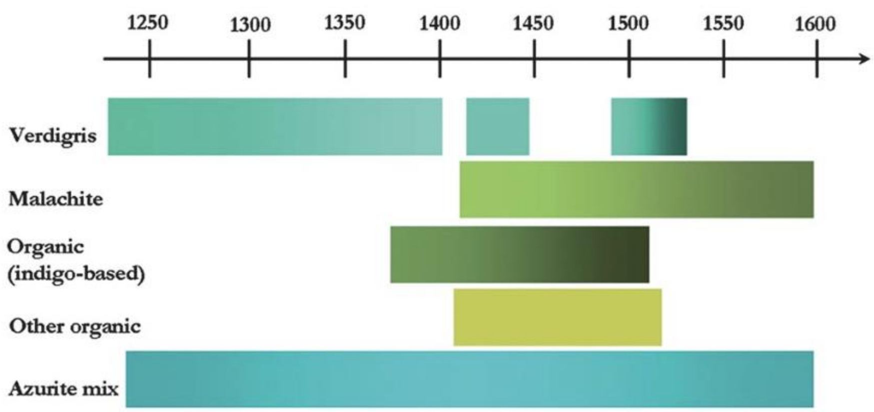


Figure 35. Timeline for the green pigments and mixtures in the French illuminated manuscripts of the 13th and 16th century. From *(Ricciardi, et al., 2013)*.

Overall, these observations suggest that the Alcobaça *scriptorium* underwent significant experimentation and transition in pigment use, reflecting broader socio-economic and cultural exchanges during the period.

CONCLUSIONS

Conclusions

This master's thesis has given an insightful analysis on the characterization of the green colour sources of Portuguese scriptoria during 12th to 15th -16th century. Aim of the thesis was to identify verdigris in copper-proteinate paints, determine the transition period to green mixtures in Alcobaça scriptorium's color palette, and outline the history of uses of green pigment over three centuries. Interdisciplinary approaches have been used to characterize the materials and produced a tentative timeline of chronological use of green pigments. Archaeometric analysis was carried out through elemental and molecular analysis, determining the elemental and molecular palette of the spots of analysis and studying the presence of functional groups.

Based on the preceding analysis, a detailed chronology of the use of green paints in the Alcobaça collections can be proposed. The paints made with copper proteinate include samples from 1175 (Alc. 433), 1185-1191 (Alc. 166), 1191-1196 (ANTT Ms 17), partly from 1197-1198 (Alc. 167), and 1210-1300 (Alc. 341), as well as all paints from the 15th-16th century (Alc. 166). Malachite was used for decoration only in 1205 (Alc. 255) and in the years 1318-1380 (Alc. 26).

Notably, certain paints from 1175-1191 (Alc. 260), 1197-1198 (Alc. 341), and 1210-1301 (Alc. 341) were found in the clusters of malachite and copper proteinate. This suggests that the period from 1191 to the early 13th century could be a transitional phase from malachite to copper proteinate paints, with a brief resurgence of malachite in the additions of the 15th-16th c. of the Alc. 166. Based on these observations, a timeline for the use of green paints was proposed (Figure 33).

The evidence presented were not enough to answer the question of the existence of verdigris, thus more investigation is necessary to dispel any doubts regarding its presence in copper proteinate.

Future research

The results gathered from this dissertation revealed significant opportunities for further research on the use of green pigments in historical manuscripts. The current study's limitations in distinguishing between copper proteinate, malachite, and verdigris using UV-Vis-NIR-SWIR FORS analysis highlight the need for more advanced techniques. Employing ER-FTIR or micro Raman spectroscopy could provide more definitive results due to their ability to yield distinct molecular signatures not reached by h-EDXRF nor by UV-Vis-NIR-SWIR FORS. Although these methods were not utilized in this framework due to their time-consuming nature (ER-FTIR) and for its inexistence in HERCULES Lab at the time of the analysis of the manuscripts (micro-portable Raman), they are essential for achieving a higher level of confidence in pigment identification.

Future research should prioritise these analytical techniques to overcome the limitations encountered with FORS. Additionally, a deeper investigation into the social and cultural context of the manuscripts could provide valuable insights into the changes in illumination practices. Understanding the broader historical, economic, and cultural influences on the scriptorium's work could enrich our comprehension of the transitions in pigment use and artistic techniques. By combining advanced scientific methods with a thorough historical analysis, future studies can build a more comprehensive understanding of the use and evolution of green pigments in illuminated manuscripts.

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Appendix 1. Analytical conditions of the scientific analysis

UV-Vis-NIR-SWIR FORS data

The FORS UV-Vis-NIR data of Chapter 2 was collected with a BWTEK i-Spec 25 portable spectrometer using a handheld reflectance probe of trifurcated fibre optic bundle series for sampling, and an extended InGaAs array sensor for data collection. The spectrometer has an integrated with a 5W tungsten halogen source as the excitation source, which is collimated with a 5 mm. The data is acquired in the 400- 2500 nm spectral range. Th iSpec4 software was used for data collection and to export.

The measuring conditions are as follows (integration time-accumulations): 95ms, 25x (detector 1, 346-1061 nm); 250µs, 50x (detector 2, 883-1718 nm); 332µs, 100x (detector 3, 1482-2654 nm), no smoothing. The spectra were plotted with Microsoft Excel 365.

PCA classification

An unsupervised approach using Principal Component Analysis (PCA) of FORS spectra was performed using MATLAB (version R2023b) and PLS toolbox (version 9.8.3) from Eigenvector Research Inc. FORS spectra of historical green paints from nine manuscripts produced at Alcobaça scriptorium (Alc. 26 – 6 spectra; Alc. 166 – 9 spectra; Alc. 167 – 5 spectra; Alc. 255 – 6 spectra; Alc. 260 – 9 spectra; Alc. 341 – 11 spectra; Alc. 433 – 4 spectra; MS 17 – 7 spectra) were pre-processed with Standard Normal Variate (SNV) for scaling the spectra (weighted normalisation), followed by Mean Centring to remove mean offset from each variable, and a Savitzky-Golay smoothing filter with 15-point window size, second-order polynomial and first derivative. The PCA model was calibrated with 57 FORS spectra of historical green paints, 12 of which FORS spectra are historically accurate paint reconstructions of copper proteinate (6 spectra) and malachite produced with egg white (6 spectra) projected into the model.

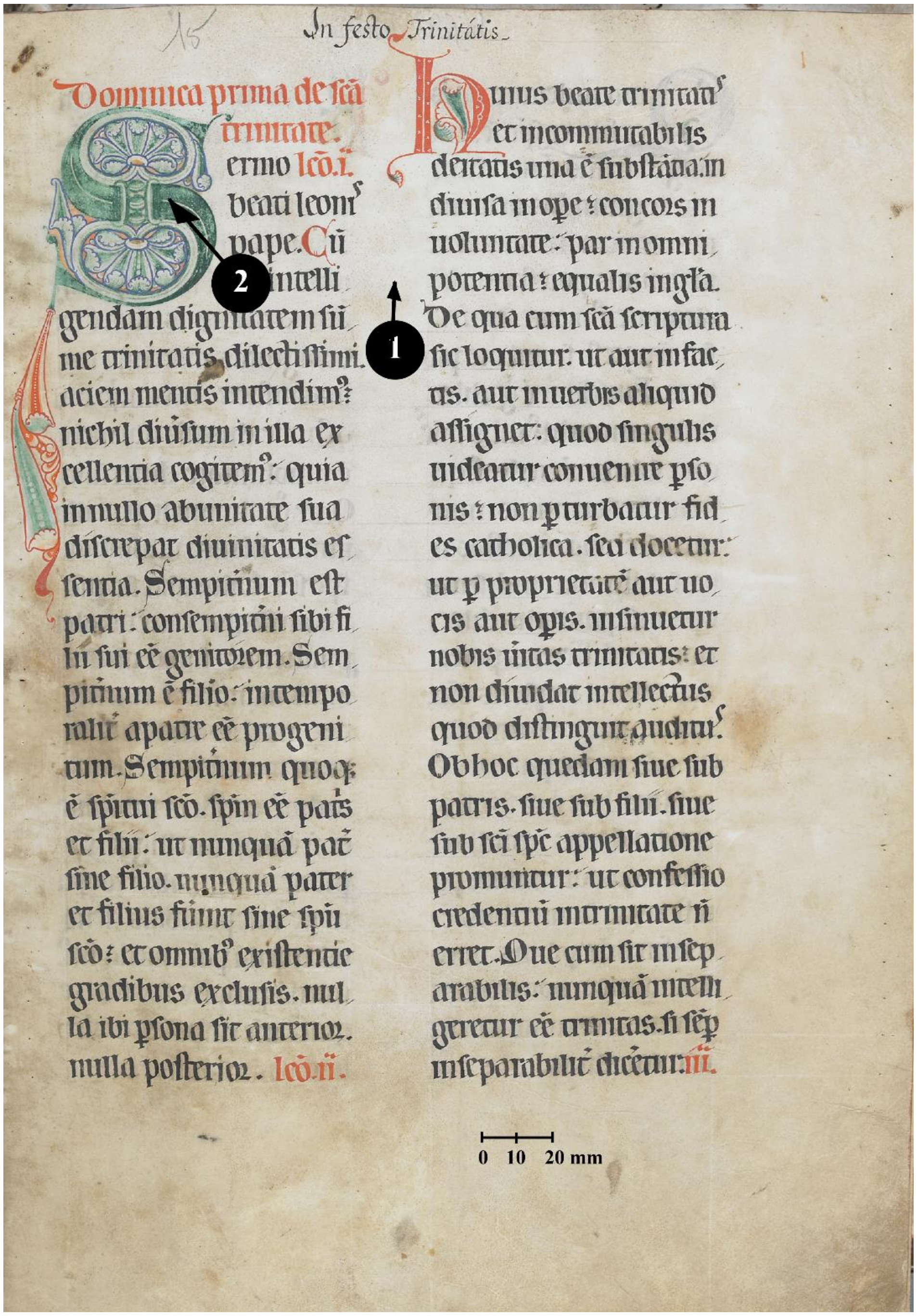
H-EDXRF data

The h-EDXRF were collected with a handheld Tracer III-SD ED-XRF spectrometer by Bruker. The spectrometer is equipped with a 10 mm² XFlash® SDD and a peltier-cooled detector with a resolution of 145 eV at 100,000 cps (2048 channels), and a Rh filament. The analyses were made at 40 keV, 11 μA, without filter, acquisition time of 30 s, and a spot size of 12 mm 2 (3 mm x 4 mm), working distance: 2-3 mm from the analysed area to avoid manuscript damaging. All spectra were collected and explored with the S1PXRF Software (Artax) and plotted with Microsoft Excel 365.

Appendix 2. Spots of analysis for the scientific analysis

BNP, Alc. 433

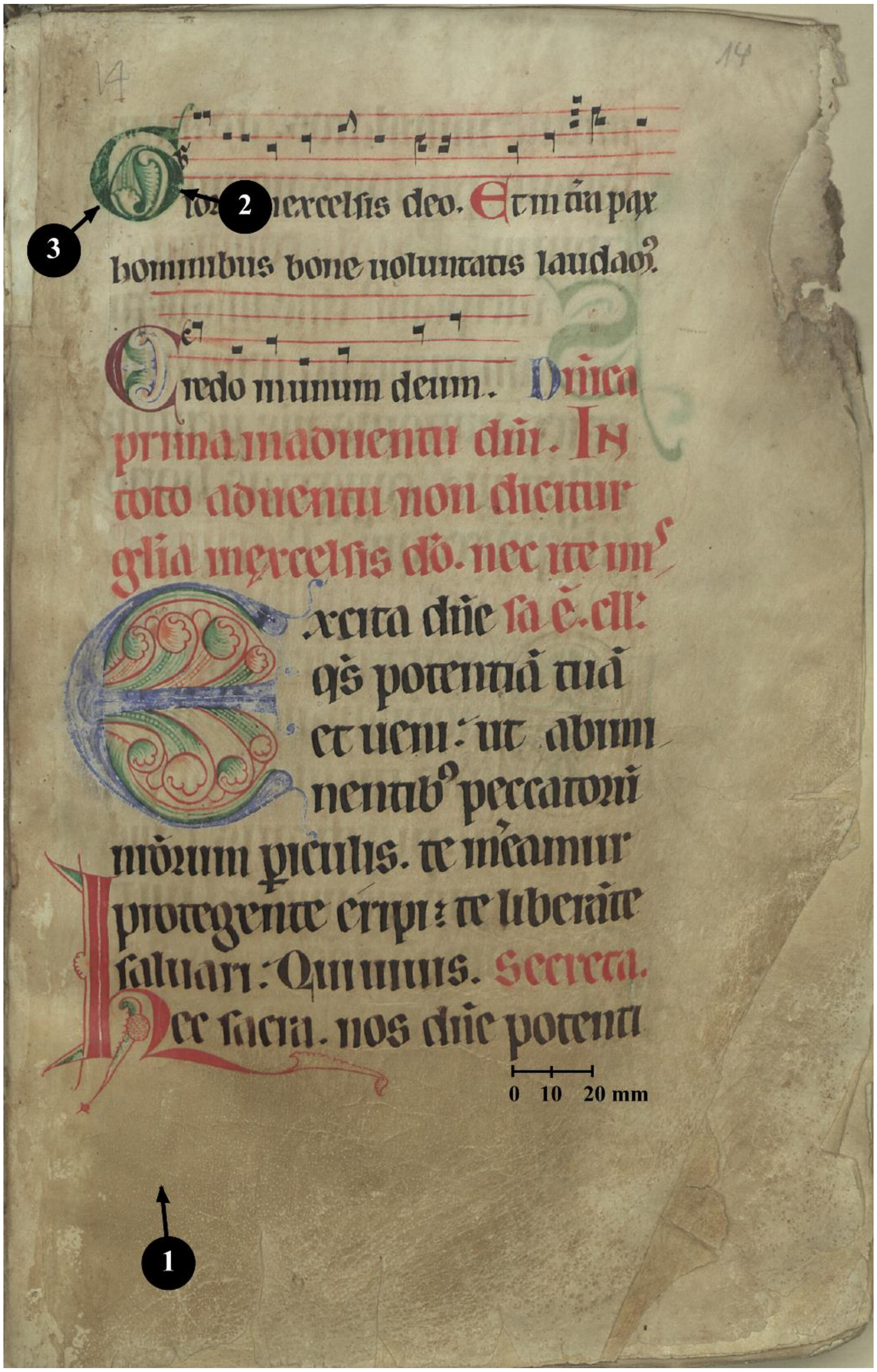
Alc. 433, f. 15r



1) Alc. 433 f.15r: Parchment (h-EDXRF)
2) Alc. 433 f.15r: Green (h-EDXRF)

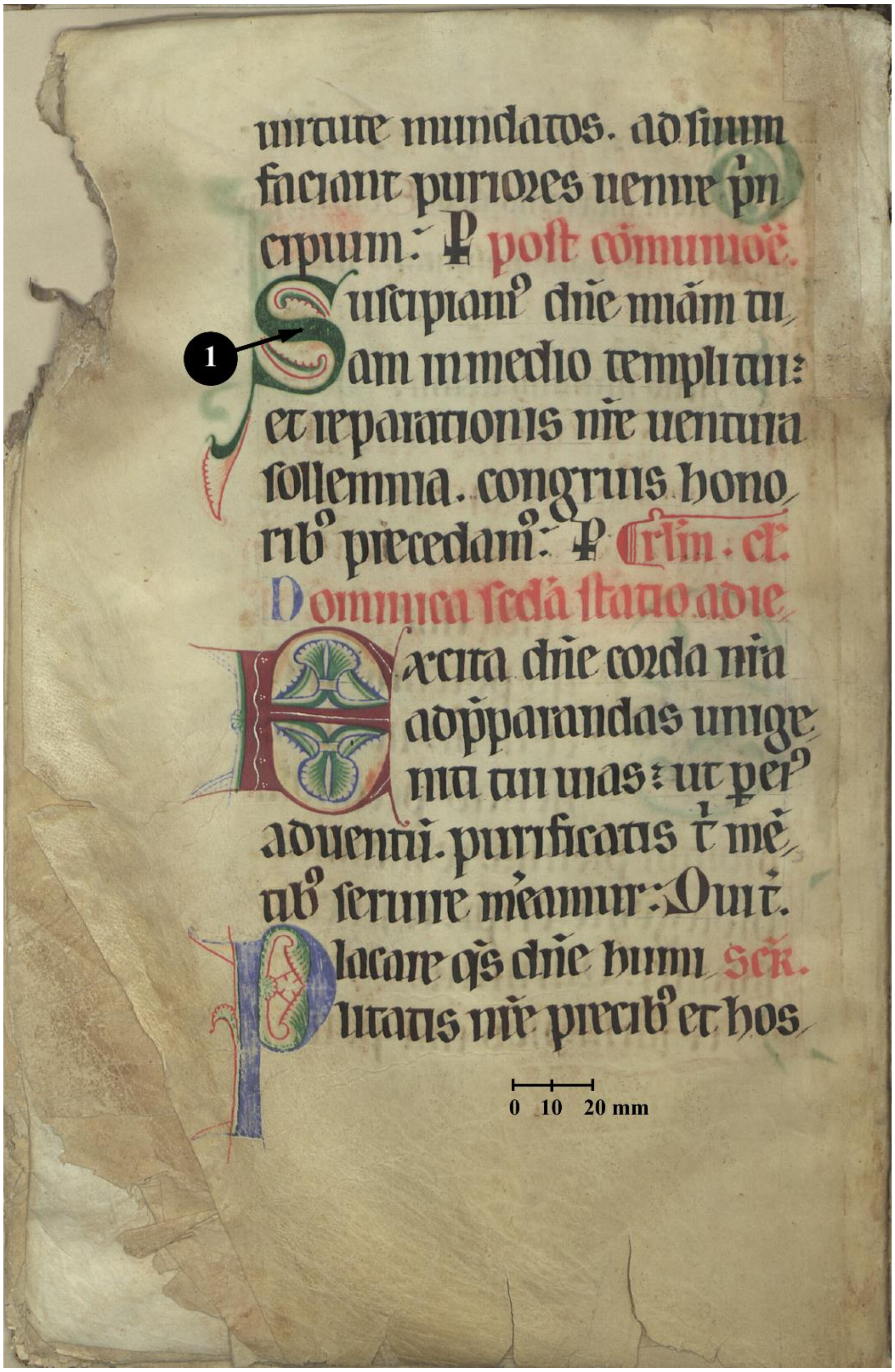
BNP, Alc. 260

Alc. 260, f. 14^{r}



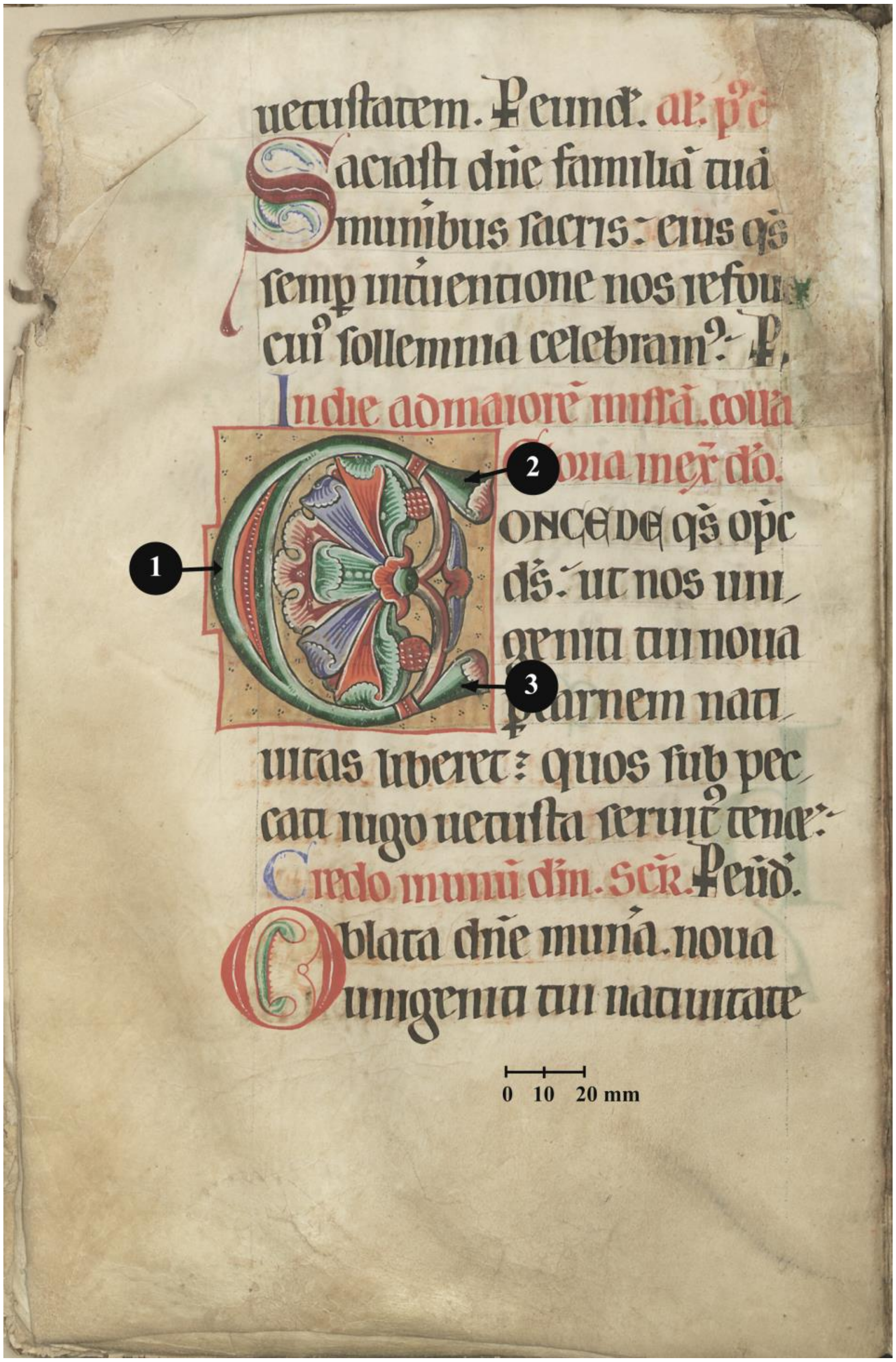
1) Alc. 260 f.14^{r}: Parchment (FORS)
2) Alc. 260 f.14^{r}: Green_1 (FORS)
3) Alc. 260 f.14^{r}: Green_2 (FORS)

Alc. 260, f. 14v



1) Alc. 260 f.14v: Green_1 (FORS)

Alc. 260, f. 21v

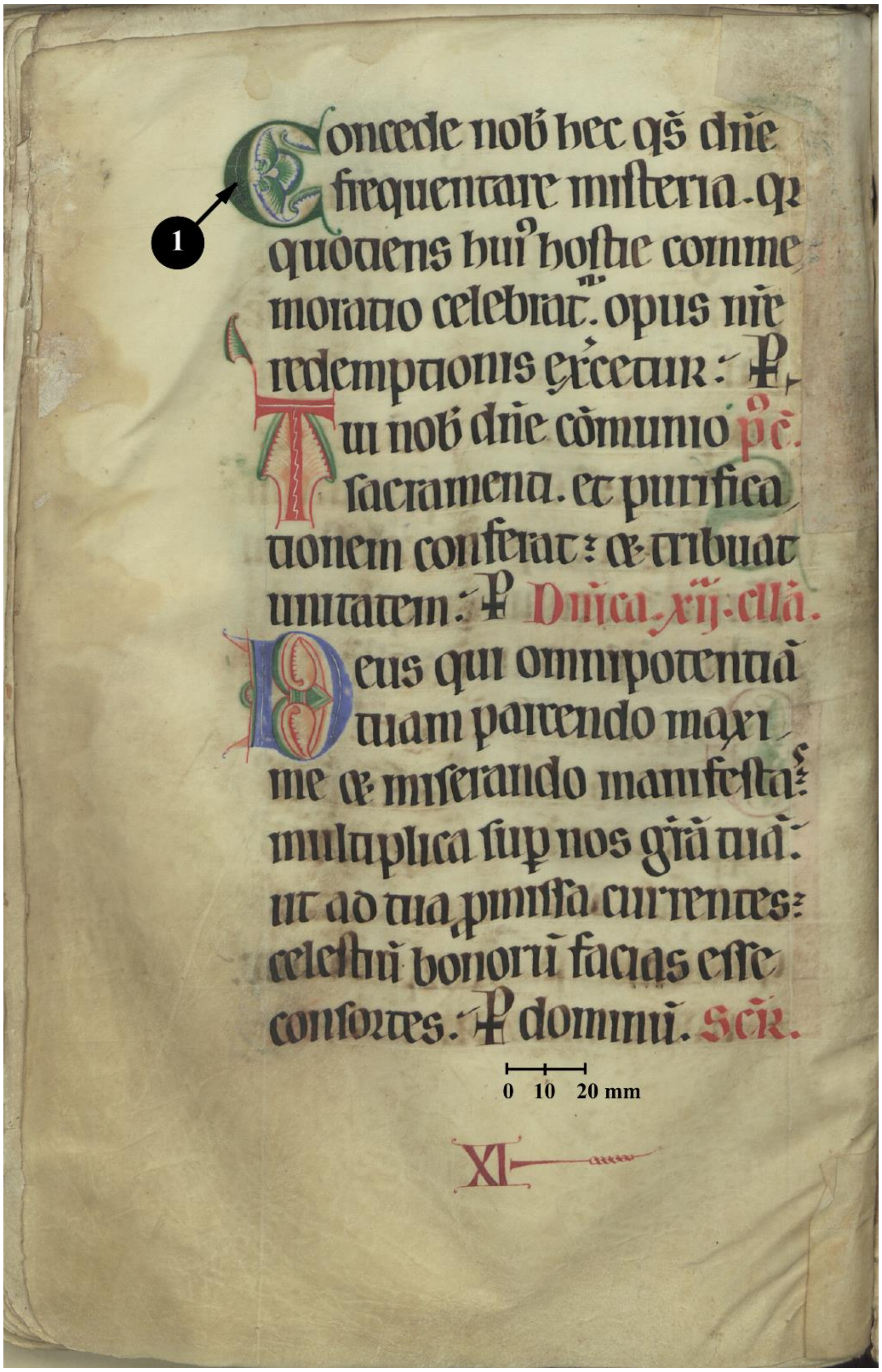


1) Alc. 260 f.21v: Green_1 (FORS)
2) Alc. 260 f.21v: Green_2 (FORS)
3) Alc. 260 f.21v: Green_3 (FORS)

Alc. 260, f. 75r

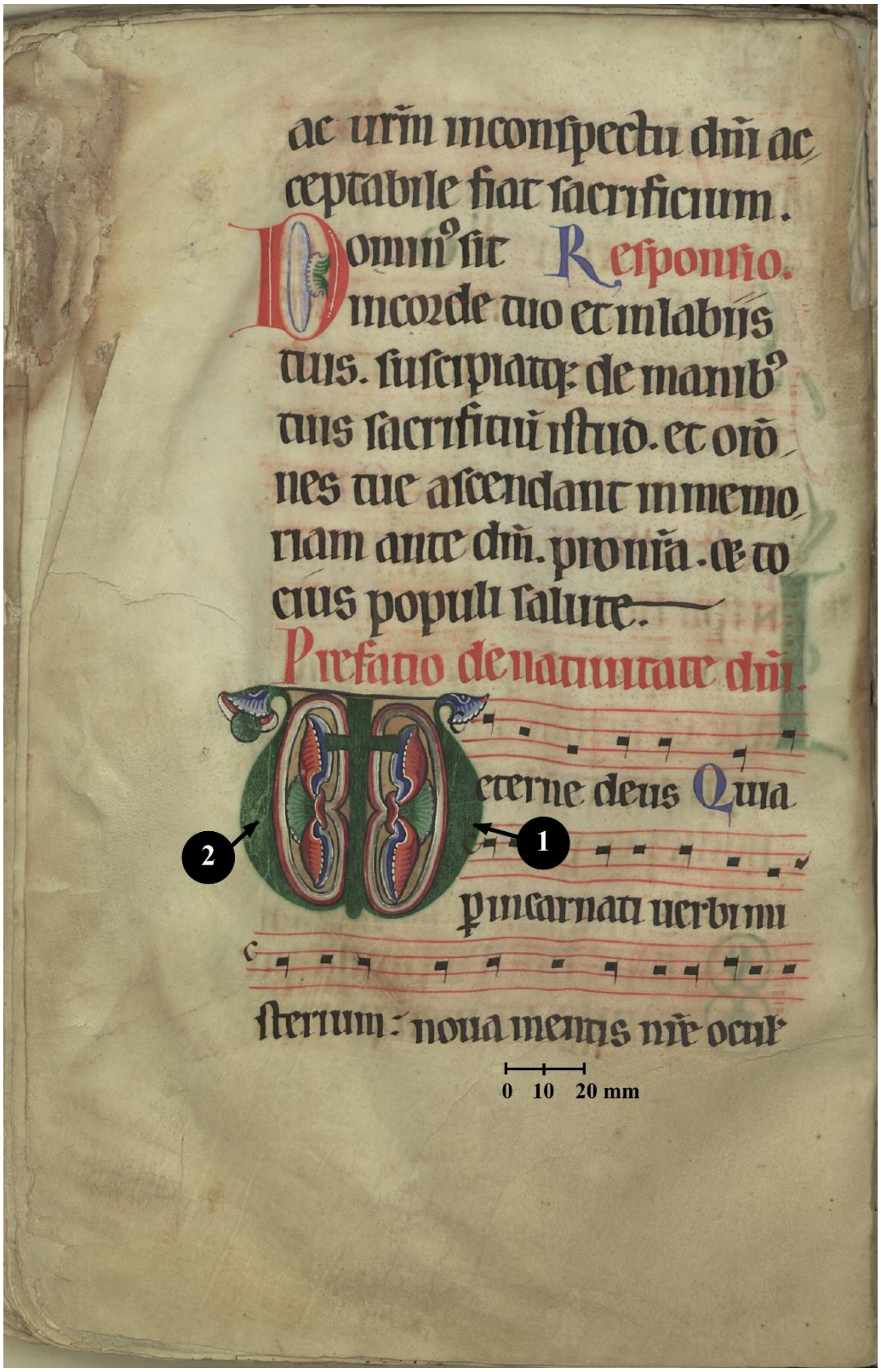
Alc. 260 f.75r: Green_1 (FORS)

Alc. 260, f. 88v



1) Alc. 260 f.88v: Green_1 (FORS)

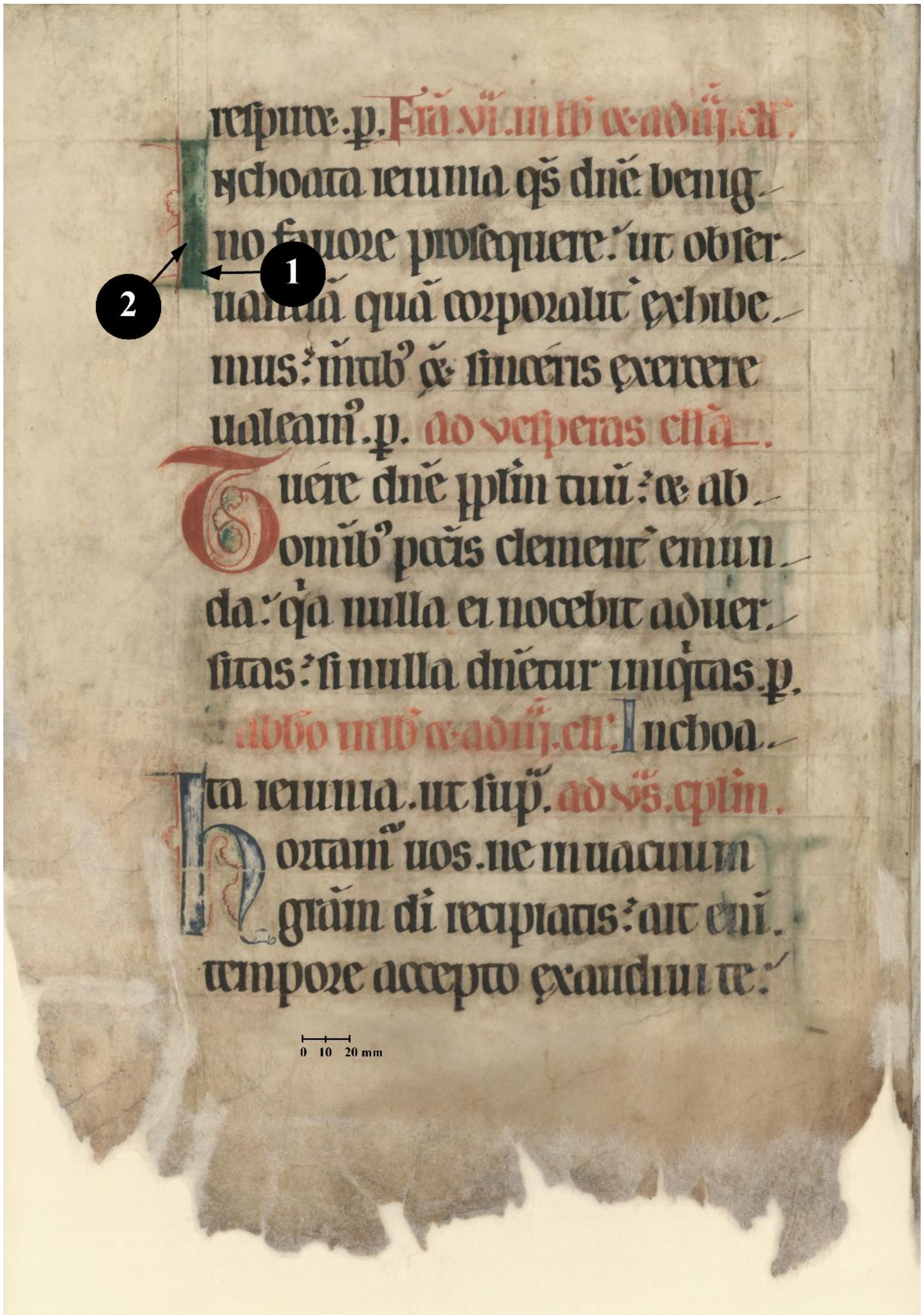
Alc. 260, f. 98v



1) Alc. 260 f.98v: Green_1 (FORS)
2) Alc. 260 f.98v: Green_2 (FORS)

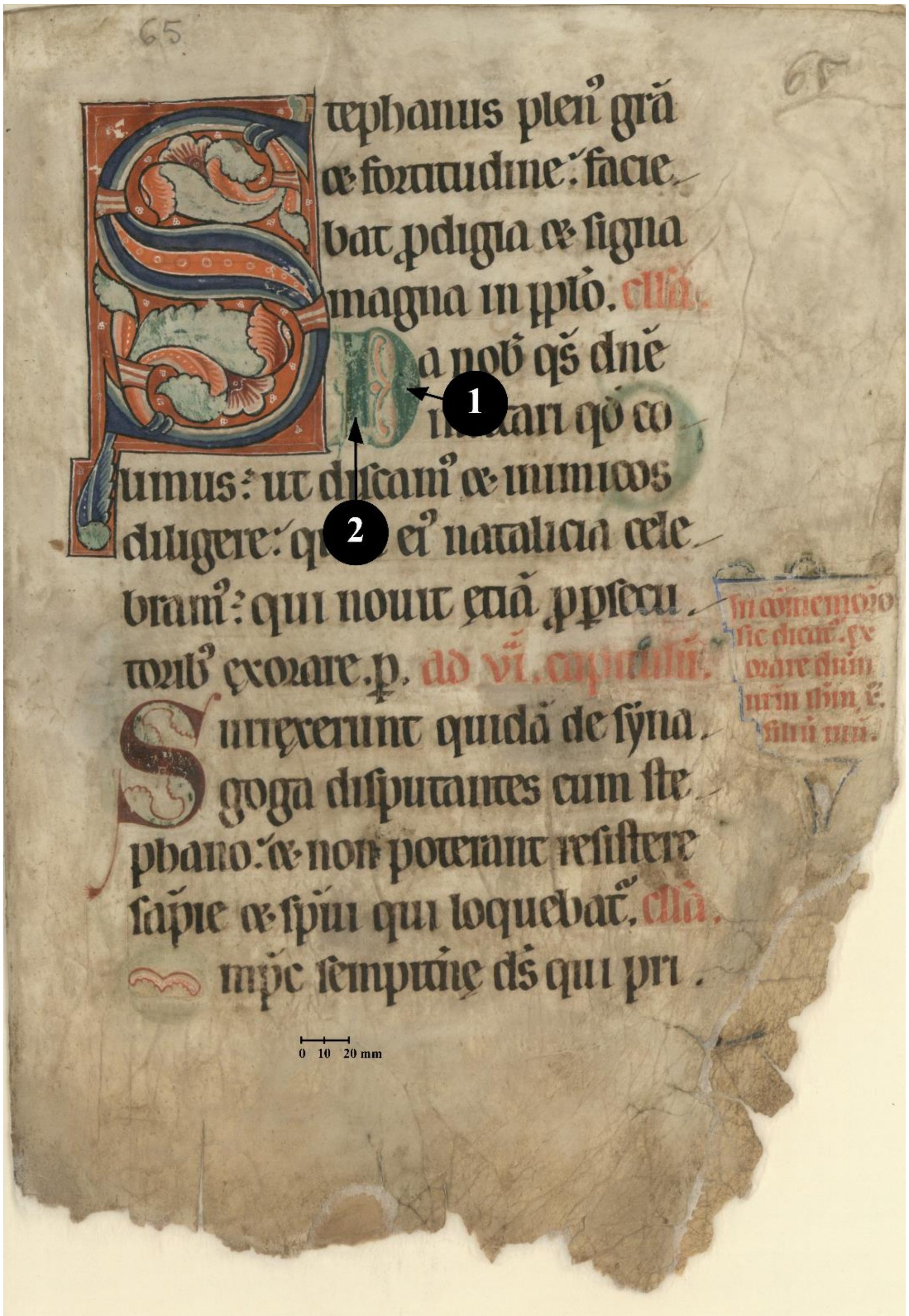
BNP, Alc. 166

Alc. 166, f. 25v



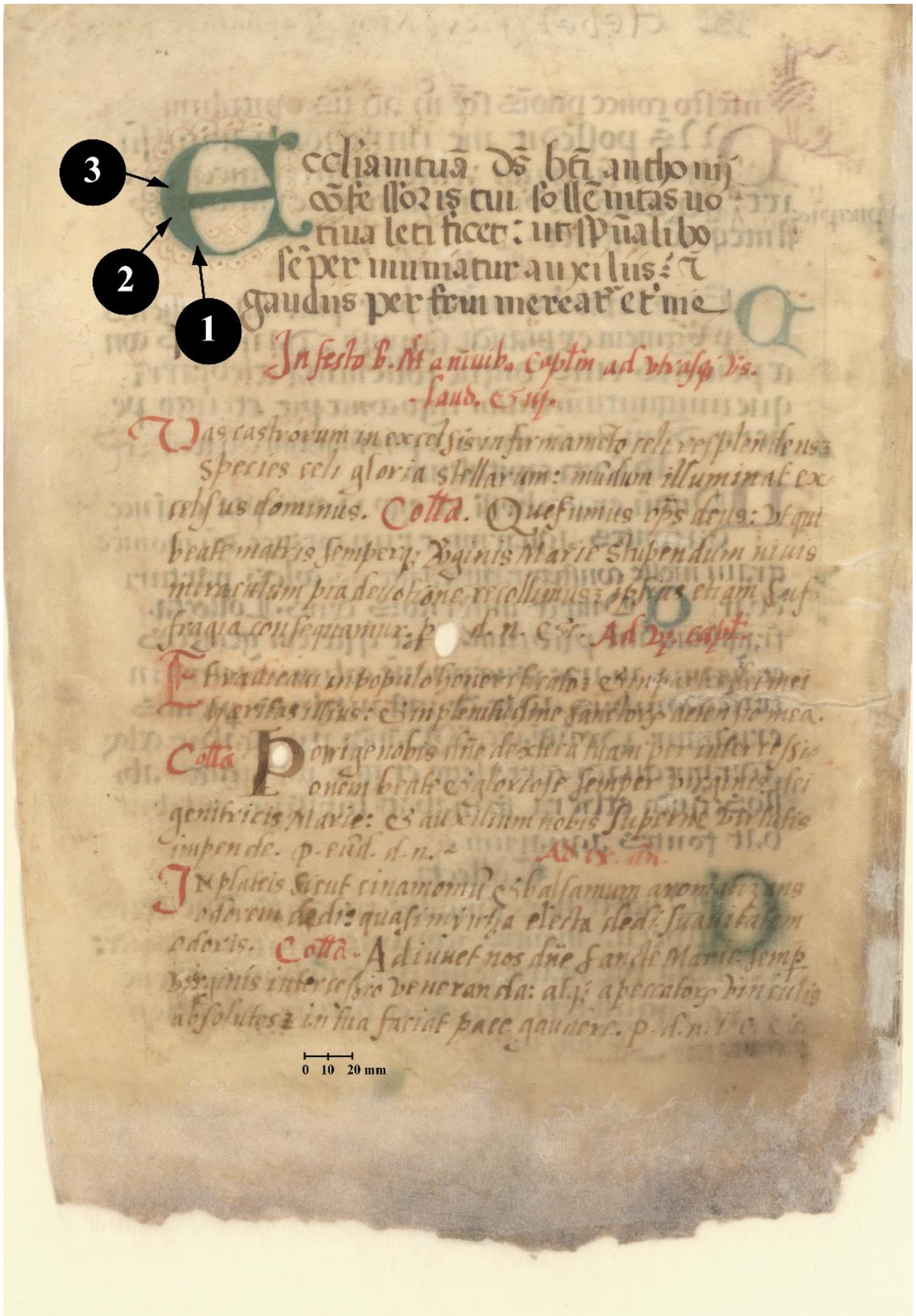
1) Alc. 166 f. 25v: Green_1 (FORS)

Alc. 166, f. 65r



1) Alc. 166 f. 65r: Green_1 (FORS)
2) Alc. 166 f. 65r: Green_2 (FORS)

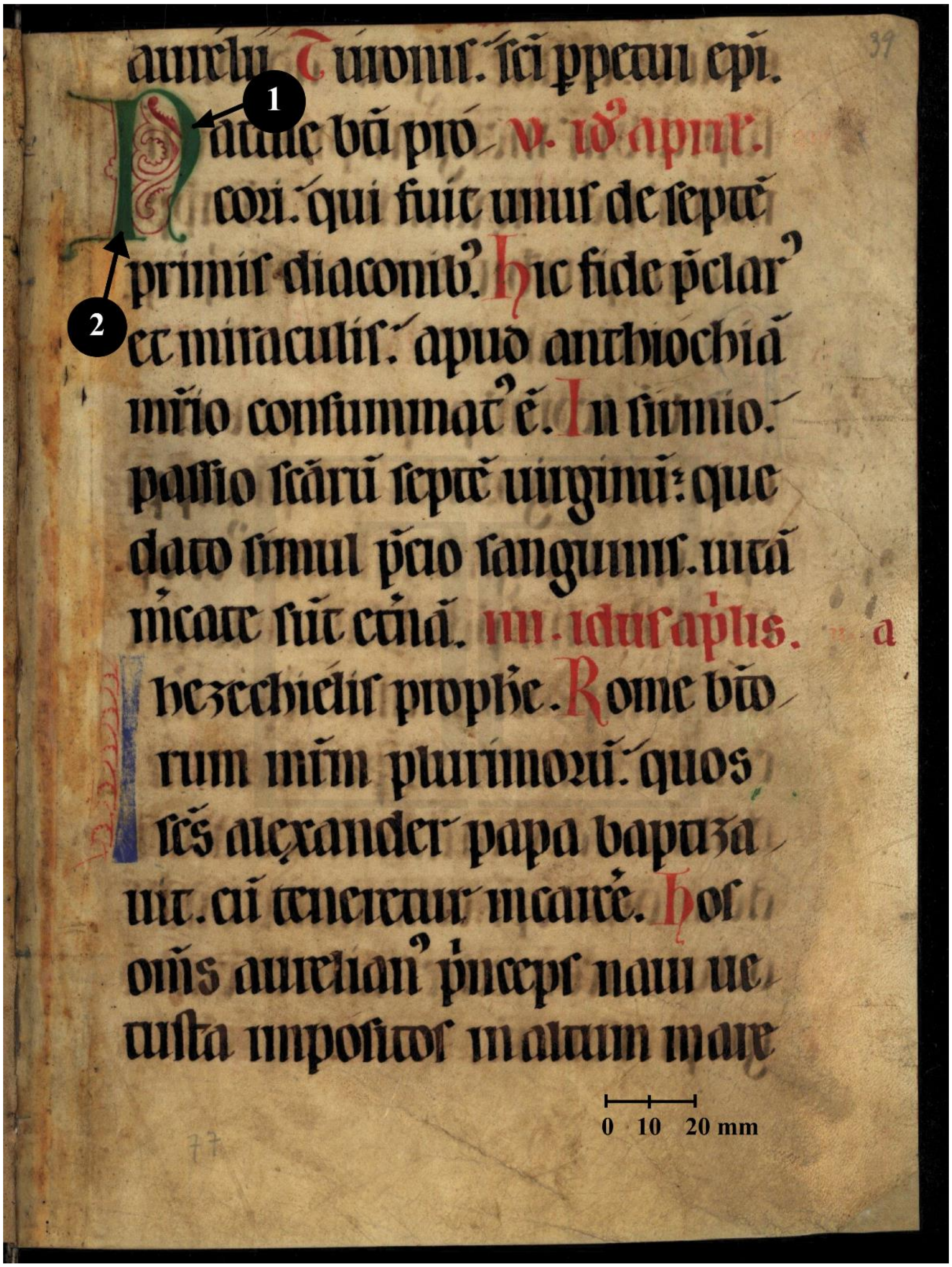
Alc. 166, f. 151[v]



1) Alc. 166 f. 151[v]: Green_1 (FORS)
2) Alc. 166 f. 151[v]: Green_2 (FORS)
3) Alc. 166 f. 151[v]: Green_3 (FORS)

ANTT, Ms 17

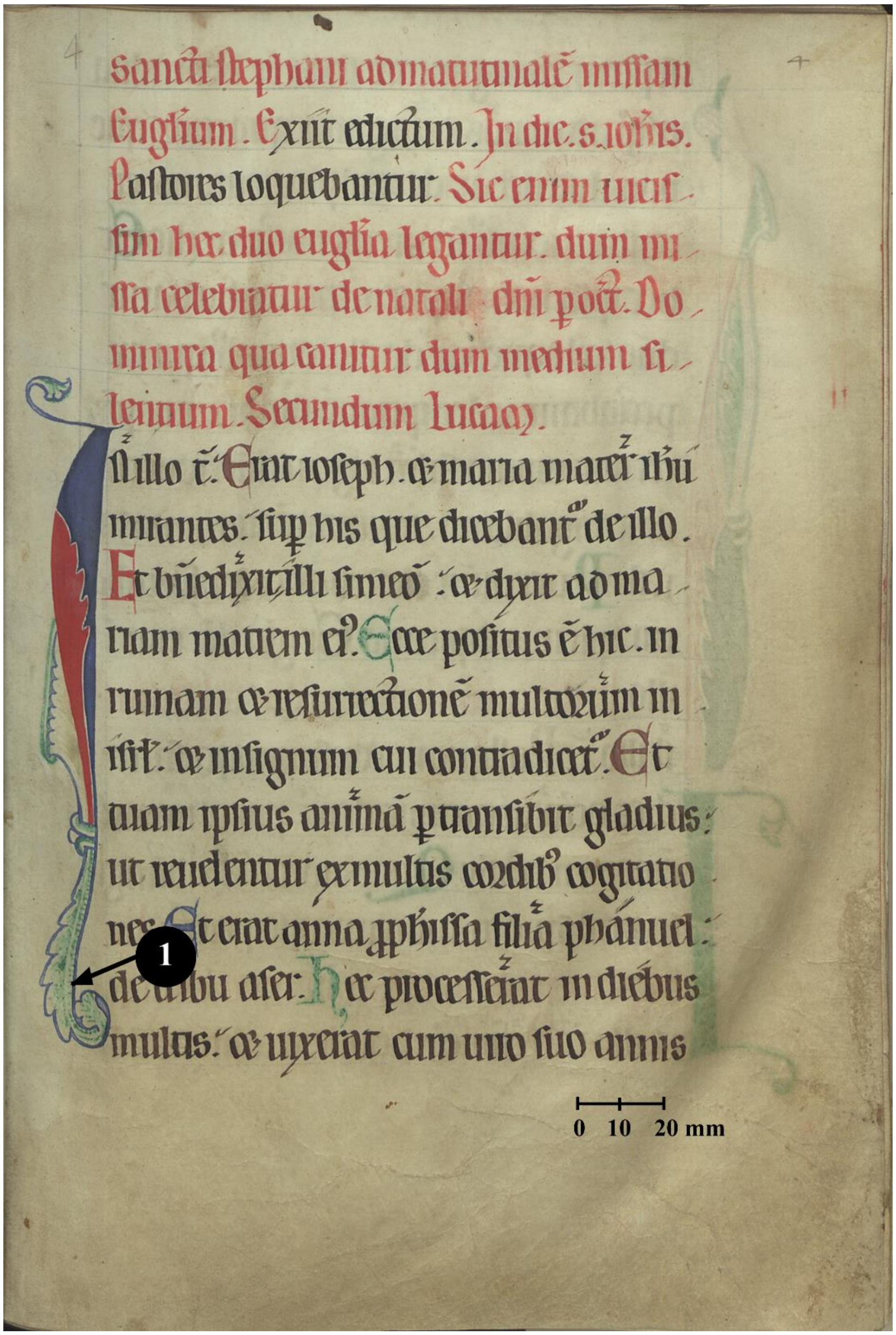
ANTT, Ms 17 f. 39v



1) MS 17 f.39v: Green_1 (FORS)
2) MS 17 f.39v: Green_2 (FORS)

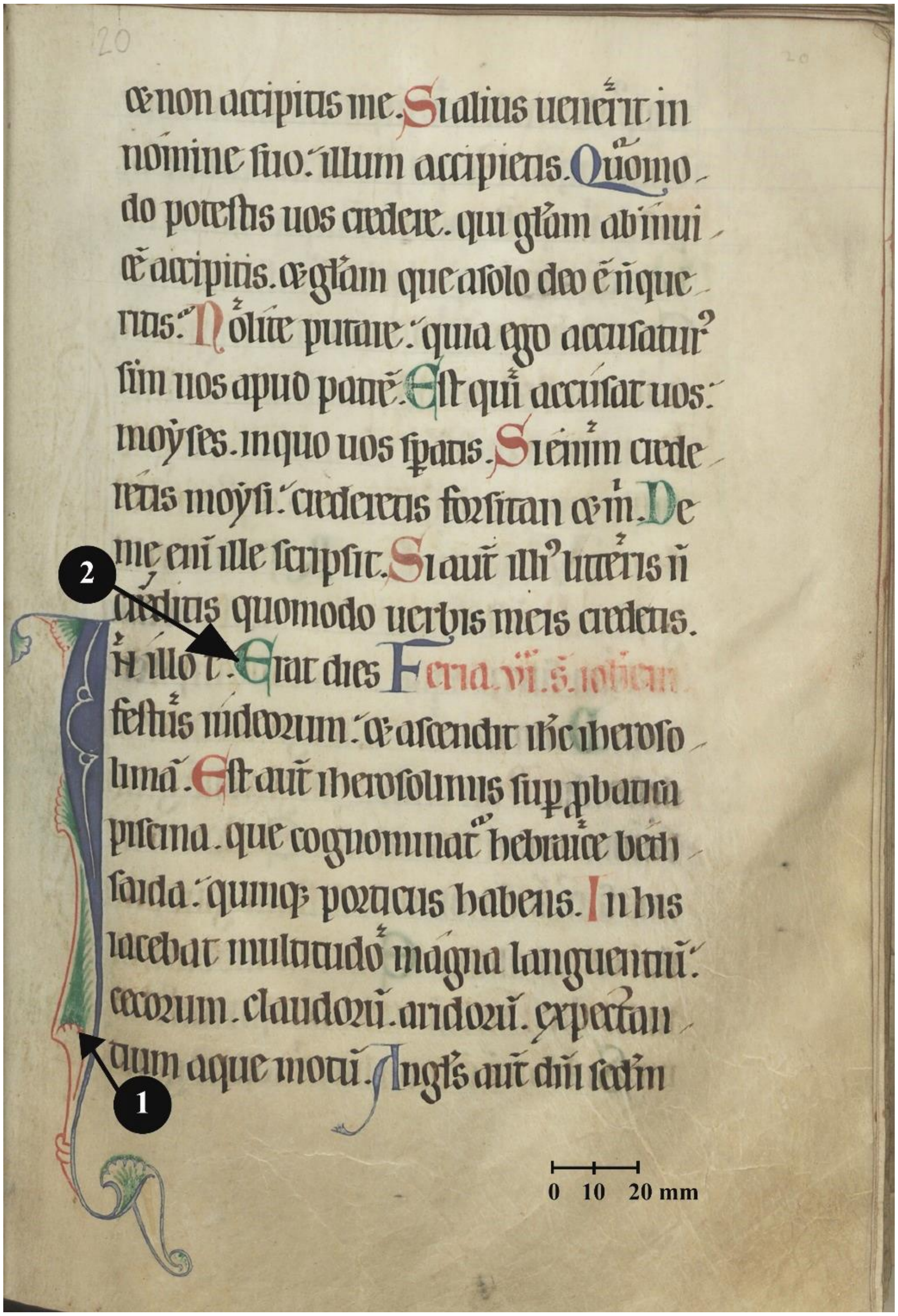
BNP, Alc. 167

Alc. 167, f.4^{r}



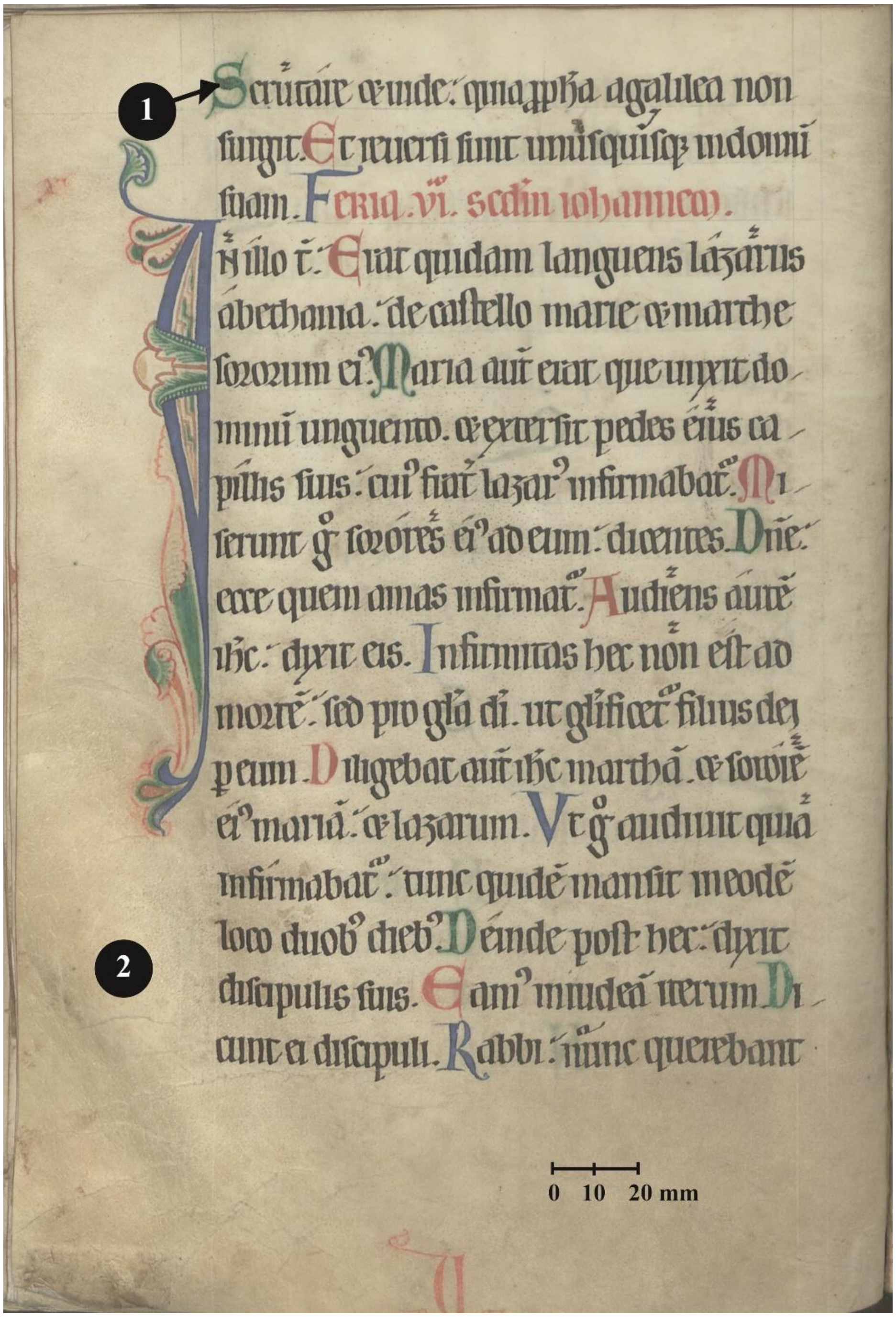
1) Alc. 167, f.4^{r}: Green_1 (FORS)

Alc. 167, f.20r



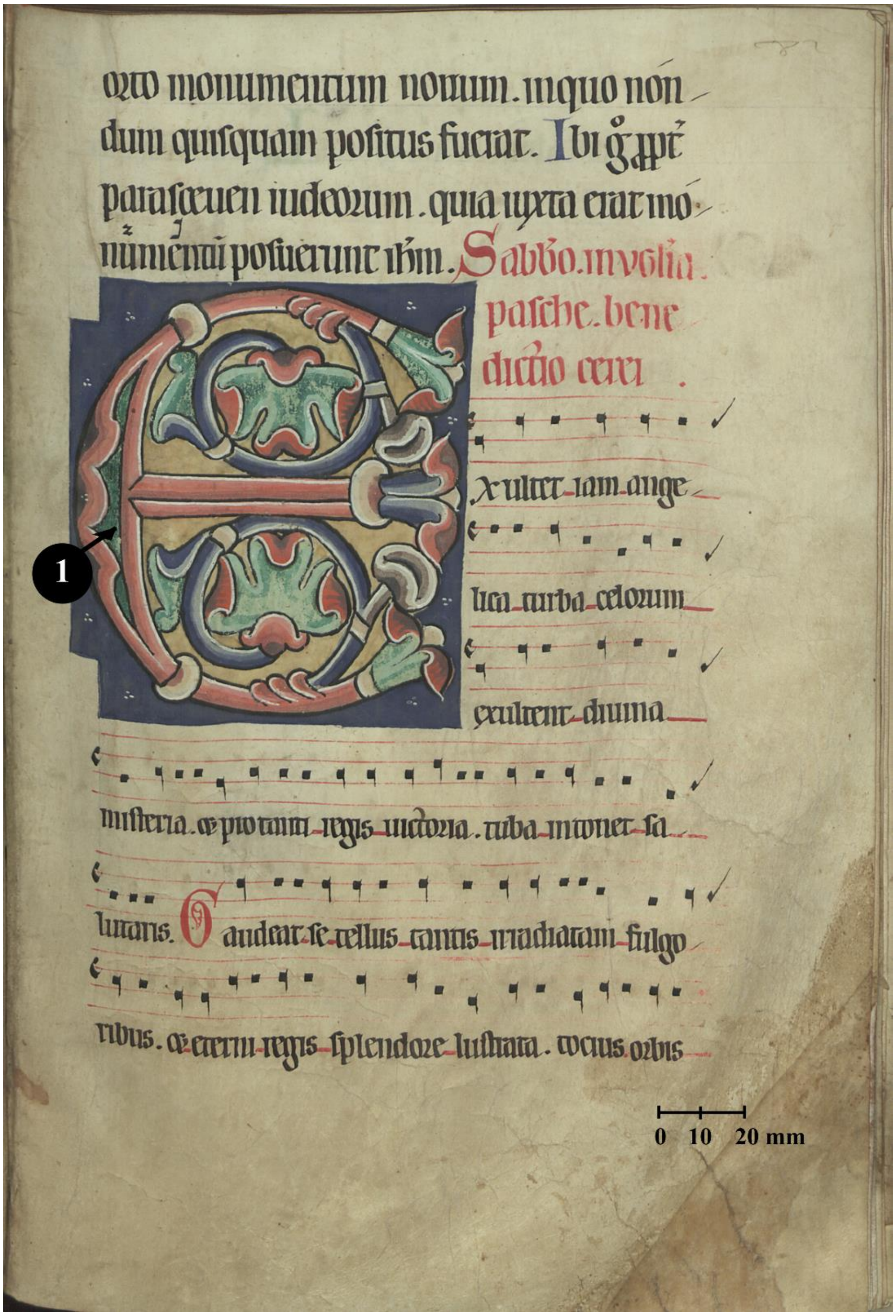
1) Alc. 167, f.20r: Green_1 (FORS)
2) Alc. 167, f.20r: Green_2 (FORS)

Alc. 167, f. 40v



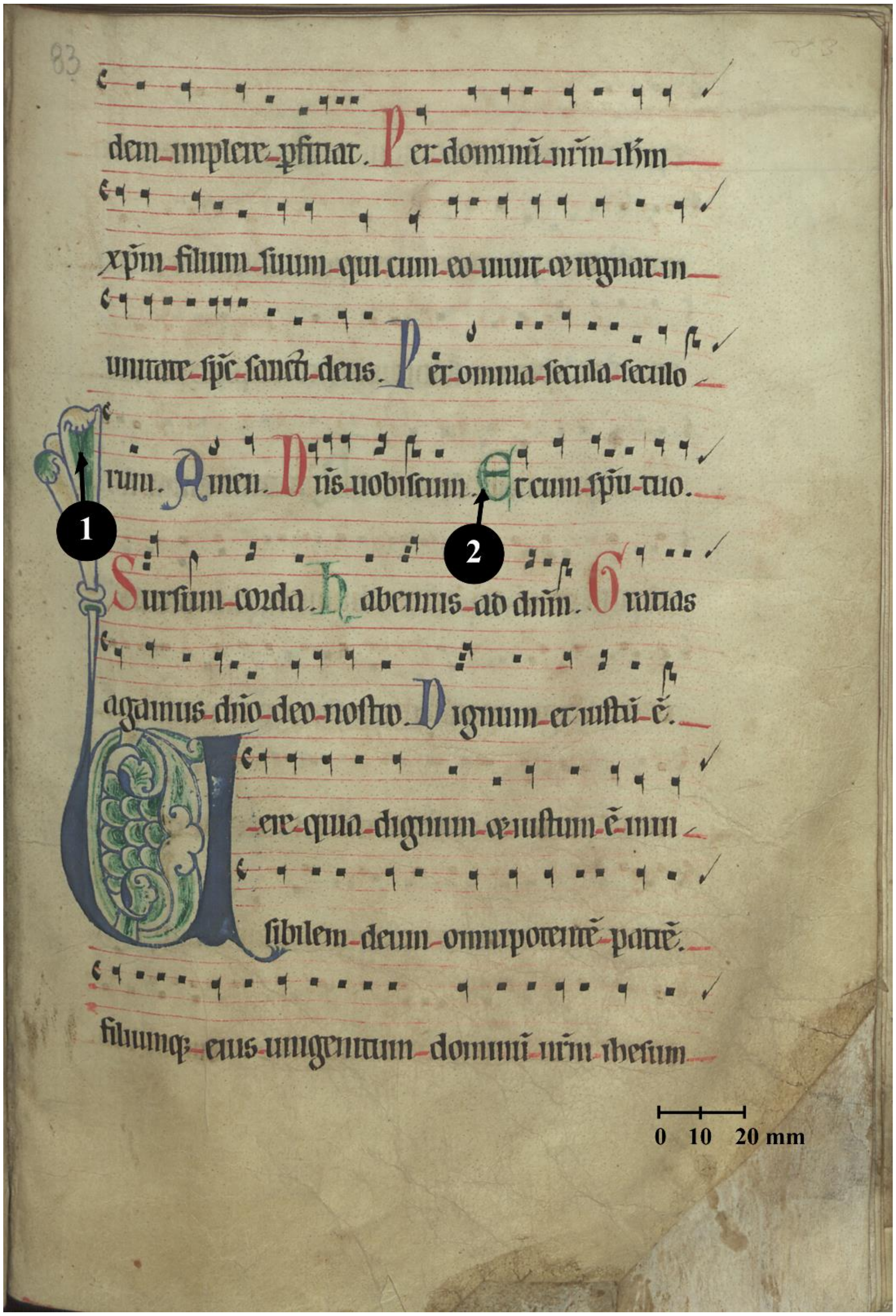
1) Alc. 167, f.40v: Green_1 (FORS)
2) Alc. 167, f.40v: Parchment (FORS)

Alc. 167, f. 82r



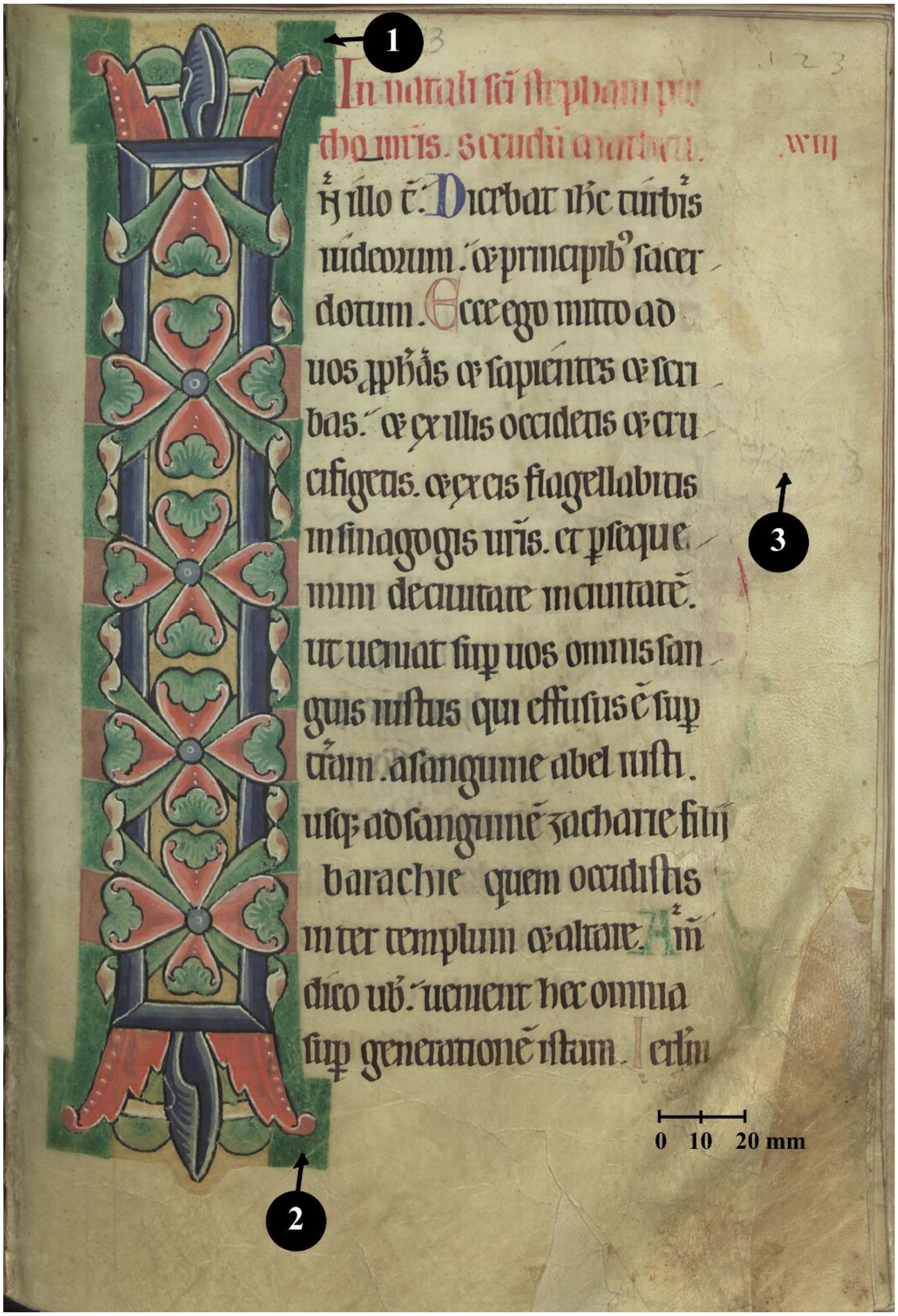
1) Alc. 167, f.82r: Green_1 (FORS)

Alc. 167, f. 83^{r}



1) Alc. 167, f.83^{r}: Green_1 (FORS)
2) Alc. 167, f.83^{r}: Green_2 (XRF)

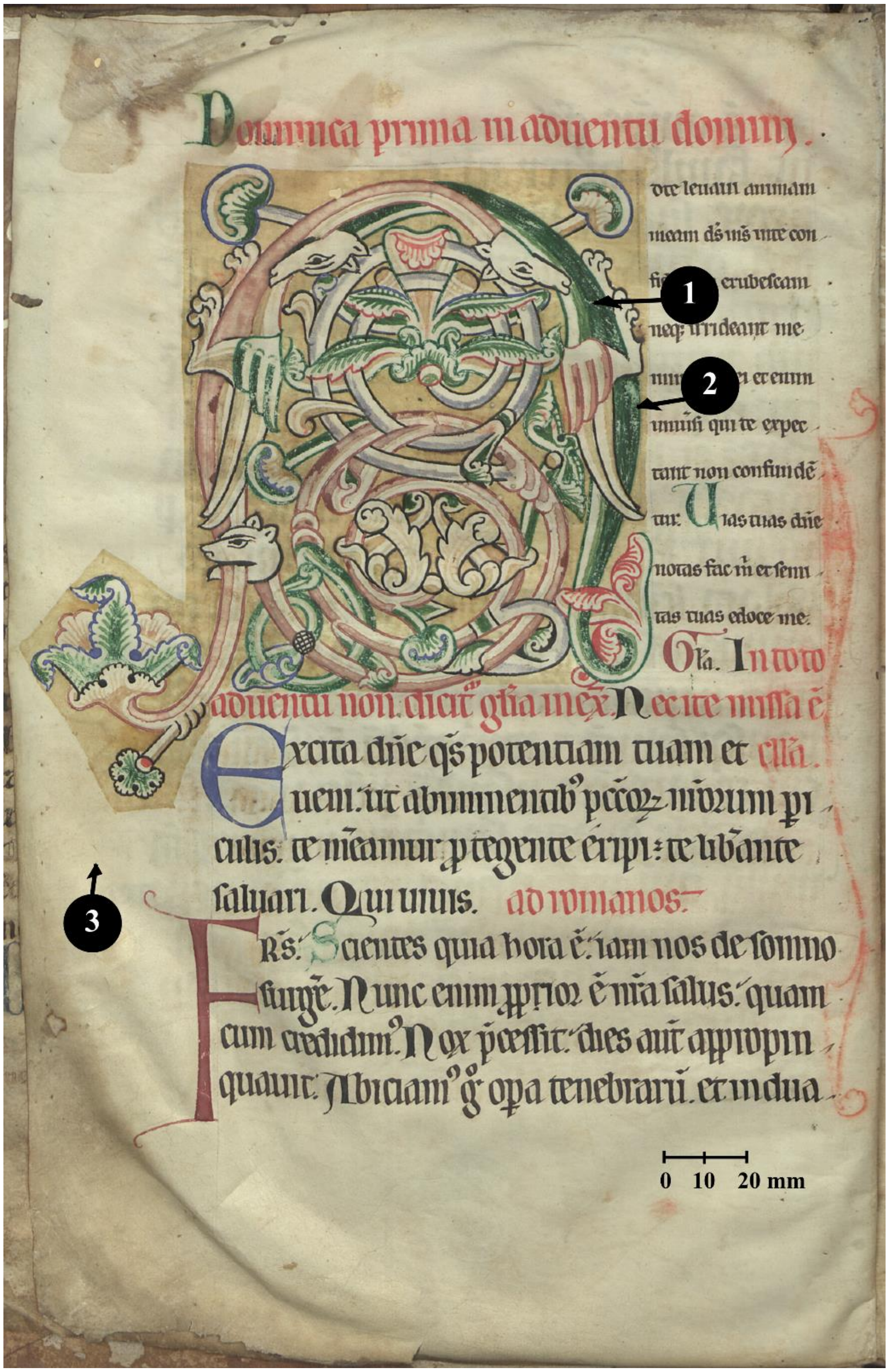
Alc. 167, f. 123^{r}



1) Alc. 167, f.123^{r}: Green_1 (FORS)
2) Alc. 167, f.123^{r}: Green_2 (FORS)
3) Alc. 167, f.123^{r}: Green_3 (FORS)

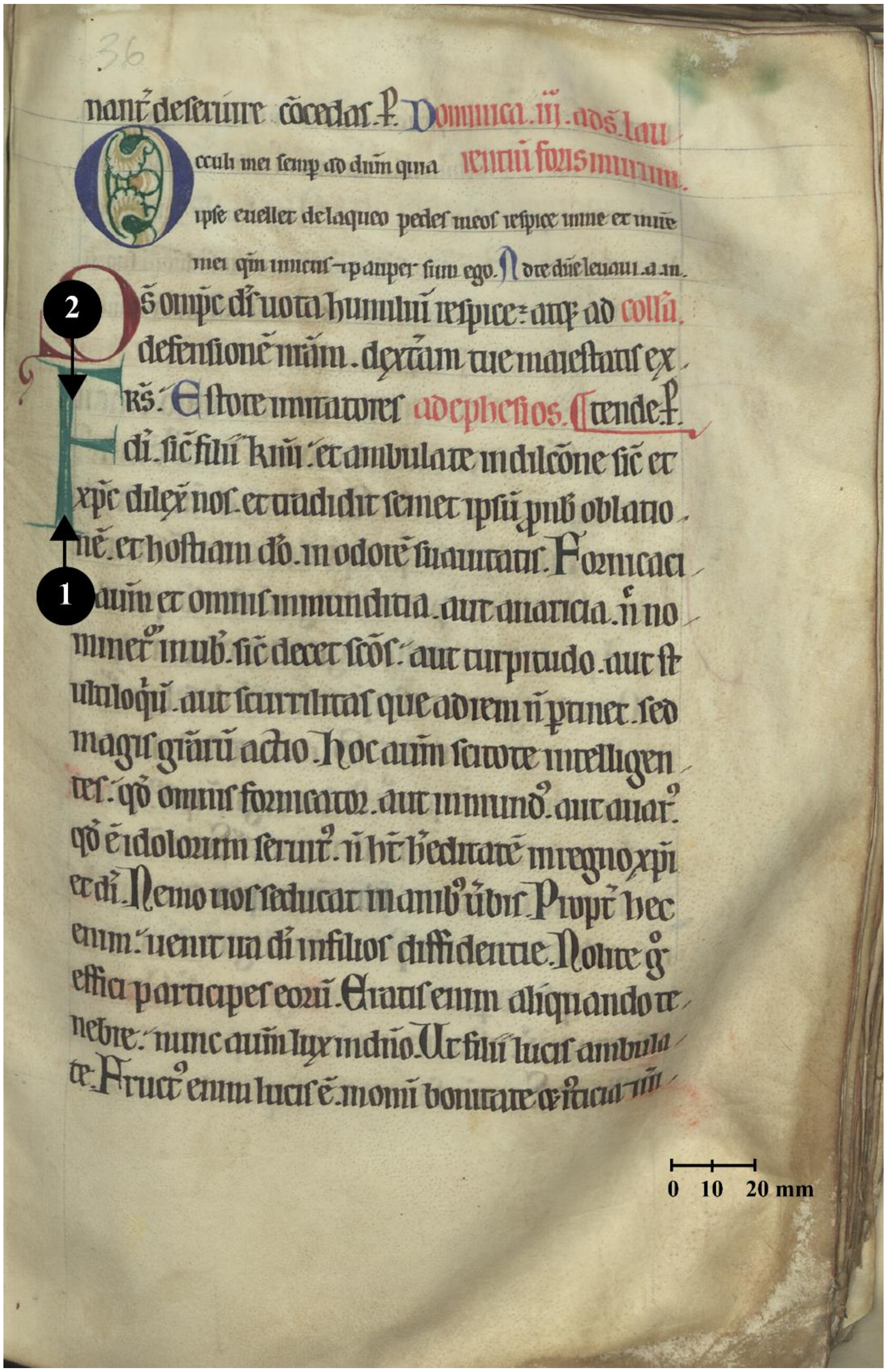
BNP, Alc. 255

Alc. 255, f. 2^{v}



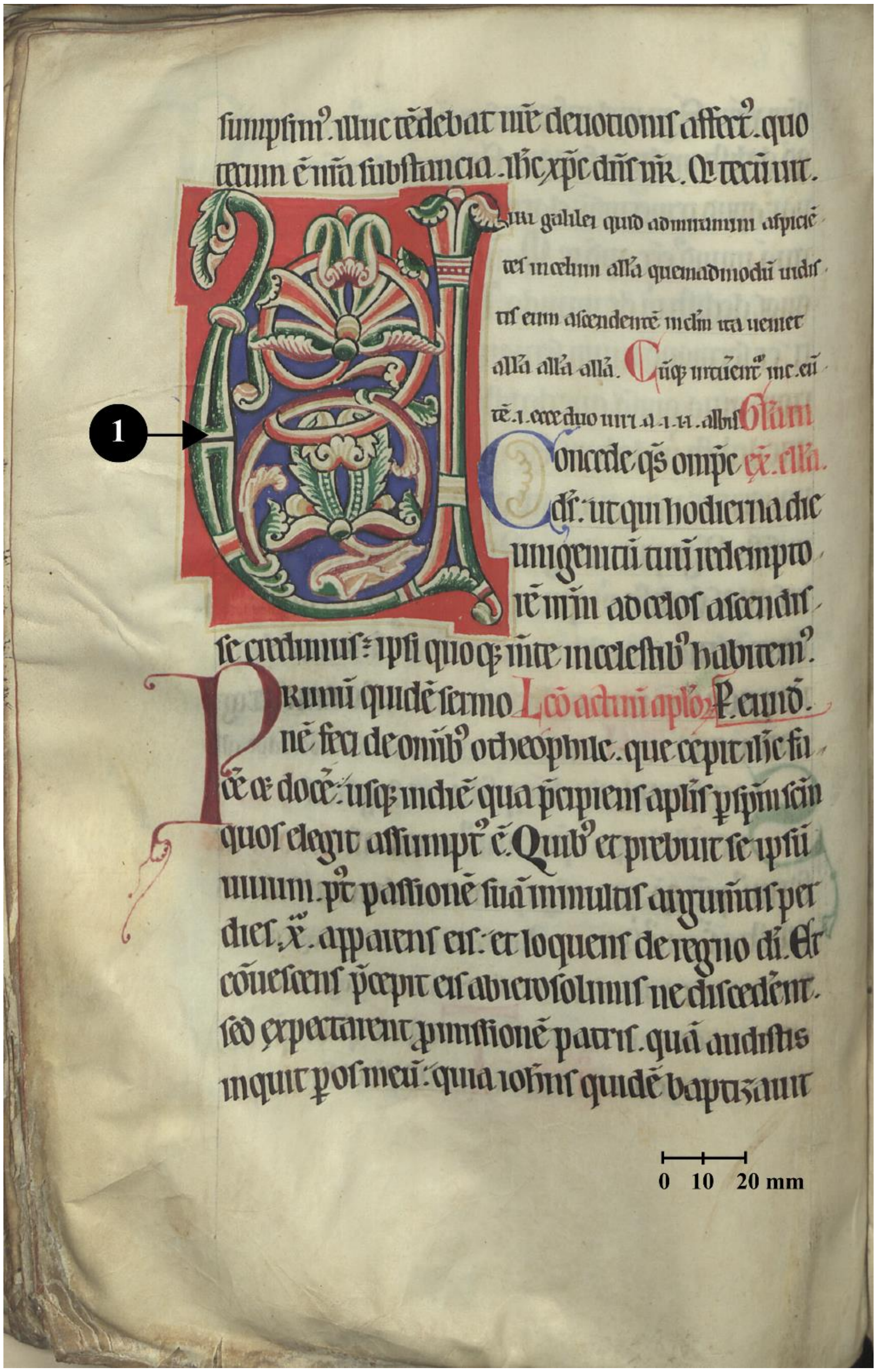
1) Alc. 255, f.2^{v}: Green_1 (FORS)
2) Alc. 255, f.2^{v}: Green_2 (FORS)
3) Alc. 255, f.2^{v}: Green_3 (FORS)

Alc. 255, f. 36r



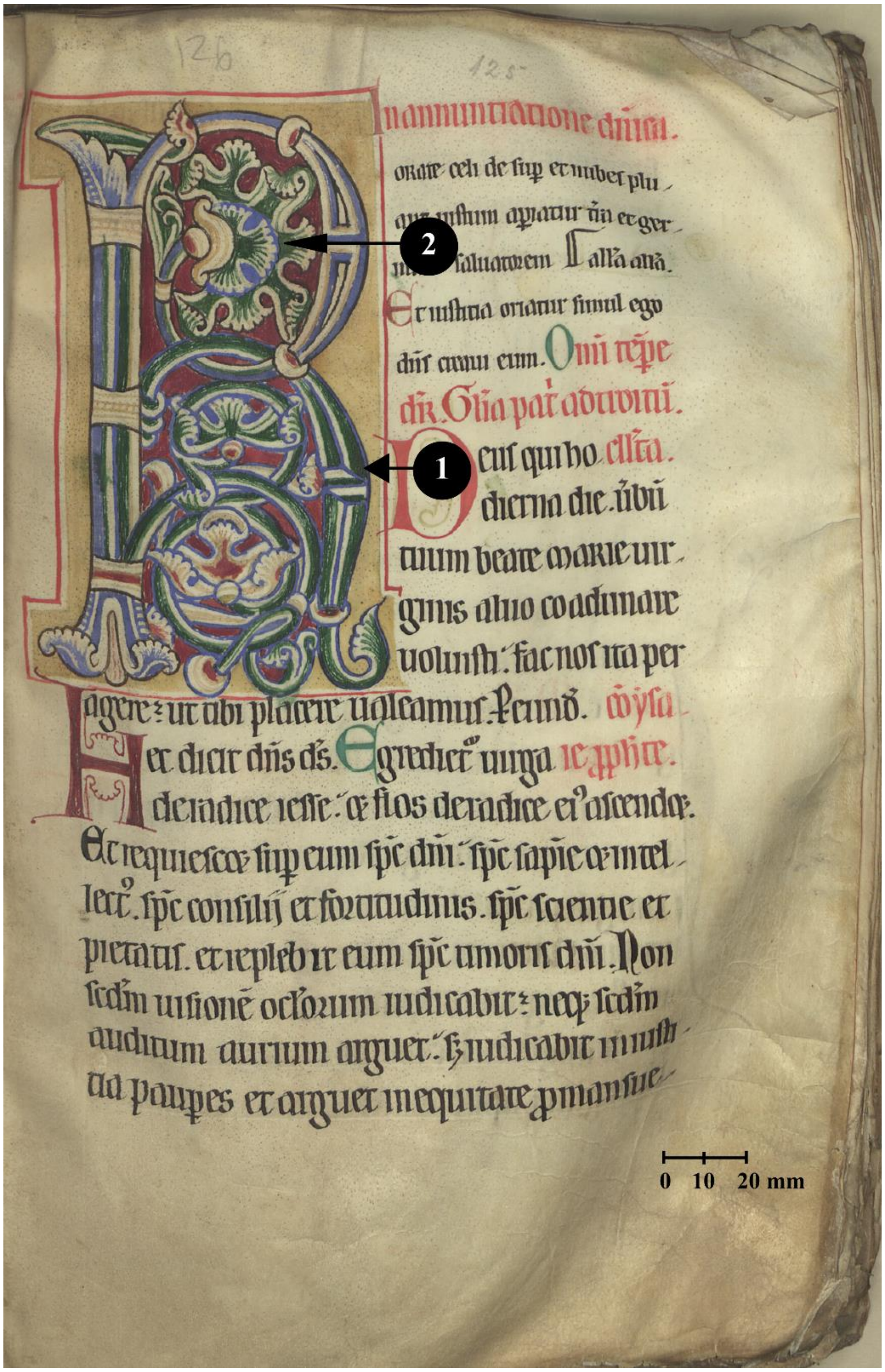
1) Alc. 255, f.36r: Green_1 (FORS, h-EDXRF)
2) Alc. 255, f.36r: Green_2 (FORS)

Alc. 255, f. 58v



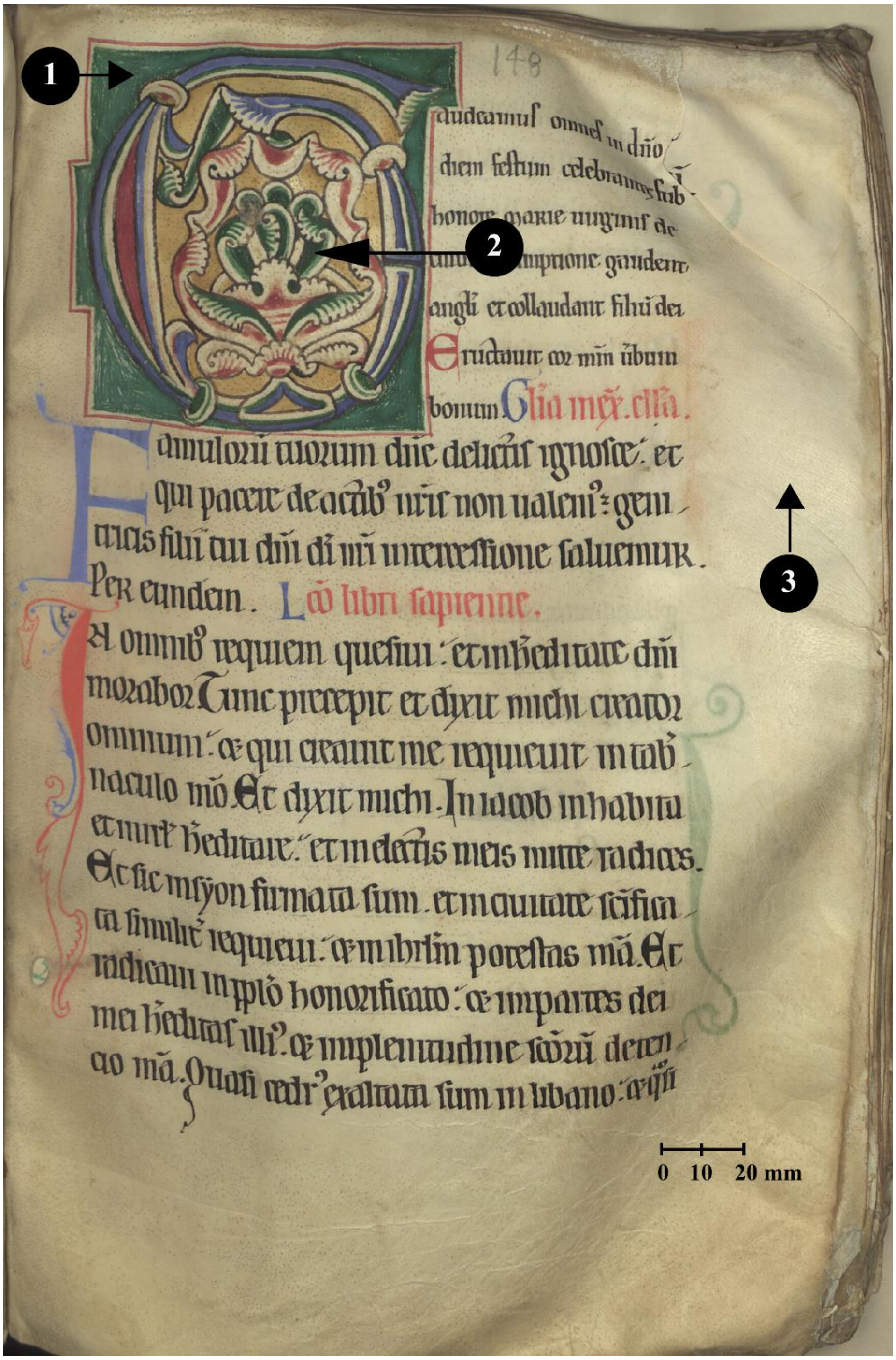
1) Alc. 255, f.58v: Green_1 (FORS)

Alc. 255, f. 126^{r}



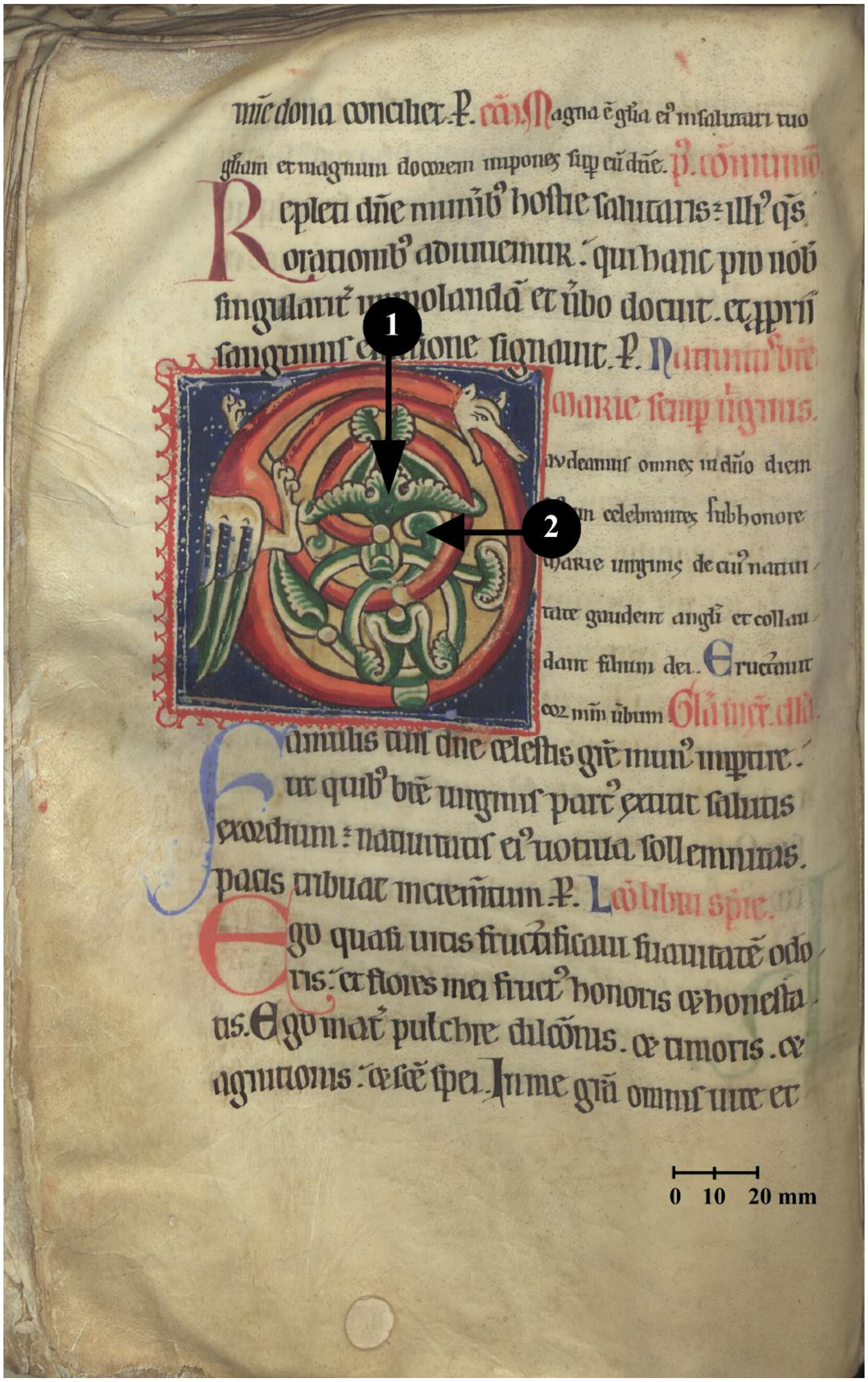
1) Alc. 255, f.126^{r}: Green_1 (FORS)
2) Alc. 255, f.126^{r}: Green_2 (FORS)

Alc. 255, f. 148r



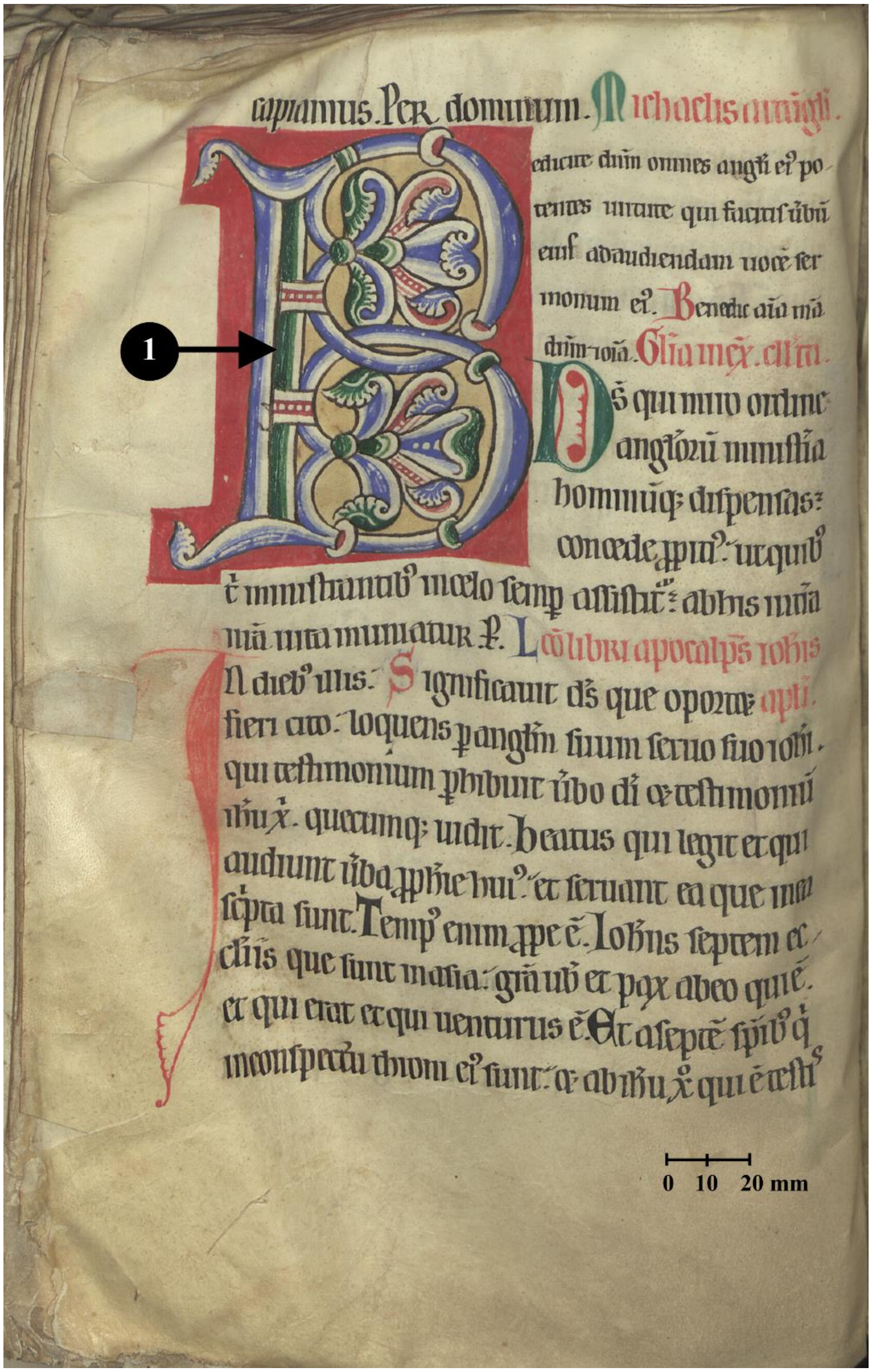
1) Alc. 255, f.148r: Green_1 (FORS)
2) Alc. 255, f.148r: Green_2 (FORS)
3) Alc. 255, f.148r: Parchment (FORS)

Alc. 255, f. 153v



1) Alc. 255, f.153v: Green_1 (FORS, h-EDXRF)
2) Alc. 255, f.153v: Green_2 (FORS)

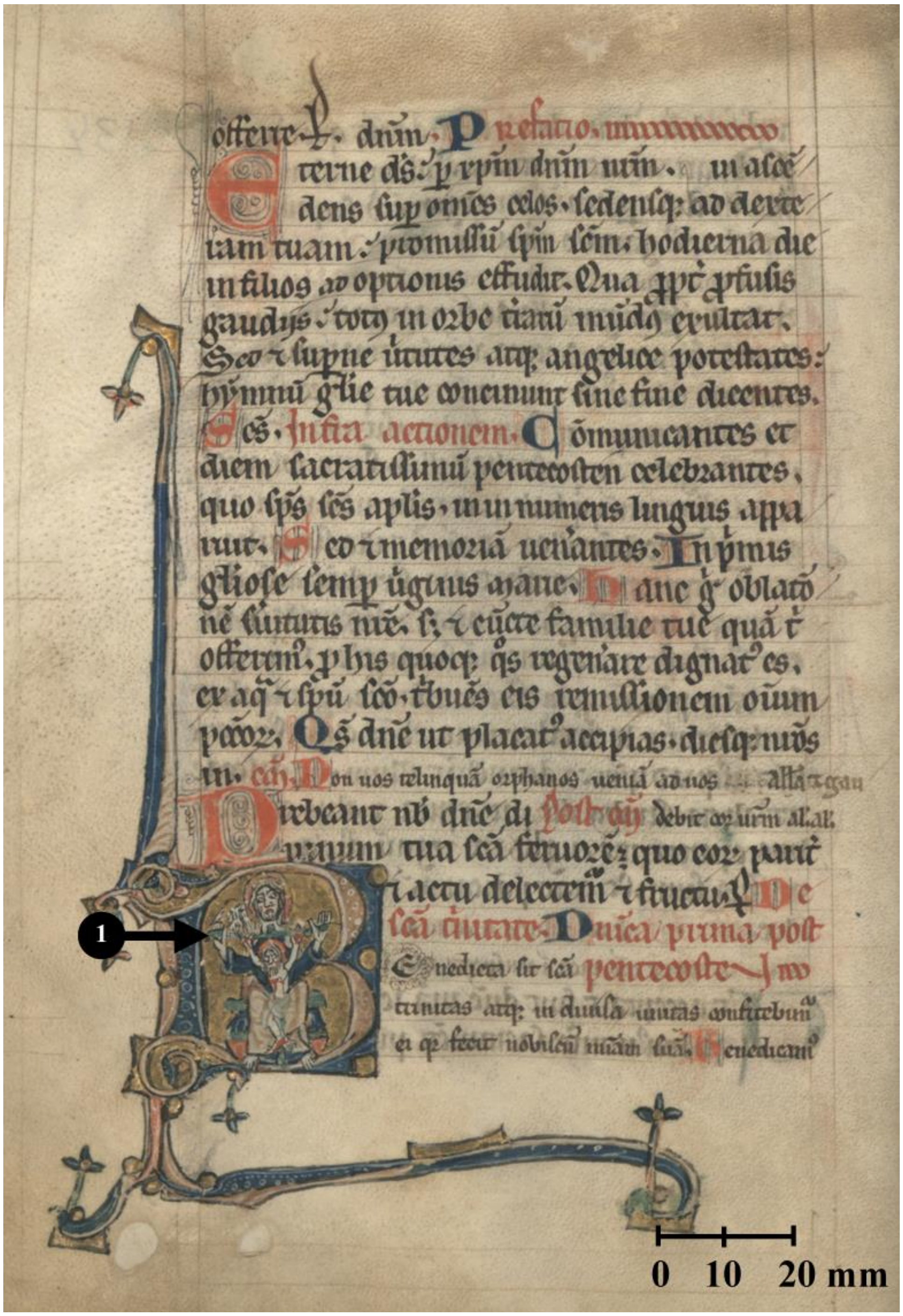
Alc. 255, f. 159v



1) Alc. 255, f.159v: Green_1 (FORS)

BNP, Alc. 26

Alc. 26, f. 101v



1) Alc. 26, f.101v: Green_1 (FORS)

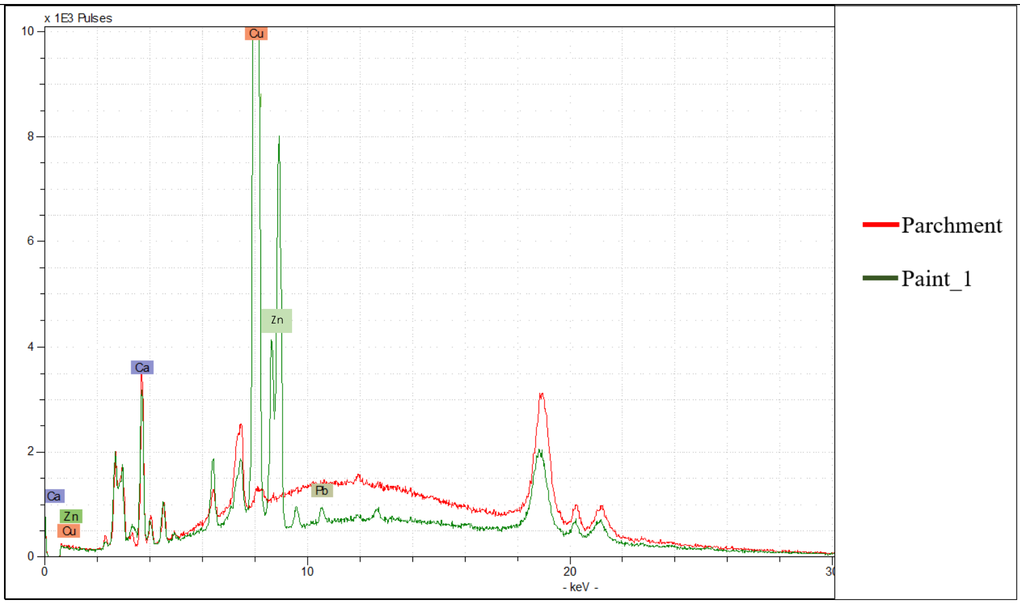
List of analysed folia through h-EDXRF

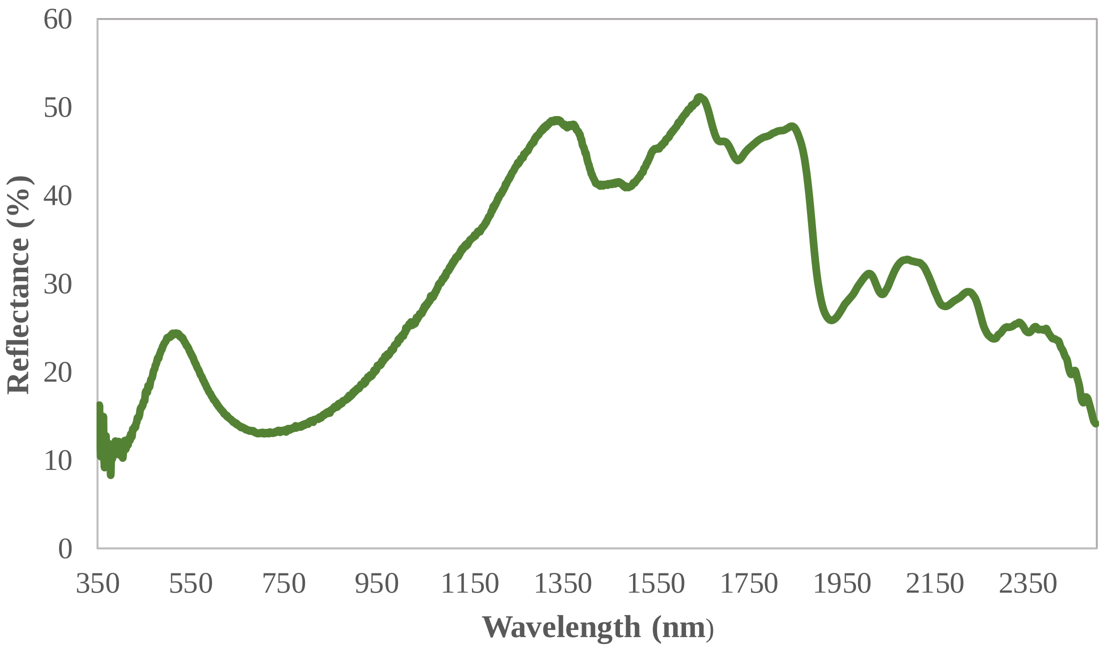
MANUSCRIPT	ANALYSED FOLIA	TOTAL FOLIA
Ms Alc. 433 **~1175-17th century**	168v, 15r	2
ANTT Ms 17 **1191-1196**	1r	1
Ms Alc. 167 **1197-1198**	83r, 98v, 123r	3
Ms Alc. 255 **1205**	2v, 36r, 153v	3
Ms Alc. 26 **1318-1380**	1v, 101v	2

Appendix 3. Molecular and elemental data

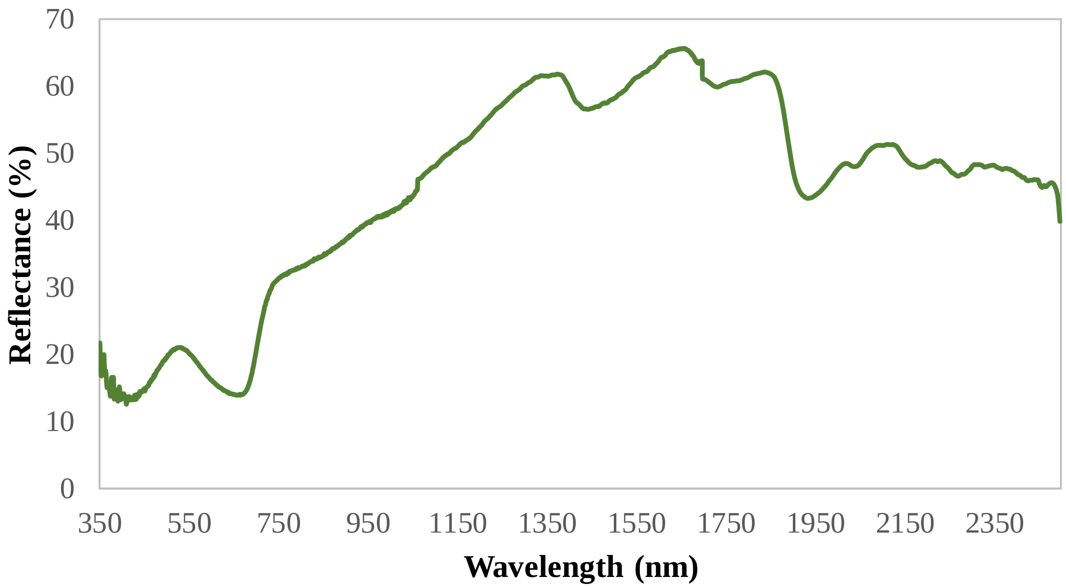
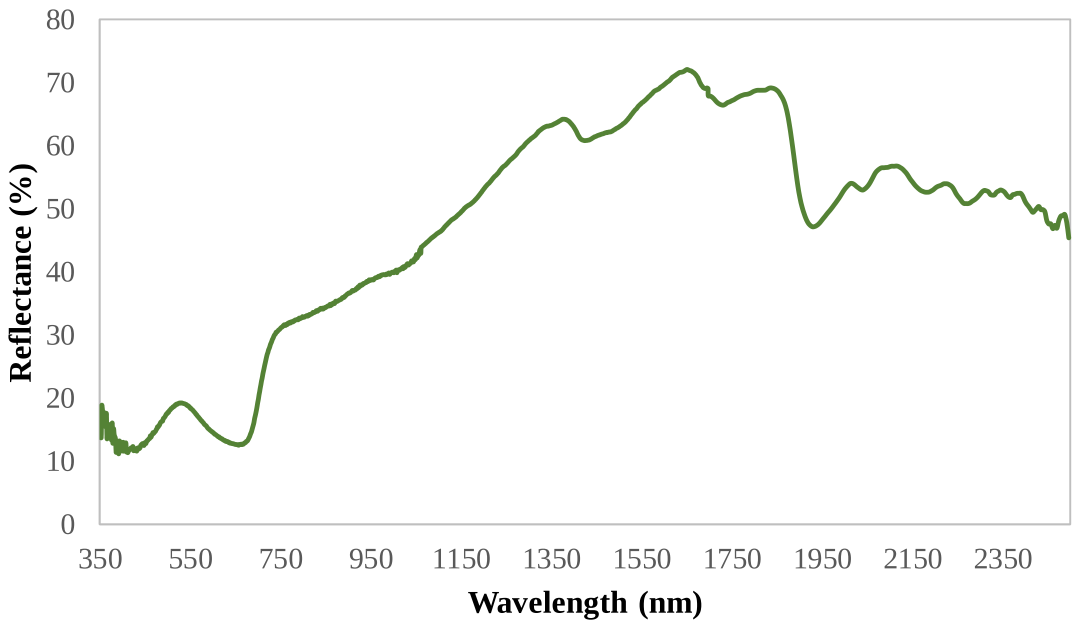
BNP, Alc. 433

f. 168ᵛ



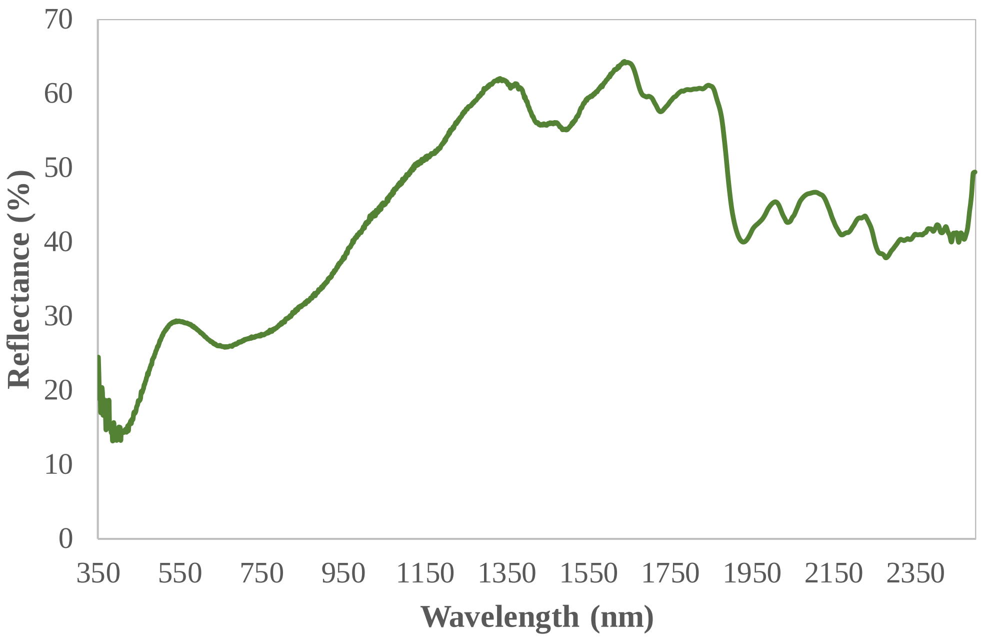


BNP, Alc. 260

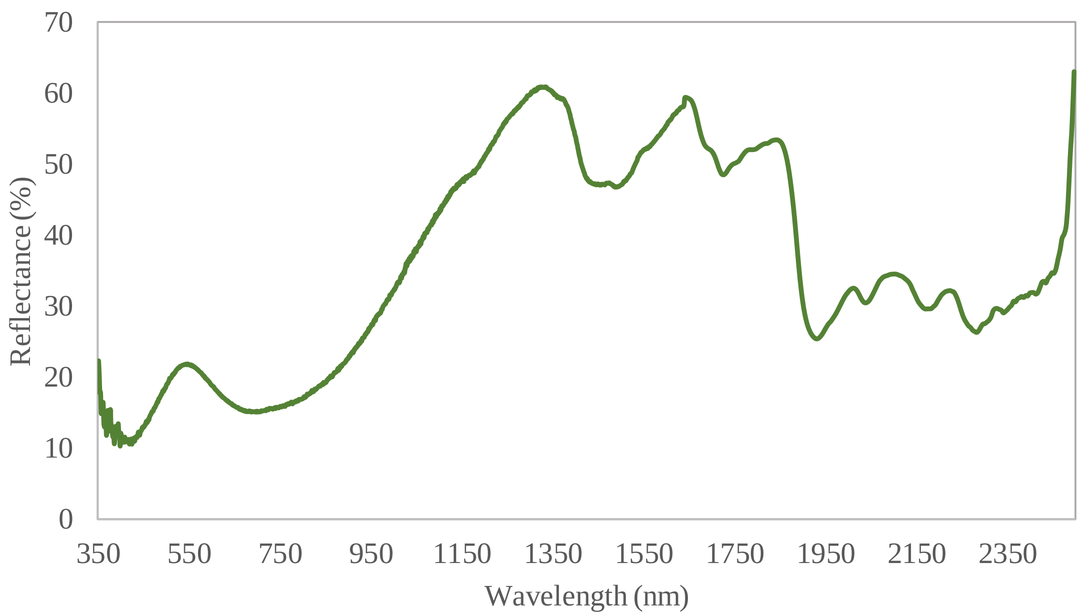
f. 75r

f. 98v


BNP, Alc. 166

f. 65r

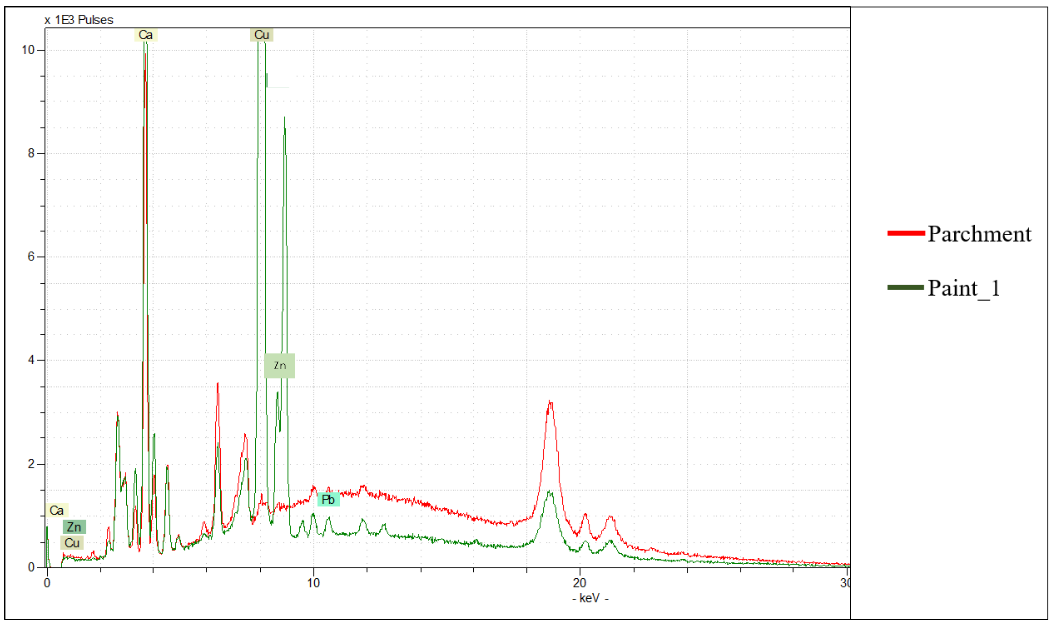


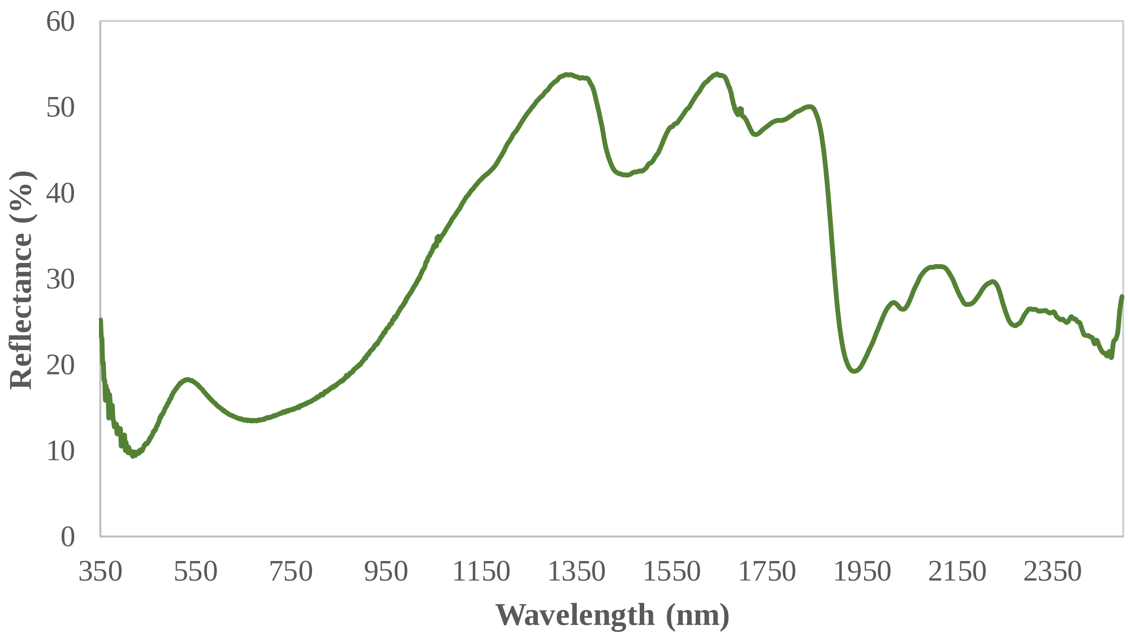
f. 151v



ANTT, Ms 17

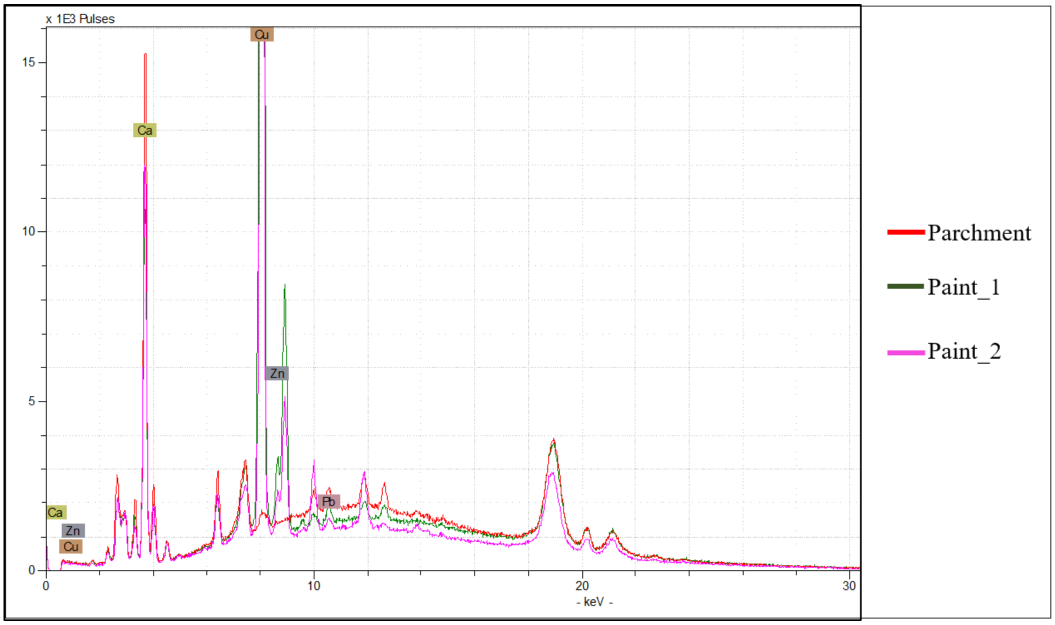
f. 1^{v}

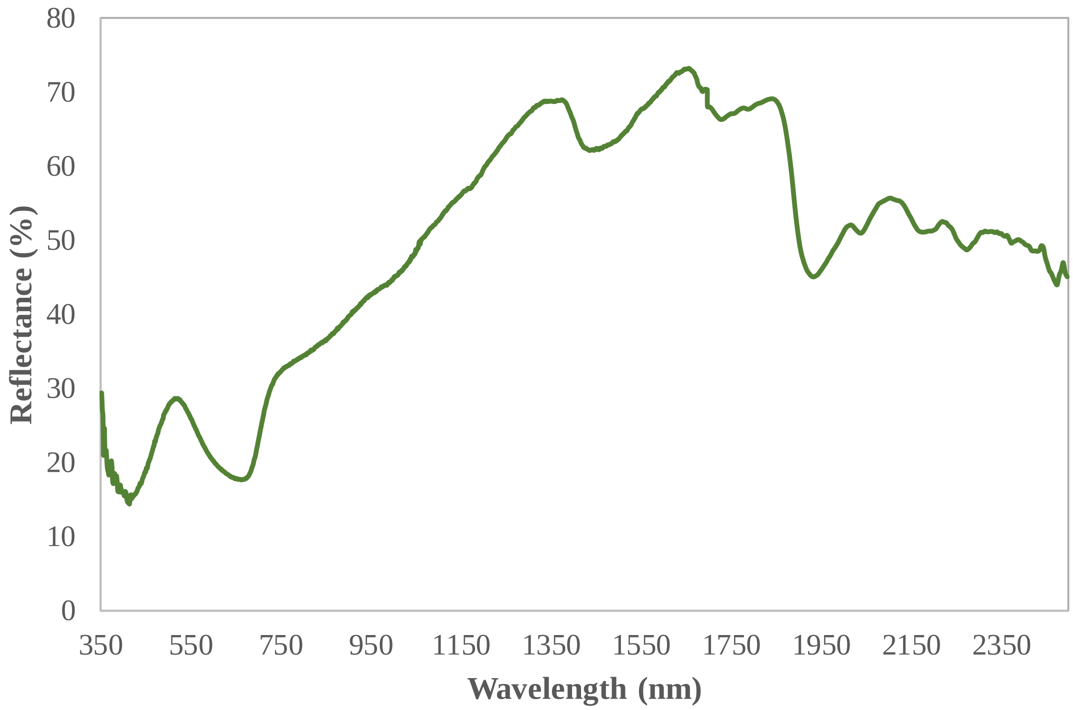




BNP, Alc. 167

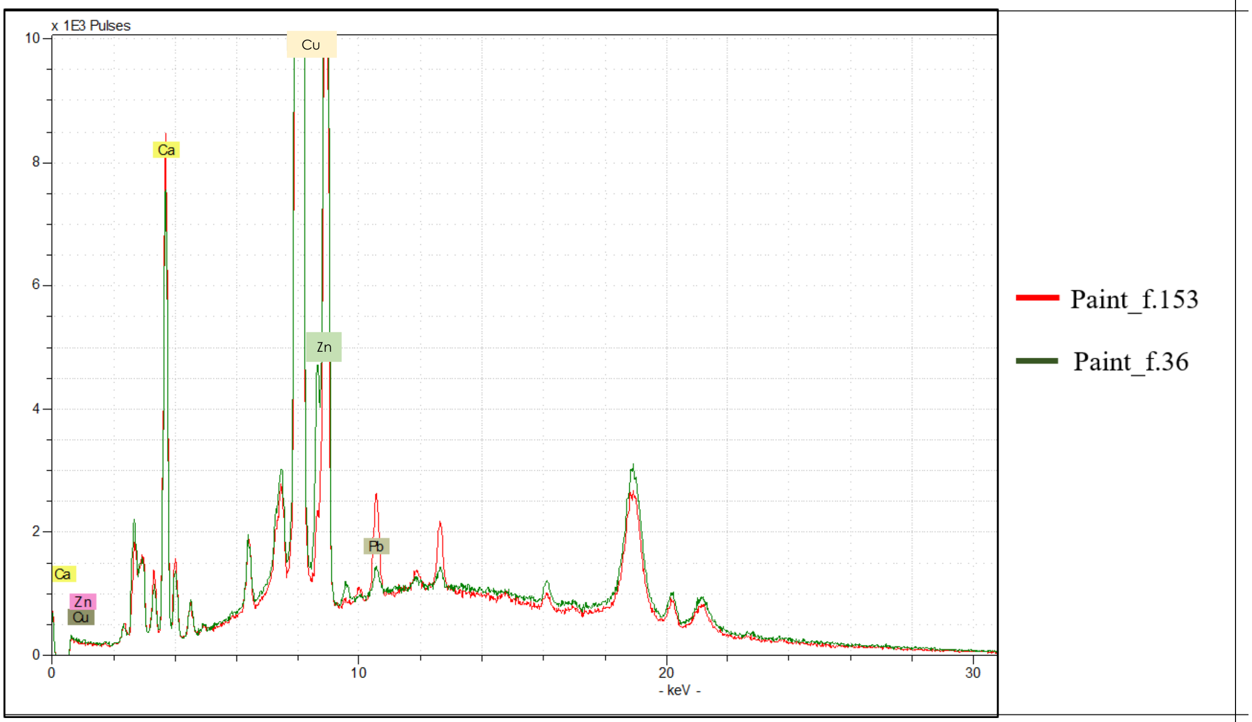
f. 83r

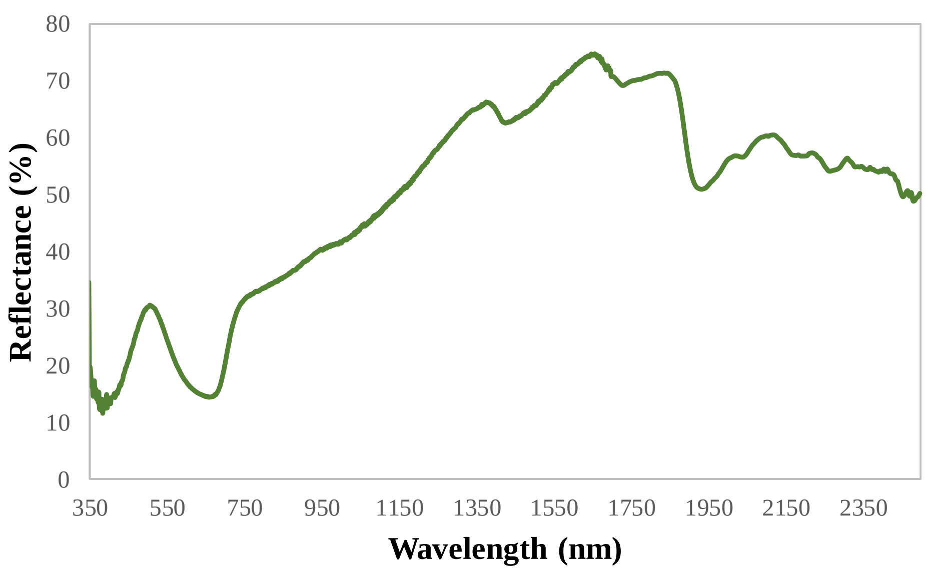




BNP, Alc. 255

f. 36r (FORS) & f. 153r (h-EDXRF)





BNP, Alc. 26

f. 101v