THE STUDY OF THE BIOGRAPHICAL TRAJECTORY OF A PORTUGUESE 12TH C. ILLUMINATED MANUSCRIPT: THE *LECCIONARIUM* ALC. 433 FROM ALCOBAÇA COLLECTION HELD BY THE BIBLIOTECA NACIONAL DE PORTUGAL

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Abstract

Medieval illuminated manuscripts are among the best testimonies of the life of medieval scriptoria. This work traces the biographical trajectory of a Lectionary according to the Cistercian rite – the Alc. 433 - through the liturgical studies and the material characterisation of its painted illuminations, with the aim of obtaining the chronological timeline of the use of colour materials in the Portuguese scriptorium of Alcobaça. For this, liturgical analysis of the manuscript combined with the material characterisation of a selection of representative folia of Alc. 433 with non-invasive in-situ analysis (h-EDXRF, UV-Vis-NIR-FORS, and hyperspectral imaging analysis) was used. The result indicates that it was produced in the last quarter of the 12th century, followed by the addition of some folia in the 13th, 14th, and the beginning of the 17th century. Materials identification revealed the use of the most common inorganic pigments for this period. As for organic colour materials, turmeric was identified as a yellow lake pigment.

Background

Between hundreds of illuminated manuscripts produced in Alcobaça scriptorium, the codex BNP, Alc. 433 leaves clear signs through its folia: it is evident that some folia

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were the initial core, while others were added years and/or centuries later. This envisioned the possibility of further and advanced research connecting this manuscript through its trajectory from one period to another with the history of Alcobaça, i.e., to trace the biographical trajectory of the manuscript as a living object that suffered continues additions as an up-to-date tool to be profoundly used by the Cistercian monks in their daily prayer. For this, an interdisciplinary approach was followed combining liturgical analysis of the texts and materials characterisation of the illuminations and writing inks. The materials used to produce Alc. 433 were analysed to investigate the production period and its changes over time. The primary structure of the bookbinding (i.e., sewing and supported materials), if not changed over time, will contribute to setting the date of the manuscript production as a whole. Within this approach, it became evident the complex chronology of the production of the Alc. 433 in terms of its colour materials, liturgical context, and bookbinding, at the same time, that allowed for broadening the research approach within the Portuguese illuminated manuscript of Alcobaça's scriptorium.[1]

Liturgical Studies

The Alc. 433 is a parchment codex that measures 460 x 329 mm (written space 346 x 225 mm) with a total of 235 folia (text in 2 columns, 27 lines). The folia are not visibly numbered. The texts were written in Latin with a Protogothic script. Even though the core of the Alc. 433 was assumed to have been produced at the end of the 12th c., it was known that some folia of this manuscript were added later in different periods due to apparent differences in the context of the liturgy and in the drawing techniques of the illumination.

In Table 1, the liturgical contents are listed only for the folia that were characterised within this research regarding its different periods of production.

Based on the liturgical contents of the different additions to the core of the codex, it becomes clear that the Alc. 433 received additions over centuries, up to the beginning of the 17th century (Fig.1). In fact, the Alc. 433 had a very long time of liturgical use by the monks: copied around 1175, shortly after the foundation of Alcobaça monastery, it received various liturgical offices as they were being authorised by the General Chapter, which was aggregated during five centuries of intensive use and received its last addition in the 17th century.

[1] Fitri, Shatila. *The Study of Biographical Trajectory of Portuguese 13th Century Illuminated Manuscript: LECCIONARIUM ALC. 433 from Alcobaça Collection held by The Biblioteca Nacional de Portugal*. **Évora:** Universidade de Évora, 2020, Master thesis; and Catarina Miguel, Shatila Fitri, Silvia Bottura-Scardina, Conceição Casanova and Catarina Fernandes Barreira, "*On the Life of a Scriptorium*: Unveiling the Interdisciplinary Study of the MS Alc. 433 Manuscript and its Unique Chronological Record of the Work at the Portuguese Scriptorium of Alcobaça" in *Drugs & colours in History*, ed. Maria Luisa Vázquez de Ágredos Pascual, Catarina Pereira Miguel and Claudia Pelosi (Valencia: Tirant Lo Blanche, 2024), in press.

Table 1. The Liturgical Content of the Alc. 433[2]

Foliation	*Liturgical Content*	*Assumed Period*	*Note*
Folio 1 (Added to the beginning of the codex)	**Corpus Christi**	Quires added to this codex in early 14th c. (between 1318-1350)	The Corpus Christi feast was authorised by the General Chapter in September 1318[1]
Folio 15 (Addition with 3 folia)	**Feast SS. Trinitate**	Folia added after 1175	The feast was instituted and authorised by the General Chapter in September 1175[2]
Folio 18v (Initial core of the codex)	**Proper of Time and Proper of Saints**	Written around 1175 (the manuscript model was written before 1175)	Most likely to be dated before 1175
Folio 228 (Addition)	*Exaltatio Sanctae Coronae Domini* (Exaltation of the Holy Cross)	Quire added after 1292	This office was authorised by the General Chapter for the French context in 1240, and authorised for the whole Christendom in 1292
Folio 232 (Quire with 3 folia and another quire with 2 folia)	Sermo in Assumptione Primus (Sermon of Saint Bernard Abbot)	Last addition, around 17th c.	This edition mentioned brother Brandão (a monk from Alcobaca who wrote the Lusitanian Monarchy in the beginning of 17th c.)

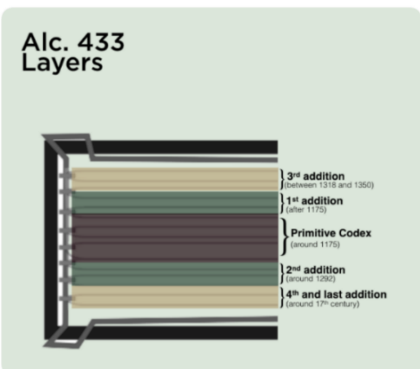

Fig. 1. Scheme of the five different sections present in the BNP, Alc. 433, according to the period of addition.

[2] Fitri, *The Study of Biographical Trajectory, and Miguel et al, "On the Life of a Scriptorium.*" The liturgical content and its connection to other manuscripts will be developed in the article of Catarina Fernandes Barreira within this book.

Bookbinding analysis

Decorations and structure shape lead us to propose that Alc. 433 was assumed to be bound around the 17th century. The bookbinding structure is sewn on five raised cords, which are laced in heavy wood boards covered by plain brown leather decorated with blind tools using a geometric pattern (Fig. 2), such as a central diamond inserted in a larger rectangle, which is very common in Portuguese 15th-17th century binding.[3] End-bands are very simple, with a round shape of a single thread on the cord, and the spine is double-reinforced with linen straps and parchment. It shows round metal bosses and squares for protection and two fastenings for text-block holding. The binding looks deteriorated, especially in the spine of the book (Fig. 3). According to Seixas' doctoral dissertation, a similar cover design with a geometric pattern can be categorised as a 'NeoManueliene' bookbinding style rather than gothic.

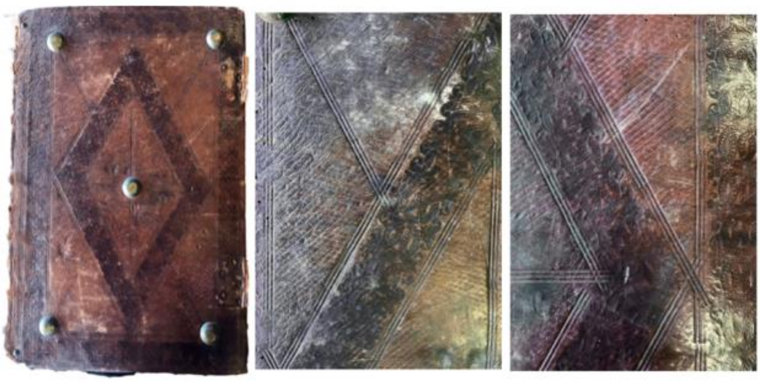

Fig. 2. The front cover of Alc 433 evidences details of decoration and embellishment in the front cover.

Fig. 3. The spine of BNP, Alc. 433, evidencing the deteriorated leather.

[3] Seixas, Maria Margarida Faria Ribeiro da Cunha de. "A encadernação manuelina a consagração de uma arte: estudo das suas características e evoluçao, em bibliotecas públicas portuguesas." Universidad de Salamanca, 2011 (PhD Thesis).

Illumination Techniques and Historical Reconstructions

Aiming to determine better how both drawing technique and colour materials were employed in the early production of Alcobaça scriptorium, historically accurate reconstructions of the illuminated capital letter present in Alc. 433 folio 18v were produced and compared with the original illumination. This choice was based on the fact that the Chapter including Alc. 433 folio 18v is in the primitive set of folia of the manuscript (meaning, in the initial core of the manuscript), and by studying it, a new approach to exploring the technique for producing illuminations in Alcobaça in its early stage of activity (second half of the 12th century) would be investigated. Moreover, the initial of folio 18v does not only presents in its colour palette the most common inorganic pigments used in the medieval period (such as vermilion, lapis lazuli, etc.) but also presents an intense light-colour yellow paint, which was assumed to be yellow lake pigments (organic dye).

The historical reconstruction of the drawing procedure of folio 18v followed several possibilities of methods, that were referenced from previous studies.[4] In total, four methods were reconstructed using transfer and freehand copy methods: stencil methods, backlight drawing, carbon and lead copy, and freehand copy. After careful reconstruction of these different techniques, the best one was the stencil method, which created similar and more detailed results (Fig. 4).

[4] Stijnman, Ad. "Oil-based printing ink on paper." *Papier Restaurierung* 1 (2000): 61-68.
Cannon, Christopher. "Chaucer and the Auchinleck Manuscript Revisited." *The Chaucer Review* 46.1-2 (2011): 131-146; Adcock, Gwenda Aleathea. *Interlaced animal design in Bernician stone sculpture examined in the light of the design concepts in the Lindisfarne Gospels*. (Diss. Durham University, 2002); Nascimento, Aires A. "Le Scriptorium d'Alcobaça: identité et corrélations." *Lusitania Sacra* 4 (1992): 149-162; Leturque, Anne. "Le savoir technique dans l'art de peindre au Moyen Âge: les modes opératoires décrits dans le Liber Diversarum Artium (MS. H277, bibliothèque de l'école de médecine de Montpellier)." *In Situ. Revue des patrimoines* 22 (2013); Cardon, Dominique. "À la découverte d'un métier médiéval. La teinture, l'impression et la peinture des tentures et des tissus d'ameublement dans l'Arte della lana (Florence, Bibl. Riccardiana, ms. 2580)." *Mélanges de l'école française de Rome* 111.1 (1999): 323-356; Kennedy, Cornelia Breugem. *A Book of Hours at the University of Iowa: An Analysis*. Diss. (University of Iowa, 1986). Kennedy, Cornelia Breugem. *A Book of Hours at the University of Iowa: An Analysis*. Diss. (University of Iowa, 1986). Antoine, Beth. "Metalpoint Drawing: The History and Care of a Forgotten Art." (2007): 3. Correia, Nuno, et al. "Design of an interactive experience with medieval illuminations: A journey into the beauty and meaning of medieval Portuguese manuscripts." *Journal on Computing and Cultural Heritage (JOCCH)* 7.2 (2014): 1-19.

Fig. 4. Left, a historically accurate reconstruction of the painted initial of BNP, Alc. 433, folio 18v; right, a scheme of the distribution of the yellow lake pigments (weld, saffron, and turmeric) applied to the illumination.

Materials Characterisation

The characterisation of the drawing technique used to produce the illuminated capital letters and the materials used to produce the colour paints of Alc. 433, such as pigments, binders, and writing ink, started with detailed observation (photography and digital microscopy), followed by elemental analysis (h-EDXRF) and molecular analysis (hyperspectral imaging analysis (HIS) and UV-Vis-NIR FORS).

A. Blue Colour Paints Analysis

Under magnified observation, the blue paint present in Alc. 433, folio1 presented higher heterogeneity, with the blue grains of the pigment dispersed in a matrix of brownish and white particles. A different morphology was identified in the blue paint present in folio 18v, where the intensity of the blue colour is considerably higher, and a higher concentration of blue pigment is present in the matrix of the paint (Fig. 5).

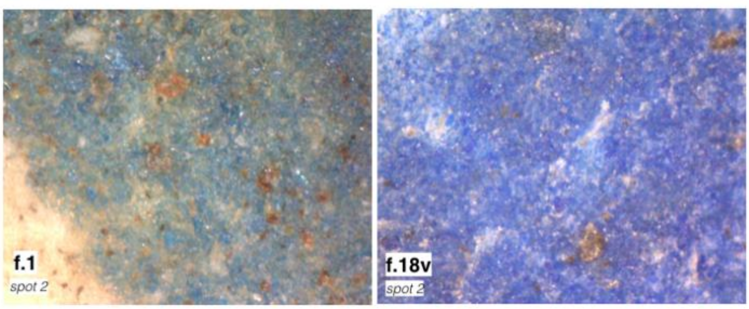

Fig. 5. The Magnified images of the blues of BNP, Alc. 433 folio1 from spot 1 (left) and of folio18v from spot 12 (magnification 430x).

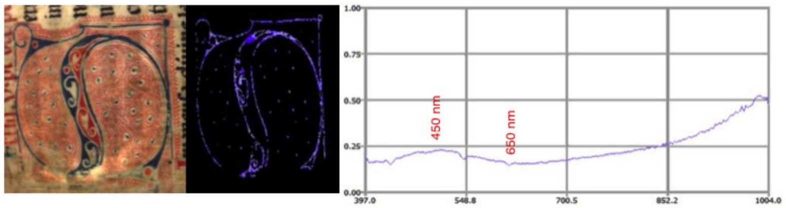

Fig. 6. Left, region of interest (ROI) of BNP, Alc. 433 folio1 analysed by HSI; centre, map of the distribution of the UV-Vis spectra of the blue paint present in the ROI; right, UV-Vis reflectance spectrum of the blue paint, where it is identified the characteristic bands

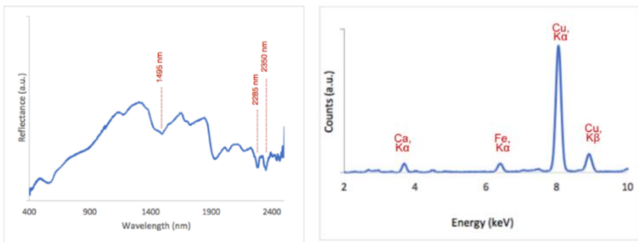

Fig. 7. UV-Vis-NIR reflectance spectra of BNP, Alc. 433, folio1 blue paint (left) and the h-EDXRF spectrum of the same folio blue paint (right).

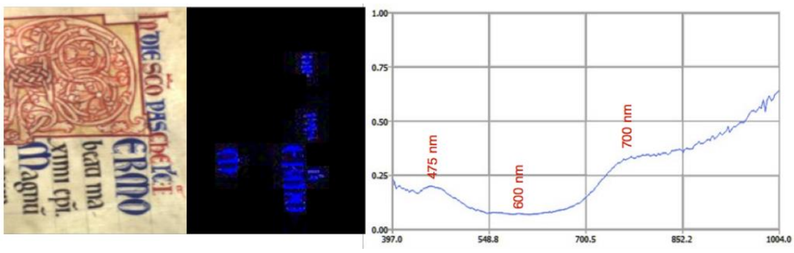

Fig. 8. Left, region of interest (ROI) of BNP, Alc. 433 folio18v analysed by HSI; centre, map of the distribution of the UV-Vis reflectance spectra of the blue paint present in the ROI; right, UV-Vis spectrum of the blue paint, where it is identified the characteristic bands.

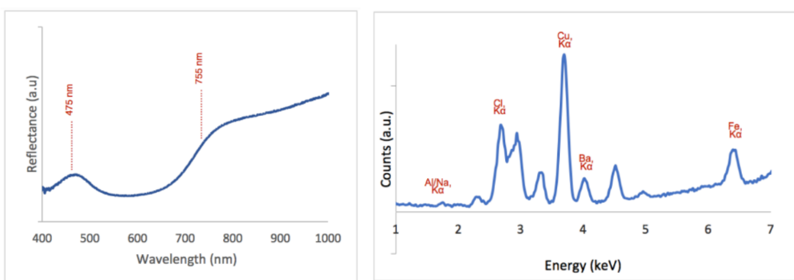

Fig. 9. UV-Vis-NIR reflectance FORS spectra of BNP, Alc. 433 folio 18v blue paint (left); h-EDXRF spectrum of the same folio, blue paint (right).

UV-Vis FORS analysis of the blue paint of the initial letter in Alc. 433 folio 1 allowed to identify the characteristic spectral profile of azurite ($2CuCO_3.Cu(OH)_2$), namely its characteristic reflectance band with a maximum at 450 nm and a maximum absorption band at ca. 640 nm related to the d- d transitions of copper (Fig. 6). Moreover, UV-Vis-NIR FORS analysis allowed to identify two specific vibrational overtones of the hydroxyl groups (-OH) and of the carbonate groups ($-CO_3$) of azurite were found: $2\nu(OH)$ at 1495 nm, ($\nu+\delta(OH)$ and $3\nu(CO_3)$ at 2285 and 2352 nm) (Fig. 7).[5] h-EDXRF elemental point analysis revealed the presence, as major elements, of copper (Cu), iron (Fe) and calcium (Ca) (Fig. 7). The presence of copper corroborates the presence of azurite ($2CuCO_3.Cu(OH)_2$). In contrast, iron might be related to the presence of pyrite (FeS_2) and calcium to the presence of calcite ($CaCO_3$), commonly associated with the mineral azurite.[6]

Regarding the blue paints present in the incipit of Alc. 433, in the folio 18v, UV-Vis FORS analysis allowed identifying the characteristic UV–Vis reflectance spectrum of lapis-lazuli ($Na_{6–10}Al_6Si_6O_{24}S_{2–4}$), namely the reflectance band at 475 nm, the shoulder at 755 nm and the maximum absorption band at ca. 600 nm (Fig. 8 and Fig. 9) due charge transfer transition inside S_3^{2-} group that is present in the lattice of the complex aluminosilicate.[7]

h-EDXRF elemental point analysis of the blue paint used for the incipit in Alc. 433 folio 18v revealed the presence, as major elements, sodium (Na), aluminium (Al), silicon (Si), sulphur (S), chlorine (Cl) and barium (Ba), often present in lapis lazuli minerals (Fig. 9). Calcium (Ca) and iron (Fe) might be related to the presence of pyrite and calcite, which can be present as minor impurities. It is worth stressing that Ca may also be present due to $CaCO_3$, commonly used to prepare parchment before the illumination process, or that could be an extender in the paint formulation.[8]

B. Red Paints Analysis

Red paints are found in folio 1 (initial letter), folio 18v (initial letter and incipit), and folio 228 (initial letter). Under magnified observation, all reds appear deep-colour intense and opaque, with a dense morphology and without a significant crack to the parchment (Fig.10). The pigment covers the parchment very well. Even in some parts of folio 1 where the paints are cracked, no parchment appeared. In folio 18v, the red paint near the ink looks cracked only in the ink area.

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[5] Ricciardi, Paola, John K. Delaney, Lisha Glinsman, Mathieu Thoury, Michelle Facini, and E. René de la Rie. "Use of visible and infrared reflectance and luminescence imaging spectroscopy to study illuminated manuscripts: pigment identification and visualization of underdrawings." In *O3A: Optics for Arts, Architecture, and Archaeology II*, vol. 7391, pp. 49-60. (SPIE, 2009).

[6] Eastaugh, Nicholas, Valentine Walsh, Tracey Chaplin, and Ruth Siddall. *Pigment compendium: a dictionary of historical pigments*. (Routledge, 2007).

[7] Bacci, Mauro, Donata Magrini, Marcello Picollo, and Muriel Vervat. "A study of the blue colors used by Telemaco Signorini (1835–1901)." *Journal of cultural heritage* 10, no. 2 (2009): 275-280.

[8] Fachechi, Grazia Maria, and Susanna Bracci. "Romanesque polychrome wood sculptures in Italy: towards a Corpus and a comparative analysis of the data from art-historical and technical studies." *Medievalista. Online* 26 (2019).

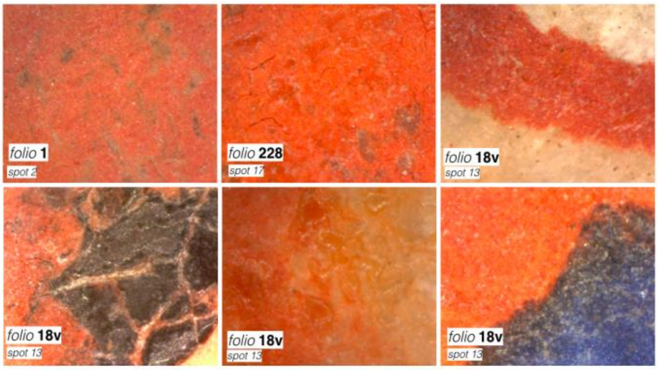

Fig. 10. Magnified images of the red paints of folio 1, folio 18v, and folio 228 with magnification 430x.

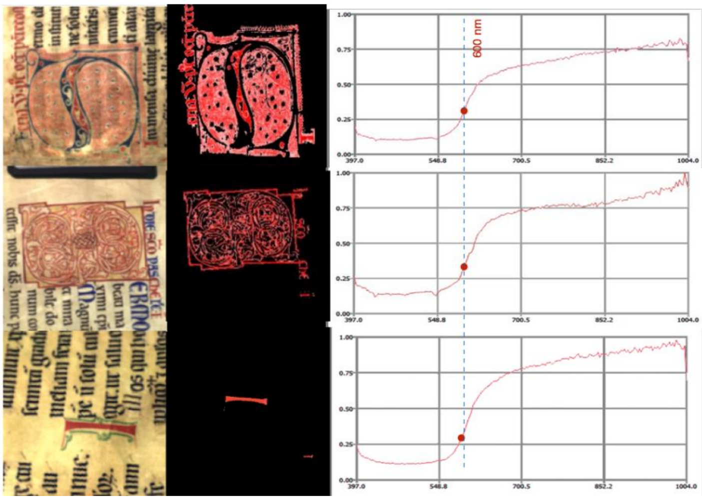

Fig. 11. Left, the region of interest (ROI) of BNP, Alc. 433 folio 18v analysed by HSI; centre, a map of the distribution of the UV-Vis reflectance spectra of the red paint present in the ROI; right, the UV-Vis reflectance spectrum of the red paint, highlighting the characteristic bands of red vermillion; from above to below: folio 1, folio 18v and folio 228.

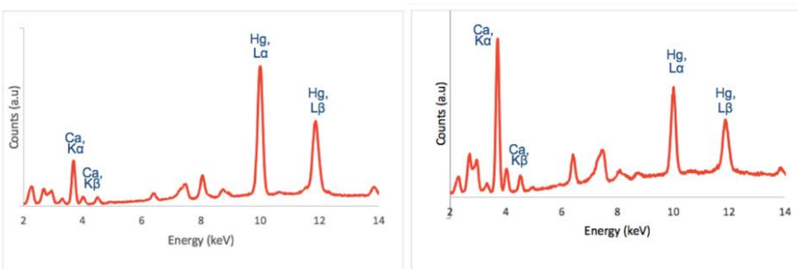

Fig. 12. h-EDXRF spectra of red paints of BNP, Alc. 433, folio228 (left) and of folio1 (right).

UV-Vis FORS analysis of this red paint allowed to identify the characteristic spectral profile of vermilion (HgS) in folio 1, folio 18v, and folio 228, where the spectral profiles for all folia show similar behaviour between 550 – 700 nm region: an inflection point at around 600 nm, characteristic of the Hg^{+} electronic transitions of vermilion (Fig. 11).[9]

h-EDXRF elemental point analysis of the red paints present in folio 228 and folio 1 exhibits the presence of the key element of vermilion: Hg ($L\alpha$ = 9.989 keV and $L\beta$ = 11.824 keV) (Fig. 12). Additionally, for the red paint present in Alc. 433 folio 1, calcium (Ca) was also identified in the paint composition through its characteristic $K\alpha$ = 3.692 keV and $K\beta$ 4.013 keV (Fig. 12). This led to the possibility of the presence of a higher amount of calcium carbonate as a filler in the paint composition of this red-vermilion paint. The presence of calcium in the vermilion-paints is ubiquitously present in the red paints of Alc. 433, although it is in folio 1, where calcium is present in a more pronounced way (Fig. 12, left).

B. Orangish-Red Paints Analysis

The red paint observed in Alc. 433, folio 15, differs from those in folio 18v, folio 1, and folio 228. The colour appears to be bright red- near to orange, i.e., presents an orangish red hue. Magnified images of the orangish-red of folio 15 show a clear hue of orange with a very dense and intense bright colour (Fig. 13).

UV-Vis FORS analysis of the orangish-red present in folio 15 allowed to identify the characteristic spectral profile of minium. The spectral profile exhibits an inflection point around 560 nm, characteristic of the electronic transitions lead (Pb) of minium (Pb_3O_4) (Fig.14).[10]

Although the results of h-EDXRF analysis present significant peaks related to the presence of lead (Pb) at $L\alpha$ = 10.551 keV and $L\beta$ = 12.614 keV (Fig. 15). Together with lead (Pb), mercury (Hg) is also highly present through its characteristic $L\alpha$ = 9.989 keV and $L\beta$ = 11.824 keV peaks (Fig. 15).

The presence of both chemical elements (Pb and Hg), together with the orangish-red hue of this colour paint, leads to place two possibilities: (1) lead (Pb) might be related to the addition of lead white ($2PbCO_3.Pb(OH)_2$) to vermilion (HgS) so that the bright red vermillion looks orangish red, or (2) this orangish-red paint was produced by mixing vermilion (HgS) with minium (Pb_3O_4). However, adding white lead to vermilion gives maximum absorbance at 560 nm[11], and white lead was likely

[9] Aceto, Maurizio, Angelo Agostino, Gaia Fenoglio, Ambra Idone, Monica Gulmini, Marcello Picollo, Paola Ricciardi, and John K. Delaney. "Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry." *Analytical methods* 6, no. 5 (2014): 1488-1500.

[10] Aceto, Maurizio, Angelo Agostino, Gaia Fenoglio, Ambra Idone, Monica Gulmini, Marcello Picollo, Paola Ricciardi, and John K. Delaney. "Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry." *Analytical methods* 6, no. 5 (2014): 1488-1500.

[11] Gettens, Rutherford J., Robert L. Feller, and William Thomas Chase. "Vermilion and cinnabar." *Studies in Conservation* 17, no. 2 (1972): 45-69.

to have been mixed with vermilion for centuries[12], supporting the strength of the first possibility.

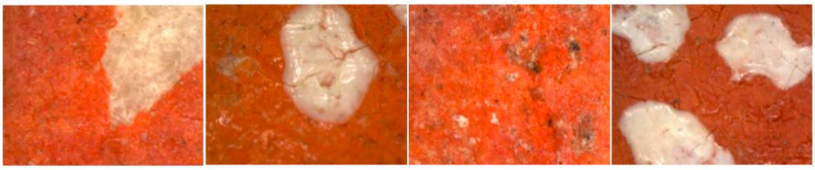

Fig. 13. Magnified images of the orangish-red of folio15 with magnification 430x

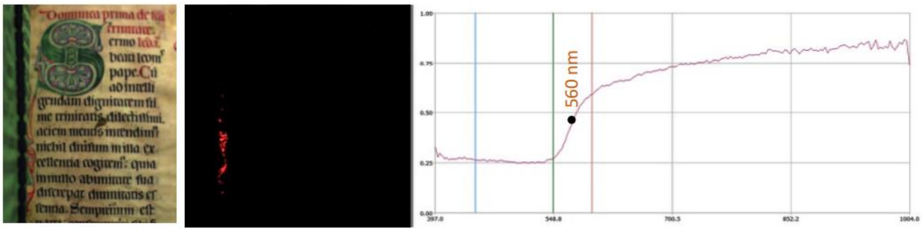

Fig. 14. Left, the region of interest (ROI) of BNP, Alc. 433, folio15, analysed by HSI; centre, a map of the distribution of the UV-Vis reflectance spectra of the orangish-red paint present in the ROI; right, the UV-Vis reflectance spectrum of the red paint, where the characteristic bands of minium are identified.

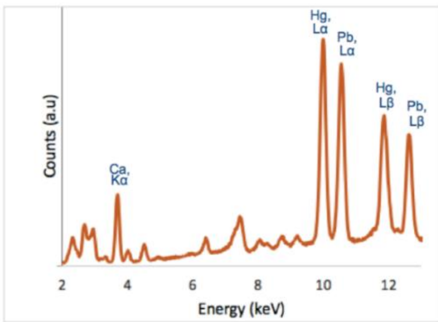

Fig. 15. h-EDXRF spectrum of orangish red present in BNP, Alc. 433, folio15.

C. Depp-glassy green Paints Analysis

Extraordinary intense, deep-glassy green paints are present in Alc. 433, namely in the initial capital letter present in folio15. The observation through digital microscopy in this green paint shows the deep green, glassy fractured appearance (Fig. 16). The green hues are not uniform; some appear intense and dark, some very light.

[12] Gettens, Rutherford J., Hermann Kühn, and W. Tom Chase. "3. Lead white." *Studies in conservation* 12, no. 4 (1967): 125-139.

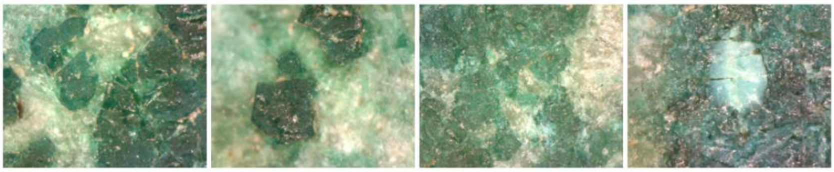

Fig. 16. Magnified images of the green paint of folio1 from spot 6 with magnification 430x.

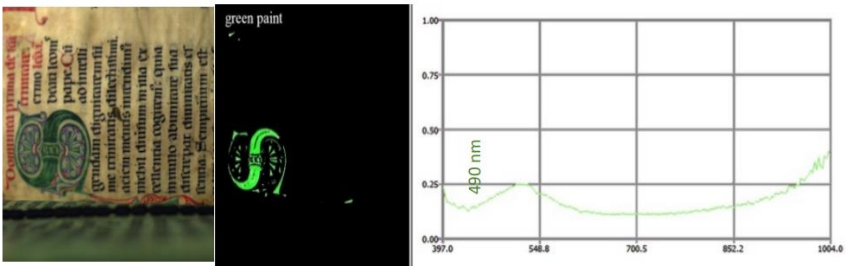

Fig. 17. Left, region of interest (ROI) of BNP, Alc. 433, folio15 analysed by HSI; centre, map of the distribution of the UV-Vis reflectance spectra of the red paint present in the ROI; right, UV-Vis reflectance spectrum of the red paint.

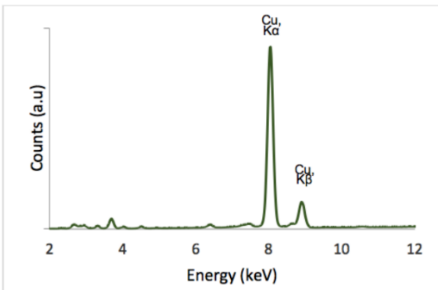

Fig. 18. h-EDXRF spectrum of folio15 green paint.

The UV-Vis FORS spectra present a maximum absorbance at around 490 nm, showing a similarity to the characteristic spectral profile of Verdigris ($Cu_2(CH_3CO)_4.2H_2O$), which presents a maximum absorbance at around 498 nm (Fig.17).[13] h-EDXRF spectrum of the green paint present in Alc. 433, folio15, exhibits two significant peaks at $K\alpha$ = 8.046 keV and $K\beta$ = 8.904 kV related to copper (Cu) (Fig. 18). UV-Vis-FORS and h-EDXRF analysis shows that the green paint in folio15 has the characteristic fingerprints of a green copper-based paint. A similar profile was found for some green copper-proteinate paints identified in a previous study, where the authors pointed to a relation between the morphological alterations of the green paints and the copper proteinate complexation, namely with

[13] Kühn, Hermann. "Verdigris and copper resinate." *Studies in conservation* 15.1 (1970): 12-36.

the modifications of the methyl and the methylene groups of the protein binder and the loss of cohesion of the paints.[14]

D. Yellow: Which Lake Pigment?

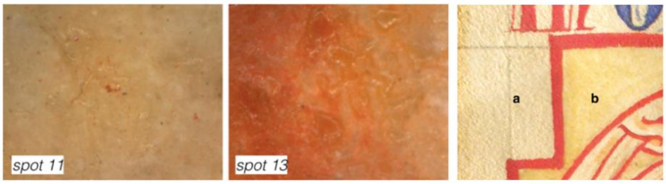

Fig. 19. From left to right: two magnified images of BNP, Alc. 433, folio 18v (yellow – spot 11; and near to a red paint – spot 13), and a detailed image of the yellow paint, capturing both blank parchment (point a) and yellow paint (point b).

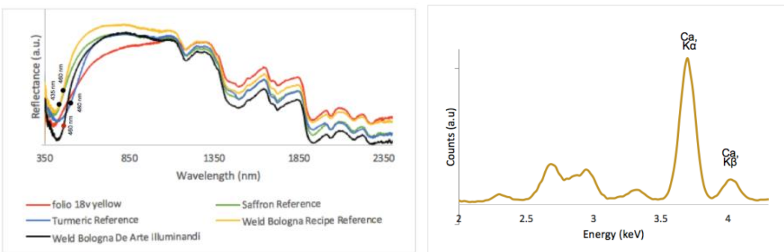

Fig. 20. UV-Vis-NIR FORS reflectance spectra of historically accurate reconstructions of yellow lake pigments and the yellow paint in BNP, Alc. 433 folio 18v (left); h-EDXRF spectrum of folio 18v yellow paint (right).

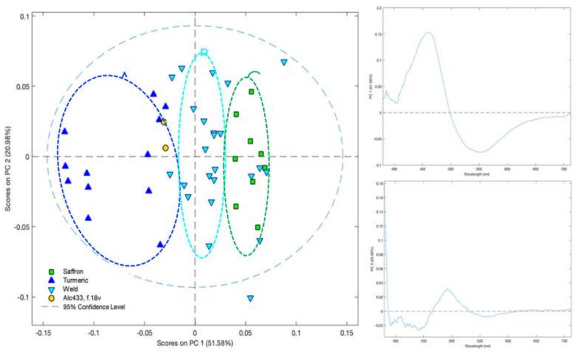

Fig. 21. Left, scores plot of PCA analysis calibrated with 51 FORS spectra of historical accurate reconstructions of turmeric (cluster A), weld (cluster B) and saffron (cluster C), on which were projected the two FORS reflectance spectra of organic yellow paints from BNP, Alc. 433 folio18v.

[14] Miguel, Catarina, Angela Nuñez-Gáitan, Maria Luísa Carvalho, and Cristina Barrocas Dias. "Scientific Study of Cistercian Illuminated Manuscripts: Techniques, Aesthetics and Religion." (2018).

A deep-light yellow paint is found in folio 18v. Magnified images evidenced the presence of a glossy pale yellow for the fully painted yellow background of this capital letter and a yellow coral at spot no. 13 (Fig. 19). Unlike intense and bright inorganic yellow pigments, the folio 18v yellow looks intense but pale. Yellow paints are not widely present in manuscripts produced in Alcobaça scriptorium in its early production stage. For this reason, this becomes the characterisation of organic yellow paints present in manuscripts produced in Alcobaça in the late 12th century.

To support and corroborate the characterisation of this organic yellow paint, historically accurate reconstructions of several yellow lake pigments were undergone: saffron, turmeric, weld (following the Bolognese recipe), and weld (following the recipe present in the *De Arte Illuminandi* treatise).[15]

The UV-Vis-NIR FORS analysis of the yellow paint's historically accurate reconstructions evidences a similar spectral profile to those found to analyse the yellow paint of folio18v in all regions (Fig. 20, left). The inflection points of each lake pigment can be distinguished clearly, with turmeric's inflection point placed at a higher wavelength (500 nm) than the inflection points of saffron and weld. On the h-EDXRF spectrum, the highest-count peak corresponds to the presence of Ca (Fig. 20, right).

Chemometric analysis has been started to be widely used in cultural heritage to recognise and identify specific samples. Principal Component Analysis (PCA) is a powerful data-mining technique that reduces data and provides a more interpretable representation of the principal component. In this case, the FORS spectra of historically accurate reconstructions of yellow lake pigments were used to produce a PCA model on which the historical spectra of folio 18v were projected, restricting the analysis to the Visible region (400-700nm).

The projection of historical spectra into the PCA model clusters its scores closer to turmeric lake pigment's historically accurate reconstructions (Fig. 21). However, this result still needs to be corroborated by other analytical techniques. Nevertheless, the use of turmeric is likely possible. It could be an interesting result if we take into account Aceto et al. 's statement that turmeric lake pigment is typically used in Islamic illumination, which can be very promising for further research in the future.

E. Ink Analysis

Iron gall ink was widely used as writing ink in Alcobaça's manuscripts, and so was for Alc. 433. Along the five different sections of the manuscript (initial core followed by four different additions), the inks present different surface morphologies (Fig. 22). The assumed earliest writing ink present in folio 18v shows a deeper cracked surface when compared with the folia representative of each of the four additions to the core. Under magnification, folio 1 and folio 15 present the more homogeneous surface; folio 228 presents a cracked surface, but it is in folio 18v where the ink crack reaches a higher effect, with some losses of the writing ink over the parchment.

[15] Pasqualetti, C., Bensi, P., & Perriccioli, A. Il" Libellus ad faciendum colores" dell'Archivio di Stato dell'Aquila: origine, contesto e restituzione del" De arte illuminandi": studio introduttivo, facsimile, testo e traduzione a fronte. SISMEL edizioni del Galluzzo. (2011).

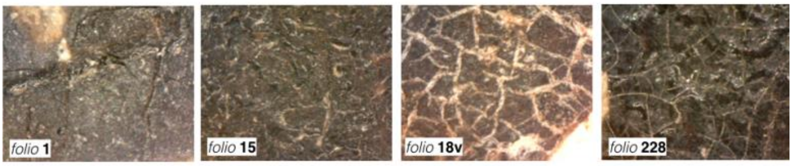

Fig. 22. Digital microscopy images of iron gall ink of BNP, Alc. 433.

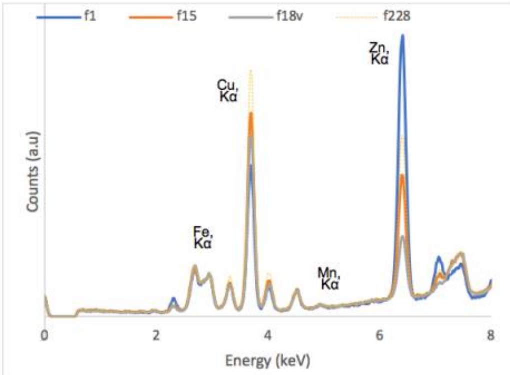

Fig. 23. h-EDXRF spectrum of iron gall inks from different folia of the codex BNP, Alc. 433.

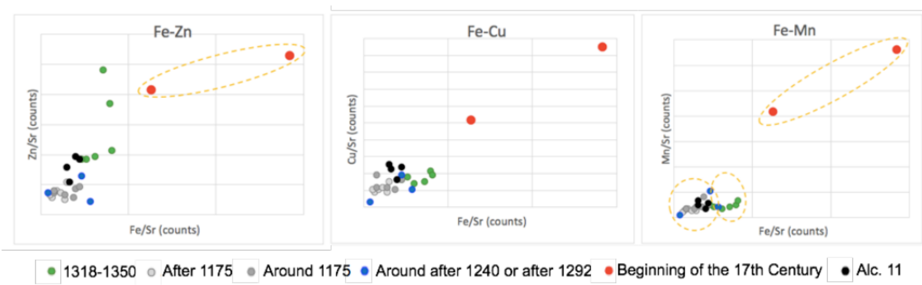

Fig. 24. EDXRF strontium normalised counts of Fe-Zn, Fe-Cu, and Fe-Mn of BNP, Alc. 433 and BNP, Alc. 11

h-EDXRF analysis of the writing inks present in folio1, folio 15, folio 18v and folio 228 revealed a similar chemical elemental composition, with Cu, Zn, Fe and Mn present in all paint's formulations, although in different composition ratios (Fig. 23). The use of iron sulphates ($FeSO_4$) for producing iron-gall inks was commonly linked to the presence of other metal ions, such as copper (Cu), zinc (Zn) and manganese (Mn) - all present in the mineral vitriol used as an iron-sulphate source to produce these inks. As a mineral, it is expected that different origins of vitriol present different chemical compositions (reflected in different EDXRF Fe: Cu: Zn: Mn counts-ratios), which means iron gall inks produced in different periods are expected to present different elemental compositions.[16]

In this sense, to evaluate the use of different iron-gall ink compositions along Alc. 433 and its link to each period of production of the manuscript already proposed according to the liturgical studies, a strontium61 normalised Fe:Zn, Fe:Mn, and Fe:Cu EDXRF counts-ratios of the writing inks present in the selected folia was analysed (Fig. 24).

The analysis of the EDXRF strontium normalised Fe-Zn counts-ratios evidenced three main clusters corresponding to the three periods of liturgical additions: one cluster corresponding to the folia linked to the around/after 1175 and after 1292 (Fig. 24, light-dark grey circles), on which iron (Fe) and zinc (Zn) are present in lower concentrations; a cluster more enriched in zinc (Zn) present in folia linked to the 1318-1350 period (Fig. 24, green circles); and a third cluster more enriched in zinc (Zn) and iron (Fe), present in folia linked to the beginning of the 17th century (Fig. 24, red circles). Interesting to notice from these results was an increment along time of the iron-zinc content to produce the iron-gall inks used in the written texts, suggesting the use of different metallic-sulphate sources (three different vitriol sources) along time in this scriptorium. As for the strontium normalised Fe-Cu and FeMn counts-ratios, two clusters are observed: one corresponding to the results of the earliest period of production (Fig. 24, light-dark grey and green circles), and a second corresponding to the latest period of production – the beginning of 17th century (Fig. 24, red circles). Even though the counts-ratio was only clustered into two groups, the production periods interpreted from these data still complimented the result of the liturgical studies and supports the use of different vitriol sources for producing the writing inks.

To evaluate the similarity of the writing inks compositions at the beginning of the activity of the Alcobaça scriptorium, a comparison between the strontium normalised Fe:Zn, Fe:Mn and Fe:Cu EDXRF counts-ratios of the writing inks of Alc. 433 and of Alc. 11[17] (also one of the oldest manuscripts produced in Alcobaça, around 1175, that has reached our days)[18] was performed (Fig. 24, black circles). Moreover, alongside with the Psalter-hymnal, Alc. 11 contextual and palaeographic studies are the primitive product of Alcobaça. In this sense, this comparison with Alc. 433 strengthens the liturgical results and the writing-inks results, which date to the first corpus of Alc. 433 back to the beginning of Alcobaça's scriptorium activity, as the

[16] Tibúrcio, Catarina, Valadas, Sara, A. Cardoso, Candeias, António, Barreira, Catarina Fernandes and Miguel, Catarina. "On the use of EDXRF and UV–Vis FORS to unveil the production of two illuminated manuscripts from the fifteenth century portuguese royal court." *Microchemical Journal* 153 (2020): 104455.

[17] About this codex, see: Arrojado, Samuel. "Contribuições para a caracterização do scriptorium de Alcobaça: estudo e preservação de um códice litúrgico medieval (BNP Alc. 11)." MA thesis, NOVA University of Lisbon, 2020; Casanova, Conceição, Samuel Arrojado, Catarina Fernandes Barreira, Catarina Miguel, Teresa Quilhó and Ana Tourais. "Narrating the Codex History: The Case Study of the Psalter-Hymnal from the Alcobaça Monastery, Portugal," *Journal of Medieval Iberian Studies* 14:1 Special Issue: Connecting the Dots (2022): 127-141.

[18] Barreira, Catarina Fernandes. "Abordagem histórico-artística a dois manuscritos litúrgicos do scriptorium do Mosteiro de Alcobaça do último quartel do século XII ou o início de "huma livraria copiosa"." *Revista de História da Sociedade e da Cultura* 17 (2017): 33-62.

EDXRF strontium normalised counts-ration of Alc. 11 ink clustered into the cluster of Alc. 433 earliest analysed set (Fig. 24).

Conclusion and Summary

The present work is a profound testimony of the importance of a multidisciplinary research team and how fruitful a research project might become if an illuminated manuscript is examined simultaneously by different perspectives and methodologies, such as liturgical studies and material characterisation.

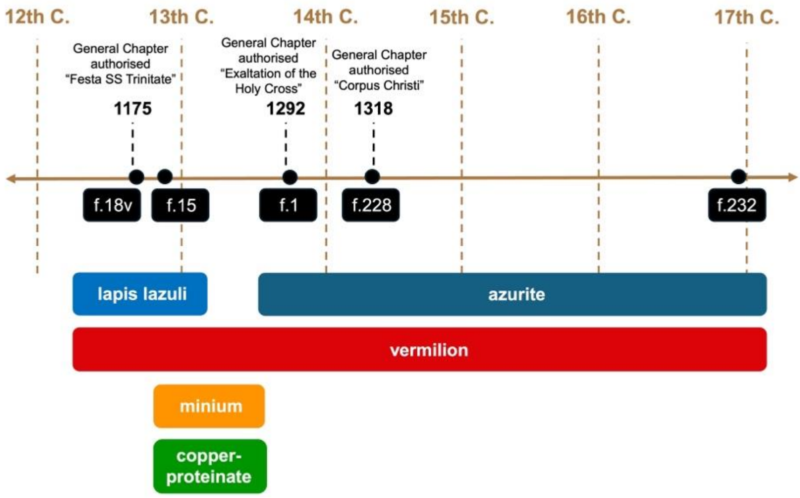

Fig. 25. Timeline of the BNP, Alc. 433 and the pigments used in its production, according to the results presented in this paper.

The Alc. 433 history (and story) is undoubtedly extraordinary, as it incorporates the fingerprint of its use throughout almost five centuries of the life of the Alcobaça scriptorium. The manuscript starts, in its primitive core, by *The Temporale*, which begins in folio 18v, with a beautiful, illuminated capital letter painted with vermilion red and turmeric yellow lake pigment, and completed by an *incipit* written using lapis lazuli blue. A subsequent feast was added: the *SS Trinitate* (folio 15 et seq.), with the initials painted by deep-green copper-based paints decorated with orangish minium. The feast of *Corona Domini* was then added at the end of the 13th century, more precisely after 1292, marked by folio 228, where vermillion was still used to paint the initial letter. In the next addition - after 1318, the feast of *Corpus Christi* material analysis of the blue paints allowed to identify that lapis lazuli was replaced by azurite. Finally, with the evidence of bookbinding, and no illumination exists in the last chapter addition started by folio 232, the Alc. 433 finished its "production" at the beginning of the 17th century. In conclusion, the result of the colour materials' characterisation, alongside the results from the liturgy studies, is clearly in Fig. 25 as the pigment timeline of Alc. 433, expresses well why "Medieval illuminated manuscripts are among the best testimonies of the life of medieval scriptoria" and why the Alc. 433 is one of the best testimonies of the life of the Portuguese scriptorium of Alcobaça.

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