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Illuminated manuscript analysis methodology using MA-XRF and NMF: Application on the Liber Feudorum Maior

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ABSTRACT

The determination of the composition of illuminated manuscripts' components is an important tool for the better understanding of their history, their origin and the procedures carried out for their elaboration, providing an insight into techniques and materials used in the times of their fabrication. By focusing on all three important aspects of an illuminated manuscript, which are their content, their decorative style and the composition of the materials used (CSM approach) a more complete vision of the manuscripts can be obtained, as the results of each field's studies complement each other. This article presents a methodology that combines the information obtained from single point measurements, Macro X-ray Fluorescence (MA-XRF) and Non-Negative Matrix Factorisation, evaluating the advantages and drawbacks each method presents, with an emphasis on the detection of minor signals and minor components and the interpretation of their contribution in the understanding the object and the artistic process carried out for its creation. The importance of adjusting the methodology according to each case's requirements is also indicated. The methodology has been applied to a late 12th century Catalan cartulary, the *Liber Feudorum Maior*, an exceptional non-religious cartulary, elaborated along more than one century, and which contains 76 miniatures painted in two different decorative styles. The information obtained from the different measurements has made it possible to establish not only a large part of the palettes used for the two painting styles but also determine small differences in the composition of the inks used to write the cartulary's text. Through this compositional study it has been possible to gain insight into the techniques used for the manuscript's elaboration, which could be indicative of the participation of multiple artisans.

1. Introduction

Medieval manuscripts are amongst the best historical sources available that describe life in the Middle Ages. Furthermore, many of them are richly decorated, meaning that they also consist in valuable works of art. The information these manuscripts offer can be organized into three categories: 1) the content of the text and the illustrations that accompany it, 2) the style the miniatures are designed in and 3) the materials and procedures used and followed to create the manuscript. These three sources of knowledge offer complementary information regarding the manuscript, the society it was created in, its authors and the techniques that were used for its elaboration. An approach focused on content, style and materials (CSM approach) is necessary, as even though the text and illustrations provide direct information on the historical events, religious beliefs and artistic tendencies of the period, information can also be extracted implicitly through the manuscript's composition, which is often the least studied field of the three. Analysis of the composition can be a source of valuable information on the manuscript's history, as it is embedded unconsciously in the object. Furthermore, the material study helps to shine some light on the accepted values and culture of the society and the availability of materials to different artists or regions.

The *Liber Feudorum Maior* (*LFM*) is an illuminated cartulary elaborated between the end of the 12th century and the beginning of the 13th and the documents it includes were compiled by Ramón de Caldes, the dean of the Barcelona Cathedral, by order of King Alfonso II of Aragon (1162 – 1196).

It is an exceptional manuscript, as it is one of the first lay cartularies made in a period predominated by cartularies created for ecclesiastical institutions, while, furthermore, being widely illuminated [1]. The documents in the cartulary include agreements, land sales, donations, oaths and betrothals and the illustrations accompanying the text depict such scenes. The majority of these scenes represent homage or vassalage

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acts, depicting the vassal kneeling in front of their lord [2]. The manuscript is in a relatively good conservation state.

One of the most interesting characteristics of the *LFM* is that these miniatures are painted in two distinct decorative styles, belonging to two different periods (Fig. 1). The differences between the two styles can be attributed to the stylistic and ideological evolution that occurred in Catalonia in the 12th century's final years, which represent the transition from Romanesque to Gothic. There is no additional information regarding their material characteristics, the order of the creation procedures or the number of artists and copyists involved in the centuries-long development of the cartulary. Instead, the dating of the manuscript has been made possible thanks to the dating of the text through the identification of one of the copyists, Ramón de Sitges, who had not begun working in the Royal Chancellery until 1179 [3]. Regarding the nomenclature of the miniature styles, even though the illustrations cannot be directly assigned to the two different stylistic categories, hereon, for simplicity reasons, they shall be referenced to as Romanesque and Gothic, respectively corresponding to Styles A (archaic) and B (proto-Gothic or Year 1200 Style) mentioned in the literature [4,5], as can be seen in Fig. 1.

The *LFM* has been subject to multiple studies throughout the years, each one focusing on different aspects of the manuscript. Issues investigated in several published works are the dating of the two decorative styles of the miniatures from an art history perspective [2,4–6]; the significance of the blank pages and the analysis of the manuscript's content from a historical point of view [1]; and an attempt to identify scribes and pin their work down to a certain time period, though paleographic analyses [3]. Nevertheless, the manuscript's composition has never been analysed, meaning that certain questions remain unanswered and the choice of adequate conservation conditions and restoration treatments becomes more difficult.

Information that would allow the better understanding of the *LFM* can be obtained through the analysis of the miniatures and the text. The composition of the pigments used to decorate the cartulary can be determined through the identification of the major and minor elements that they are made of.

For the better conservation of the LFM, as well as many other similar cartularies, it is recommended to use non-destructive analytical techniques and portable instruments that can perform the analysis *in* situ, so as to avoid any kind of physical deterioration [7]. An analytical technique that complies with these requirements is X-ray Fluorescence (XRF), which provides information on the elemental composition of the sample. Due to the penetrative properties of X-rays, XRF allows the gathering of information from the layers located underneath the illustrations' surfaces, giving a deeper insight into their structural characteristics and the techniques used to achieve them, in comparison to other surface techniques [7].

Nonetheless, like all analytical techniques, XRF also presents some disadvantages and certain difficulties. The technique's incapacity to detect light elements, such as carbon or oxygen, means that organic materials cannot be identified. In the case of illuminated manuscripts, such materials include the parchment or colourants of vegetal or animal origin. It must be highlighted that even if light elements were detectable, it would be impossible to characterise the organic compounds present based only on their elemental composition. The procedures based on single-point analyses and the acquisition of high-quality spectra can also be time-consuming and not always representative of the whole illustration. Furthermore, minor signals originating from lighter elements must be studied carefully, as they may correspond to the main element of the pigment, whose identification is vital for the correct

Fig. 1. Representative miniatures of the two decorative styles found in the *LFM*. Miniatures (a) from folio 83v and (b) from folio 19r belong to the Romanesque style. Miniatures (c) from folio 82v and (d) from folio 41r are painted in the Gothic style and (e) 109r is painted with elements from both styles.

identification. Weight must also be given to minor elements, as they can provide further knowledge on the nature of the pigments or the composition of mixtures. Moreover, changes in signal intensity can help with understanding the structural distribution, when multiple materials have been used, and reveal information on procedures and techniques used by manuscript illuminators. Equivalent information regarding the text found in the manuscript can also be gathered through the determination of the ink composition.

A step forward is the Macro X-ray Fluorescence (MA-XRF) mode that yields elemental distribution maps and guarantees a higher representation degree of the illustration's composition. This makes interpretation easier by allowing direct correlation between composition and colour zones and can reveal information not easily identifiable through simple comparison of single-point spectra [8–15].

Taking into account the high amount of data provided by the MA-XRF maps and the high amount of information included in them, the procedure followed for its extraction is of paramount importance. This procedure can be carried out using the different programmes associated with the commercial instruments, but a complement to these, which are of particular interest in order to obtain information about the minor signals, would be the use of specialized data treatment programmes, which further allow the application of multivariate techniques. Techniques such as Principal Components Analysis (PCA) [16–18], Multivariate Curve Resolution – Alternating Least Square (MCR-ALS) [19,20] or Non-Negative Matrix Factorisation (NMF) [21] have sometimes been applied in the field of artwork analysis, proving their capabilities of providing a better understanding of the MA-XRF data, through the reduction of their dimension by foregrounding the most relevant aspects of the maps.

The aim of this work is the establishment of an analytical methodology for the determination of the composition of the pigments and inks used in medieval manuscripts, as well as the study of the structural distribution of the materials used, when possible, by paying special attention to the information provided by the minor signals.

The effectiveness of the methodology will be tested by applying it on the analysis of the *Liber Feudorum Maior*, in order to establish the composition of the pigments and inks found within it, thus deepening the existing knowledge on the cartulary's history.

2. Materials and methods

2.1. Sample

The *LFM*, conserved at the General Archive of the Crown of Aragon in Barcelona, has suffered many changes throughout its existence. Historical descriptions of the *LFM* mention that it was made up of two volumes, the first one consisting of 499 numbered pages and the second one of 405 numbered pages [4,5]. Currently only 120 folios are conserved, of which 89 (59 from the first volume and 30 from the second) were rebound in 1807 [4]. Some pages without text were used as covers of other books conserved at the Archive and twenty-seven of them were discovered in 1944 [22], while four more were discovered in 2014 [23]. The size of the folios is thought to have been manipulated over the years as well, with them being cropped [4], leading to a reduction of the dimensions.

The *LFM* contains 76 miniatures, of which 23 are painted in the Romanesque style and 51 are painted in the Gothic style. Two miniatures in the manuscript are decorated with characteristics of both styles, where gothic elements were added onto unfinished Romanesque miniatures. Of the 51 gothic miniatures, several are unfinished: in some only the golden or silver leaves have been placed, while others are further developed and also include painted areas.

Due to the large number of miniatures found in the manuscript, elaborated using different pigments and presenting multiple structural characteristics, a thorough study of the cartulary implicates the selection and analysis of a representative number of miniatures. This selection includes 4 Romanesque, 10 Gothic and 1 mixed miniatures, with the analysis focusing on selected areas of these miniatures. These zones were chosen so as to represent the palette used for the decoration of the whole manuscript and were large enough in order to recognize the design and motifs of the miniatures. The analysis of 8 decorated capital letters, of which one is illuminated provided further information on the pigments used.

Regarding the compositional study of the inks used in the cartulary, 17 black letters and 4 red ones were analysed. The letters chosen represent groups of text with different aspects, which were determined from certain changes found between these groups, such as the calligraphy style or the colour of the ink.

2.2. X-ray Fluorescence

The XRF measurements were carried out using a portable commercial XRF spectrometer (Elio, XGLAB Srl), equipped with a Rh anode X-ray tube, a 12.5 μm thick Be window and a 25 mm^2 active area Silicon Drift Detector with an energy resolution of 135 eV at the Mn Kα line. The analysis range of the instrument lies between 1 and 40 keV, which allows the analysis of elements from Si to U.

A 2 cm thick methacrylate plate was placed under the folios analysed for all measurements in order to block emissions and interferences from lower folios. Furthermore, the areas analysed were chosen carefully and after having checked the reverse side of the folio, in an attempt to avoid spots where the back side was painted and thus limit interferences.

2.2.1. Single-point analyses

The measuring conditions for the point analyses were maintained at 50 kV, 80 μA and an analysis time ranging between 20 and 120 s, with 40 s being the measuring interval mostly applied. One replicate was obtained for each analysis. The sample was always kept at a distance of 1.4 cm from the detector [24].

2.2.2. MA-XRF

For the MA-XRF analyses the measuring head of the same equipment was fixed onto an XY motorized stage. The scanning process is performed automatically through consecutive 1-second point analyses of 1 mm^2 areas, every 1 mm. The result of this procedure is an elemental analysis map and a single XRF spectrum which includes the data found in each one of the points analysed. The 1-second point analysis spectra can also be accessed. The generated map uses a chromatic scale to represent element intensity in each pixel of the map.

The analyses consist of the creation of visual maps that express the elemental distribution of a specific area as a result of the sequential recording of XRF spectra

2.3. Data treatment

The datasets acquired via the XRF scans are treated with the open source PyMCA software (Software Group of the European Synchrotron Radiation Facility (ESRF)) [25], using the "Fast XRF Stack Fitting" and "PyMca NNMA" tools. The first one allows the generation of deconvoluted maps of certain specified elements, whereas the second one allows the treatment of the acquired data via non negative matrix approximation techniques.

The technique used in this article is NMF, which allows the approximation of a matrix, such as the XRF data matrix, into two new non-negative matrices. The non-negativity of the technique has the advantage of producing results that respect non-negative physical quantities [26], such as peak intensity, thus facilitating the comprehension of the generated spectra.

However, NMF also presents a drawback, which is its non-reproducibility. Due to the fact that the two newly generated matrices are initialized with random non-negative values, NMF decomposition is not unique and the final result of each iteration is slightly different. The randomness of NMF caused by the lack of normalisation or regularisation methods [27] can be corrected by changing certain parameters, which however are not included in PyMca and for which reason multiple iterations of the technique must be carried out.

3. Results and discussion

3.1. Methodology development

The establishment of a reliable analytical procedure included the evaluation of four methods: single-point measurements, ROI imaging, deconvoluted maps and NMF analysis. They are proposed as successive steps that can help deepen knowledge of miniatures' material composition, with a special emphasis on minor signal contributions.

The first method evaluated are the single point measurements, which consist in the most basic form of XRF data. The spectra retrieved were found to be reliable and an accurate representation of the spots analysed, thus providing a good first understanding of the materials present and allowing the identification of most of the major elements found in the manuscript. However, some drawbacks were observed as can be appreciated in Fig. 2. Minor Hg signals were visible in some blue pigment and ink spectra, including the ones presented in the figure. Their absence in other analysed areas and their strong presence in some parchment spectra suggest that they could come from the cinnabar used on the reverse side of the parchment. Contrary to the parchment spectrum, where the error is relatively obvious due to the low probability of having such a strong mercury signal originating from the parchment, the weak mercury signals found in the other two areas could easily be mistaken as important when determining material composition if just one measurement was performed. Another problem related to the identification of blue areas was that no strong element signals were observed. The Si, S and K signals could indicate the use of ultramarine, but the two latter elements are also present in the parchment. Even though these elements display a strong signal in the blue pigment spectrum, the comparison with the also strong signals detected in the parchment and ink areas make it difficult to single it out as an identification agent. In order to be confident that the elevated signal intensity is indeed related to the presence of the pigment, multiple measurements of both blue and non-blue areas would be necessary.

Therefore, an important drawback related to these measurements appears to be that some minor elements, some minor signals or some small changes in signal intensity may be ignored, thus overlooking relevant information. Single point spectra can be directly compared in order to avoid such occurrences, but this is a time-consuming process, and often it is necessary to recur to chemometric techniques. If no attenuating precautions have been taken, errors may also occur from misinterpreting signals belonging to the other side of the parchment, or underlying folios.

A step forward from single point spectra are elemental distribution maps. These maps display the varying intensity of elements in the different parts of an analysed area and can help overcome some of the aforementioned issues. In this work, b maps generated through Region of Interest (ROI) imaging software and deconvoluted maps were evaluated.

ROI imaging, which consists in the selection of certain regions of the spectrum corresponding to different elements, shows the distribution of these elements in the map and can be carried out using the software that accompany modern commercial XRF equipment (in this case Elio Software, XGLab Srl). These types of software allow the visualization of elemental maps and also a preliminary analysis of the general spectrum that corresponds to the whole analysed area. ROI imaging offers the advantage of being able to check element distribution in the same interface in which the analysis is being carried out, proving to be a useful tool for on-the-spot analysis, which may be necessary when there are time limitations associated with "in situ" or routine studies.

With ROI imaging, issues such as the identification of pigments with weak signals or the confusion generated by signals emitted from the parchment or the reverse side of the folio are solved, as the small differences in intensities between neighbouring measurements are easily detectable. However, a new problem arises regarding the overlapping of peaks, which can be understood by studying the maps corresponding to five regions of an analysed area's general spectrum, presented in the top row of Fig. 3. In some cases, such as the Hg Lα map, the determination of the element is easy, due to the lack of other peaks in the specific spectral area. However, in other cases, such as the broad peak found in the 2.05 – 2.50 keV region, which includes the Hg Mα, S Kα and Pb Mα peaks, or the peak found in the 10.45 – 10.70 keV region which coincides for the Pb Lα and As Kα emissions, determination of the element present can be difficult, or impossible. For example, the study of the 2.20 – 2.30 and 10.45 – 10.70 keV maps could indicate that the yellow-beige area of the

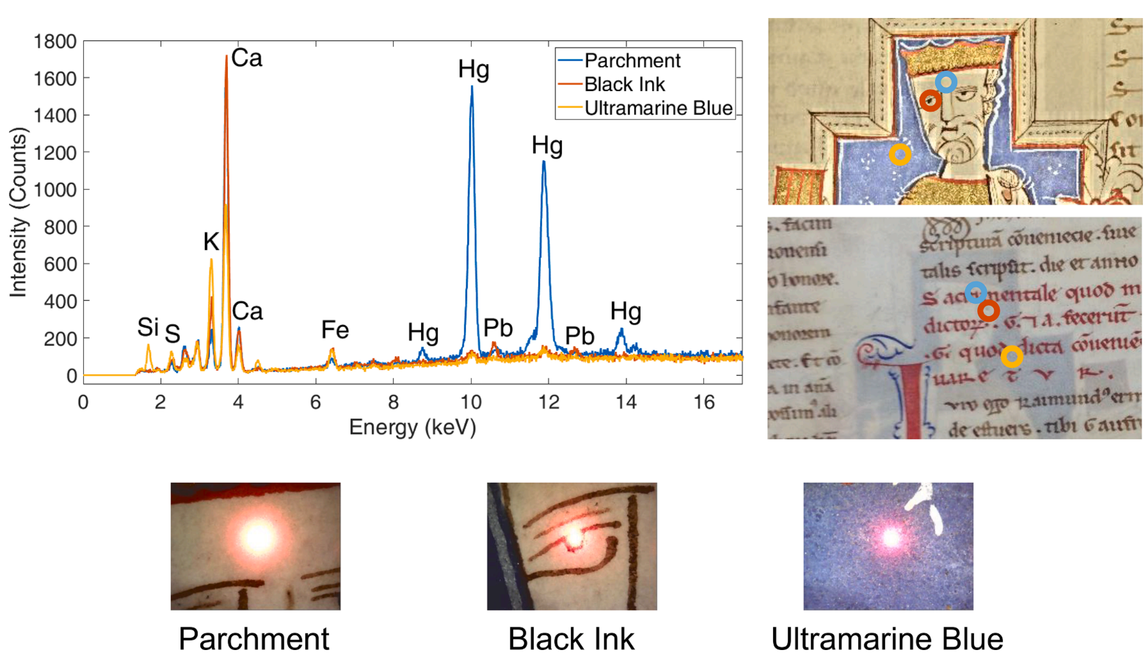

Fig. 2. Single point measurements on a Romanesque miniature on folio 74v.

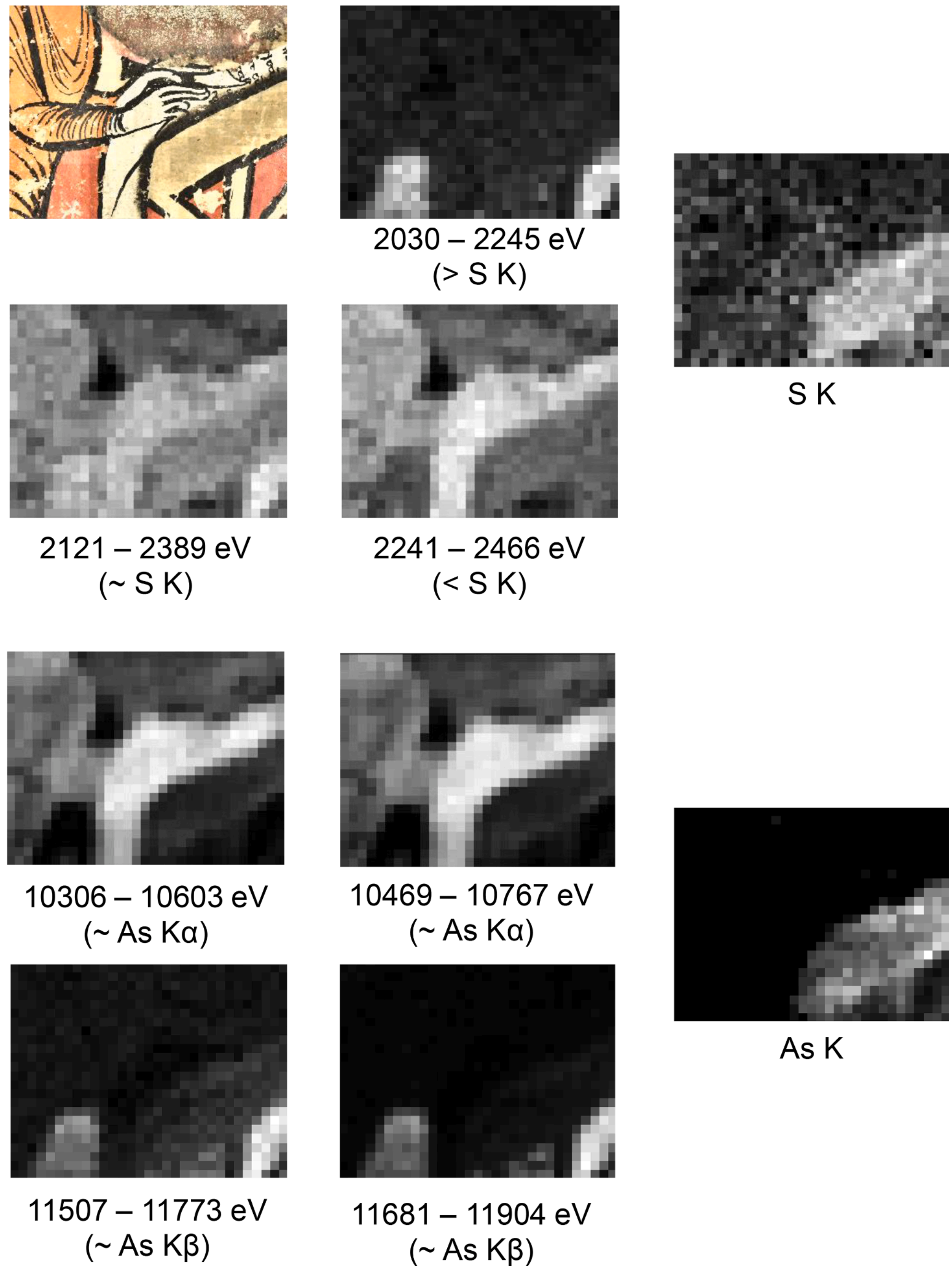

Fig. 3. Comparison of ROI (top) and deconvoluted (bottom) maps of the S, As, Hg and Pb peaks for an analysed area of the Gothic miniature on folio 1r. The regions selected for the ROI imaging correspond to energy areas surrounding the expected peaks.

analysed region, corresponding to the scribe's desk shows a slight S and As presence. However, the fact that Pb peaks appear inside of or close to both areas, it is impossible to know if the signal is correlated solely to this element.

As can be deduced from the example, a major disadvantage of this tactic is the lack of peak deconvolution. The regions selected may include more than one element and elements with minor signals can be missed due to the stronger signals of neighbouring element peaks. This problem can sometimes be avoided with the realisation of multiple single point analyses. Often the overlapping peaks are only present in the general spectrum of the whole map, since the elements responsible for them are found in different areas of the zone analysed. However, once again, the process of comparing the single point spectra with the general one can be time-consuming and requires experience.

Data treatment software, such as PyMCA, prove to be a useful and easy-to-use alternative. With integrated tools, such as Fast XRF Stack Fitting it is possible to quickly generate deconvoluted maps of selected elements, in order to provide well defined information and reveal the distribution of elements whose peaks were overlapped by other neighbouring ones and could not be identified with ROI imaging, thus providing a more in-depth perception of the materials used. The knowledge necessary prior to the application of this tool mainly regards the composition of pigments commonly used during the time period the analysed object belongs to, as not including certain elements in the analysis could be detrimental to the quality of the results. Hence, it is advisable to use this tool after having conducted, at the very least, a preliminary analysis of the general spectrum and having thoroughly researched on the history of the pigment's use. A configuration file can be saved and applied to multiple maps, but it is important to deal with each case in an independent way as miniatures even from the same era may have been elaborated with different materials or been restored with posterior in time pigments.

The advantage deconvoluted maps offer over ROI imaging ones can be appreciated in Fig. 3 (bottom row). In the case of deconvoluted maps, the spatial distribution of the four elements can be seen clearly and they are all free of interventions from nearby elements. The presence of As and S in the yellow-beige area is now clear, indicating that it is orpiment or realgar.

In both map types, it was found that the chromatic scales allow the identification of even minimal changes between intensities from one spot to another, which could indicate compositional differences. Elements that in a single spectrum might have seemed irrelevant gain importance if they are detected in an extended area, especially when this area clearly corresponds to a well-defined colour zone.

Finally, it must be noted that although the contribution of two elements in one area can often be deduced manually, as in the case of As and S, there are cases where this can also be achieved automatically through multivariate techniques. These techniques help in the reduction and reorganization of large data volumes into components that correspond to the most important and relevant information and can reveal correlations between elements. PyMCA provides several of these techniques, including PCA and NMF, which were assessed in this work. The results PCA offers cannot always be interpreted easily, due to the negative weight that is given to some variables and the fact that many principal components correspond to noise.

An example of an NMF application can be seen in Fig. 4. Component 1 shows the areas where Pb is present in the miniature, while Component 3 shows the association between As and S, with more weight being given to the As K peak. A similar zone is marked in Component 9, which however gives more weight to the S K peak. Component 4 indicates the zones with a high Hg content, whereas although Component 8 also gives importance to Hg, weight is also given to Ca, meaning that areas with a higher Ca/Hg ratio are highlighted. These include the areas where the red pigment has become detached from the surface and the bare parchment is visible. However, areas where no red pigment can be seen are also marked. Finally, Component 10 shows the correlation between Ag and Pb. There seems to be a red preparation layer under the silver leaf containing lead. Components 2, 6, 7 and 8 have been omitted from the figure as they do not provide relevant information.

It can be deduced therefore that NMF can provide reliable results, has the capacity to differentiate zones with unique compositions and thus helps deepen the knowledge available. Even though multiple iterations of NMF can provide slightly different results and not all components provide useful information, many of them reveal interesting data correlating elements.

As is clear from the above, a number of methods to analyse XRF maps is available, each one with its own advantages and disadvantages, which provide different levels of information depending on the needs and experience of the researcher. The complementary nature of these methods indicates the importance of having access to a wide range of tools and knowing how to combine them when analysing such data.

It must be highlighted that every case must be treated as unique and the tools used must be adapted to the necessities of the case. It is however advisable to follow a structured procedure when analysing a manuscript, which should include the following steps:

1. A preliminary analysis based on single point measurements, in order to determine the artwork's major components and formulate hypotheses regarding potentially used pigments and materials. This step ensures the existence of well-defined spectra, which may be needed to complement information deriving from MA-XRF analyses.
2. A brief review of the artwork's history, including a bibliographical research into pigments and techniques used in the time period of the work's elaboration.
3. The MA-XRF analysis, focusing on representative zones of the miniatures regarding their composition and the procedures followed to create them. A preliminary ROI imaging analysis of the accumulative spectrum can ensure that all elements appearing in these zones are included when selecting the elemental maps to be generated. This

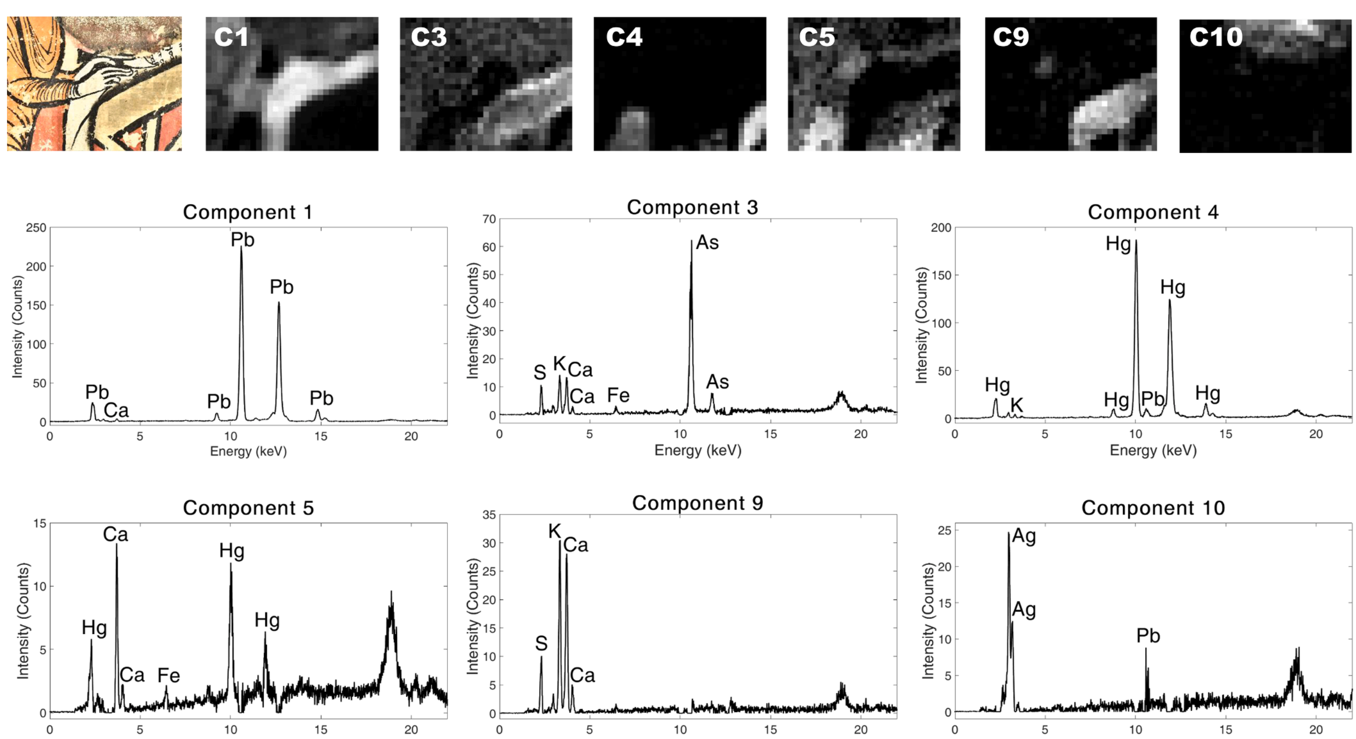

Fig. 4. NMF maps and corresponding spectra for the same analysed area of the Gothic miniature on folio 1r (as in Fig. 3).

step is followed by the deconvolution of the maps obtained and their analysis in order to establish the pigments present.

4. Application of multivariate techniques, such as NMF, in order to establish correlations between different elements. This step helps evaluate previously made hypotheses, highlights the importance of relations between certain elements and more importantly offers knowledge on the composition of specific areas, which do not necessarily consist of a sole pigment, thus revealing important information on artistic techniques, such as material mixing.

Nevertheless, it must also be noted that there are some cases that cannot be solved using any of the aforementioned procedures, and which require additional data processing or compositional contribution by complementary techniques.

3.2. Determination of the composition of Romanesque and Gothic miniatures

The proposed/established combined methodology of single point analyses, deconvoluted maps and NMF maps is applied to determine the composition and the structure, where possible, for the two styles of miniatures found in the LFM.

3.2.1. Parchment

An essential step before the determination of the colour palettes used to decorate the manuscript is the identification of the elements whose presence is attributed to the writing support, the parchment. Knowing which these elements are allows for a better understanding of the spectra corresponding to painted areas. Many times, pigments whose composition consists of light elements do not have the capacity to attenuate signals originating from the parchment, meaning that they can also be detected in the spectrum, possibly causing confusion.

Elemental distribution maps can contribute positively to the determination of the parchment's composition. Although it is easy to achieve a clear single point analysis of parchment, it can sometimes be challenging to determine which elements are relevant and which not. The constant presence of certain elements in all revealed parchment areas can eliminate doubts. The elements present in the parchments used for the folios analysed are Ca, K and Cl, as can be seen in both Figs. 2 and 5. Single point spectra also detected Fe, but as can be seen in the corresponding map, its presence is not associated with the parchment areas. Due to the fact that parchments are organic materials, the identified elements are indications of the procedures and tools used for their elaboration [28]. Calcium most probably comes from the lime baths the animal skins were put in to facilitate hair removal [7] or the chalk used by some illustrators and scribes to whiten the parchment before painting or writing on it [28,29]. Potassium or sodium chloride was used to dry the skin after hair elimination, but also pH was adjusted using ammonium chloride or sulphate, which could explain the presence of K and Cl [30,31]. Regarding iron, its detection could be attributed to the tools used to elaborate the parchment, such as the knife used to eliminate the hair [28], or the migration of iron gall inks used for the text [32,33]. The fact that all these elements are related not to the parchment's composition, but to the processes used for its fabrication explains the spatial heterogeneity of their distribution.

3.2.2. Romanesque miniatures

The determination of the colour palette used in Romanesque miniatures has been achieved using the procedure described: the combined study of single point spectra, deconvoluted maps (Fig. 5) and the application of NMF.

Certain materials or pigments can be identified more easily than others, such as white lead, which is identifiable by the presence of the double Pb peak and is used for all the white details found in the illustrations, or the golden leaves used for the elaboration of the golden areas. Another relatively easily identified pigment is cinnabar. The presence of Hg in the areas that correspond to the red details of the illustrations, accompanied by the detection of S in the same areas indicates the use of the pigment cinnabar (HgS). Mercury signals originating from the text on the reverse side of the page can also be observed. Being able to visualise the text responsible for these signals helps avoid confusion regarding the composition of other pigments. The comparison of the Hg-L and Hg-M maps is also of interest, as the second one does not allow the visualisation of the text signals, due to the lower

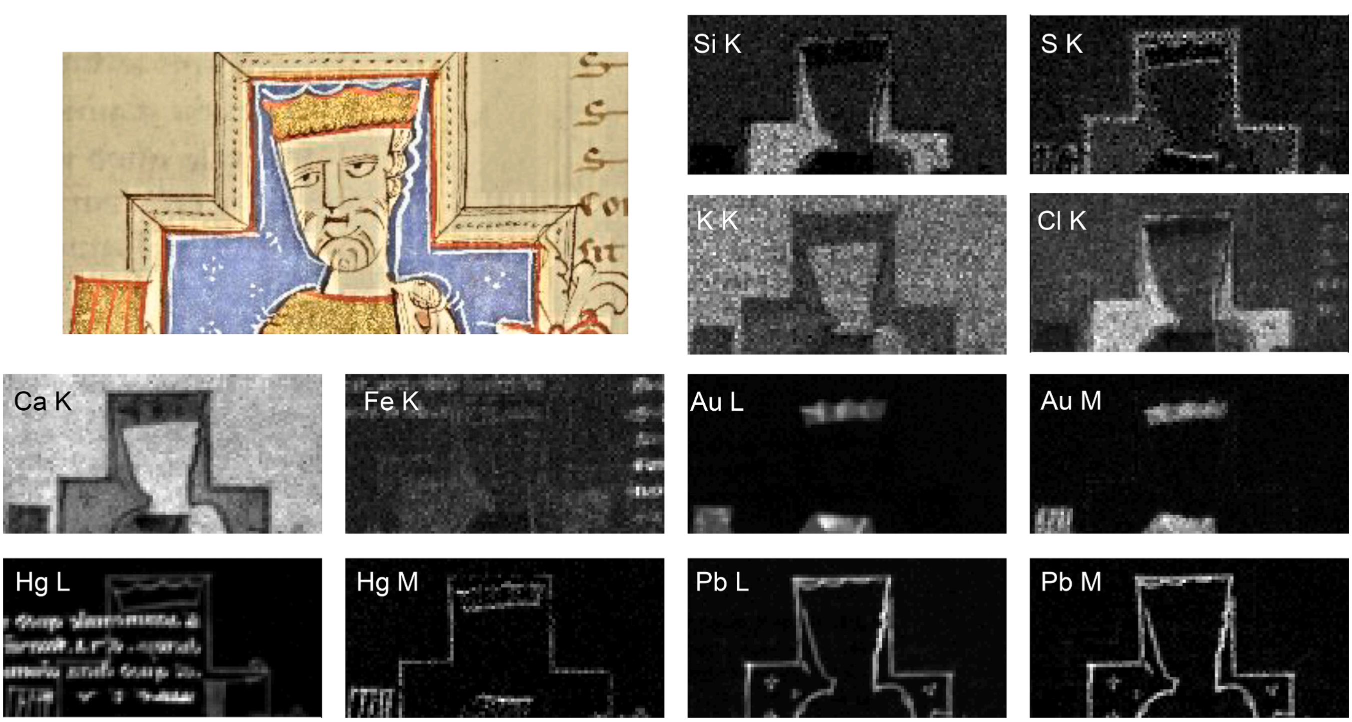

Fig. 5. Deconvoluted maps of the elements detected in the Romanesque miniature found on folio 74v.

intensity of the Hg-M peak, which is attenuated by the parchment. The comparison of peaks of different intensities of the same element can often provide useful information regarding the stratigraphy of a painting, as peaks with a stronger intensity normally reveal the composition of its surface, whereas lower peaks tend to reveal information regarding inferior layers of paint and materials. These differences in peak intensity, however, could also be related to the amount of pigment used. For example, cinnabar seems to have also been used to achieve the pale red details found on the vassals' outfits. The Hg and S signals in this case are very weak, which indicates that the pigment was used very scarcely (Fig. 6).

Other pigments require the simultaneous presence of multiple elements in an area in order to be identified. Such is the case with ultramarine blue, which could only be confirmed through the identification of Si, K, Ca and Fe signals in all blue areas. The presence of Si is a strong first indication of the presence of ultramarine blue, which is reinforced by the weaker presence of S, another element found in the mineral's molecular structure ($Na_{8\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$). The Ca and Fe signals are probably caused by the calcite and pyrite impurities found in natural lapis lazuli. In the case of Ca, the signal could also originate from the parchment found under the layer of paint, seeing that it would not be heavily attenuated by the light elements that make up the blue pigment. The presence of K is also ambiguous as it is an element not found in the structure of lazurite. One interpretation of its presence could be that it could originate from hauyne, a mineral which it is associated to, as they both belong to the group of sodalites. This mineral is primarily found in lapis lazuli stones in Afghanistan, the principal source of ultramarine blue [9]. However, potassium could also originate from a purification process, such as the one suggested in Cennino Cennini's treatise, which includes the use of lye [34,35]. Although the treatise is posterior to the *LFM*'s elaboration, it is probable that the purification technique applied is the same.

On the other hand, there are some pigments that cannot be identified using only XRF and demand the use of complementary techniques. The yellow pigment used to paint some details in the miniatures does not emit any signals, a fact that would indicate that these areas have been painted with an organic colourant, frequently used in the Middle Ages to imitate gold. Another pigment that cannot be fully identified is the one used to paint the green details found in one of the Romanesque miniatures. Although Cu can be detected in those areas, the lack of further knowledge does not allow the exact identification of the pigment, due to the abundance of copper containing green pigments used in the Medieval Times.

Finally, the nature of the black pigment or ink used to design the outline and details of the miniatures is also interesting to identify. The pale brown hue of the pigment is reminiscent of the iron gall ink used to write the manuscript's text, but the signals emitted from it are unlike those emitted by the text ink. In fact, as can be seen in Fig. 7, the Fe-K signal originating from the ink found on the reverse side of the folio by far surpasses the one originating from the miniature outline on the analysed side, where only very few slightly more intense pixels can be determined. This is the case in all the Romanesque miniature maps available and only in one occasion can the iron corresponding to the miniature ink be identified more clearly, due to the nearly complete lack of other elements present in the area.

As a summary, the palette used for the Romanesque miniatures found in the LFM is quite limited and repeated in all miniatures, without many variations (Table 1). The palette is made up of lead white, cinnabar, ultramarine blue, an organic yellow colourant and golden leaves. The only chromatic change to this palette can be seen in the miniature found on folio 110r, in which several details have been painted with a green copper-based pigment. It is possible that these green details were added later in time by the gothic miniaturists, whose use of green is more extended.

3.2.3. *Gothic miniatures*

The proposed analytical procedure was also carried out on the Gothic illustrations. These miniatures are more complex than the Romanesque ones when it comes to content and style, a quality that is partially achieved through a wider colour range.

3.2.3.1. Repeated pigments. As expected, certain of the pigments used in the Gothic illustrations are pigments that had already been used for the elaboration of the Romanesque miniatures (Fig. 8). The detection of Si, S, K, Ca and Fe in the blue coloured regions indicate the use of ultramarine blue; cinnabar, identified via Hg and S signals, was used for the red areas, while the strong presence of Pb in all white areas meant that the pigment present was white lead. Other previously seen materials, such as golden leaves and the copper-based green pigment are also used in Gothic miniatures. However due to certain peculiarities regarding their composition, they are presented in more detail in comparison to the other repeated pigments.

3.2.3.2. Golden leaves. The study of the golden areas in the Gothic-styled illustrations is particularly interesting due to the compositional differences detected between the miniatures. In the case of miniature 1r (Fig. 9), apart from gold, which had also been detected in the Romanesque miniatures, lead can also be detected in the entire golden-covered area. The Pb-M map confirms that the lead is located under the golden layer, as the signal of this peak tends to be attenuated by overlying layers of heavy elements, such as gold. This attenuation can easily be appreciated by comparing the two Pb maps of the illustration. A visual study of these areas at a larger scale shows that in some more deteriorated zones, the golden leaves have become unstuck, revealing a red-coloured layer underneath them. Preparatory layers like this were used to achieve a better adhesion of the golden leaves to the parchment and allowed them to be burnished [10]. Coloured preparation layers were often chosen by medieval artists to give a warmer hue to gold. The lead-based layer found in this miniature could have been made with red lead or white lead mixed with a red pigment, such as bole, a material often used by medieval artists.

However, this is not the case with all Gothic miniatures, as there are some where instead of lead, calcium is detected in the areas decorated with gold. This calcium signal is unlikely to originate from the

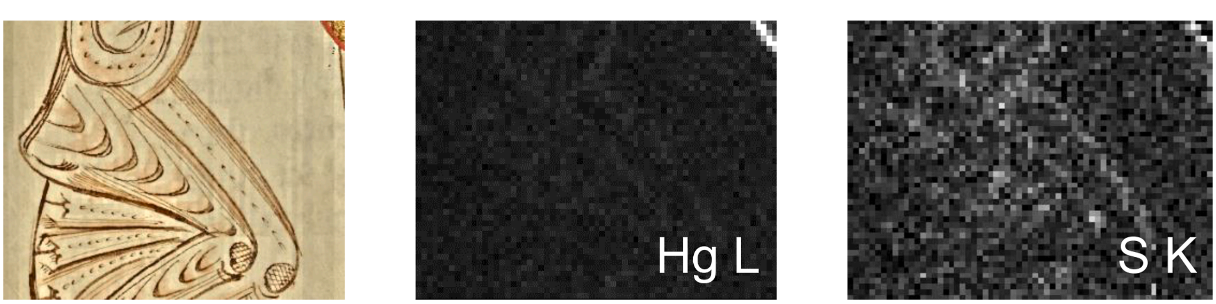

Fig. 6. Weak Hg and S signals related to small amounts of cinnabar found in the Romanesque miniature on folio 74v.

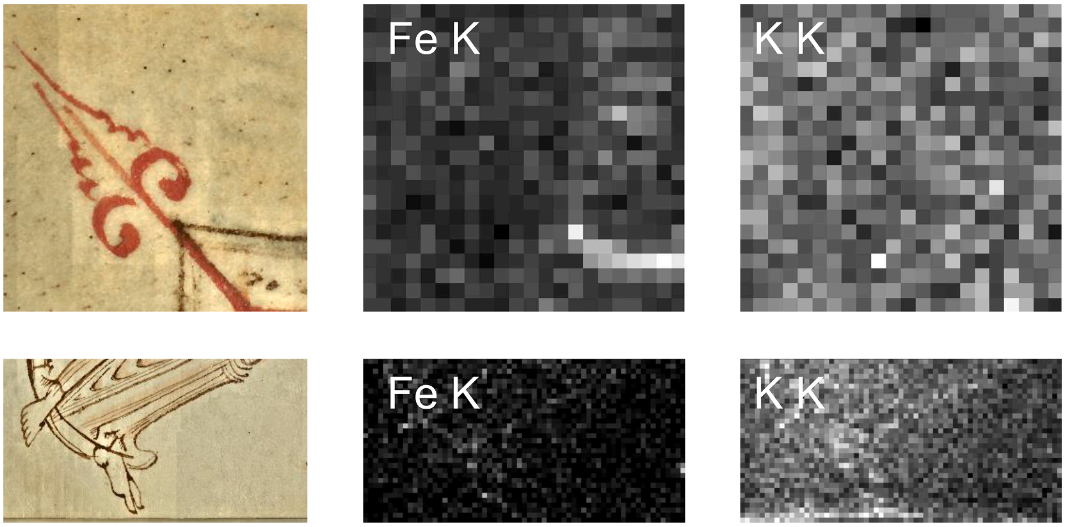

Fig. 7. Analysis of the black pigment used in Romanesque miniatures 114r (top) and 74v (bottom).

Table 1
Elements and materials detected in the Romanesque miniatures. (● Major signal ◍ Minor signal ○ No signal).

Colour	Si	S	Cl	K	Ca	Fe	Cu	As	Au	Hg	Pb	Pigment
Blue	●	◍	○	◍	◍	◍	○	○	○	○	○	Ultramarine Blue
Red	○	◍	○	○	○	○	○	○	○	●	○	Cinnabar
White	○	○	○	○	○	○	○	○	○	○	●	Lead White
Gold	○	○	○	○	○	○	○	○	●	○	○	Golden leaves
Green	○	○	○	○	○	○	●	○	○	○	○	Unidentified copper-based pigment
Black (Ink)	○	○	○	○	○	◍	○	○	○	○	○	Unidentified iron-based ink

parchment, as the study of Romanesque miniatures showed that parchment signals cannot be detected when covered with gold. Instead, this would indicate the use of a calcium rich material, such as lime, as a preparation layer or that the golden areas were covered with a calcium-based substance after being applied. However, similarly to before, the more deteriorated zones reveal a white layer under the golden leaves, which is most probably the origin of the calcium signal.

NMF consists in a useful tool for the differentiation of preparation layers, as it manages to correlate the signal coming from the golden leaves to those originating from the layers under them, producing components that correspond to exactly these areas. This fact is especially important as it indicates that NMF can provide useful structural information.

Gilding techniques in the Medieval Times could slightly vary according to each artist's experience or creativity, even though in general, there was a strong tendency to follow traditional practices [36]. The difference detected between the two types of preparation layer could be an indication that the Gothic miniatures have been elaborated by at least two different illustrators, each one following a different technique to accomplish the same goal.

3.2.3.3. Yellow pigments. Unlike the Romanesque miniatures, yellow has a more prominent role in the decoration of the Gothic illustrations, where it is used for clothing, backgrounds and architectural features, such as columns and arches. The extensive use of yellow in the illustrations, however, calls for a wider variety of hues, which is achieved through the use of multiple pigments and colourants.

The beige-yellow colour used for one of the vassals' clothing in Fig. 8 once again demonstrates the importance of choosing the correct analytical approach when identifying pigments. The maps generated through a preliminary but methodical ROI imaging study allow the observation of S and As, without, however, depicting their exact distribution, as signals from neighbouring elements also appear in the maps. Furthermore, a less exhaustive study, focusing only on clearly defined peaks, without analysing every part of broader peaks would have caused them to be ignored. Arsenic detection can be especially

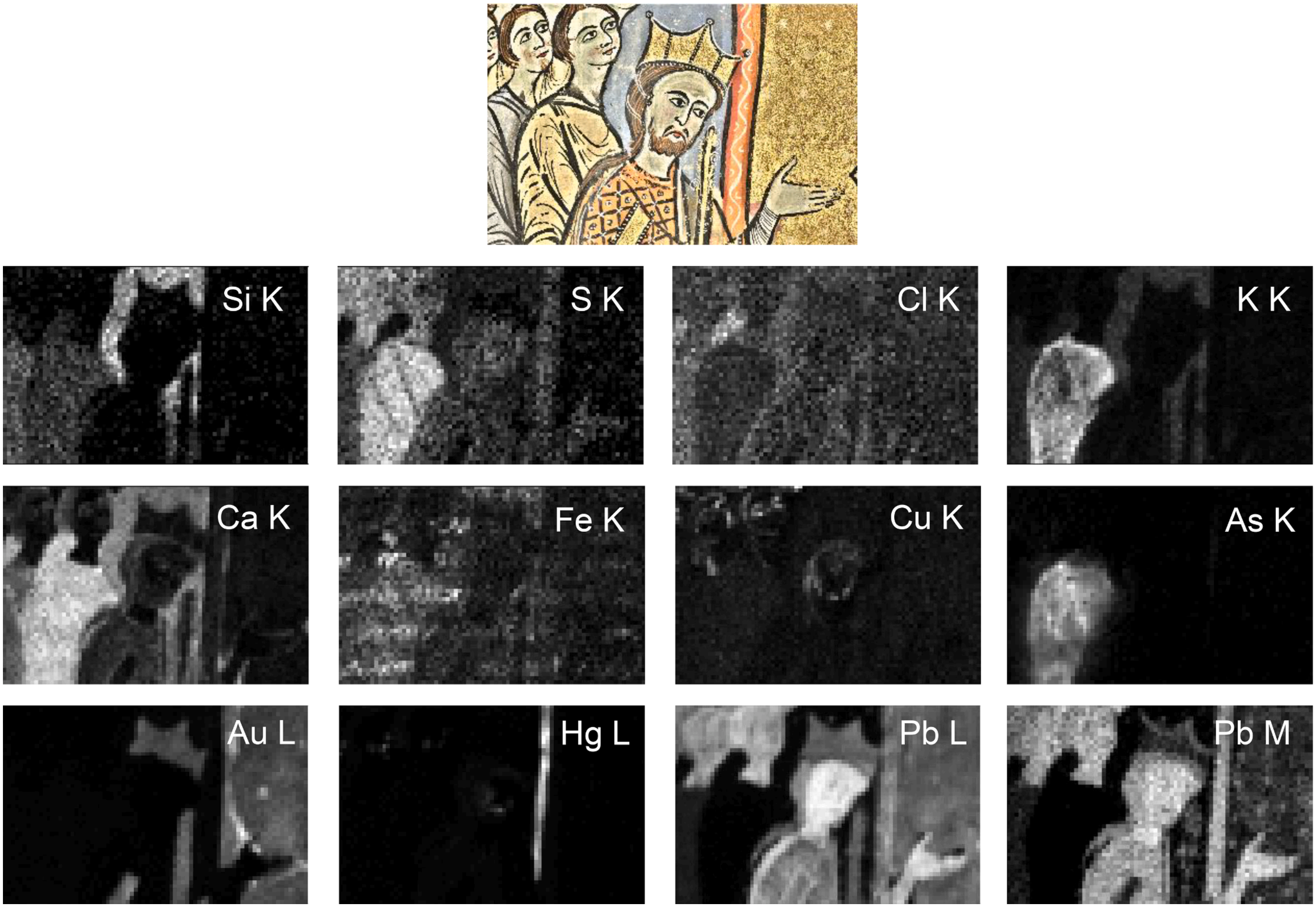

Fig. 8. Deconvoluted elemental distribution maps of the miniature found on folio 1r.

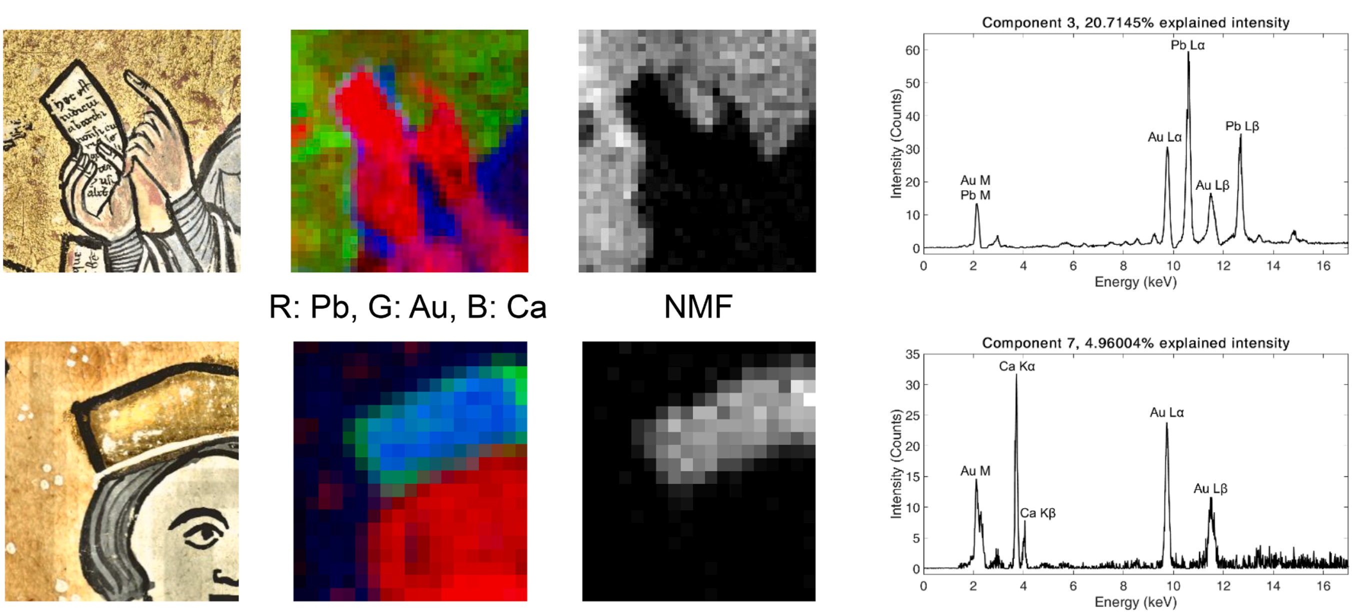

Fig. 9. Determination of the composition of the golden areas in Gothic miniatures 1r (top) and 37v (bottom). In the RGB diagrams red represents the Pb-L line, green the Au-L and blue the Ca-K line. The black and white diagrams are NMF maps presented together with the corresponding spectra.

difficult in samples that contain both Pb and Hg, as both of its peaks coincide with peaks of the latter two elements. The study of single point spectra of the area allows the identification of As and S peaks; however, the generation of deconvoluted maps or the application of NMF are preferable, as they both allow the direct association of composition and colour zone, leaving a smaller margin of error.

An additional two yellow pigments can be observed when comparing the NFM maps that correspond to two seemingly identical, but compositionally distinct yellow zones (Fig. 10). The map corresponding to the yellow pigment used to colour the figure's clothes demonstrates that the biggest weight is given to calcium and potassium. These two elements correspond to the parchment's composition, meaning that the signal detected could originate from the support found under the paint layer. This would indicate the use of an organic yellow colourant, which cannot be identified using only XRF. The yellow pigment used for the circular decoration displays a clearly different composition. It is based primarily on lead, but a calcium signal is also visible. This calcium signal differentiates the yellow zones from the white areas of the miniature, as can be seen in the third map of the figure, whose spectrum practically consists of the principal lead peaks. This could demonstrate that the colour was achieved by mixing white lead with a yellow colourant or by using an unknown lead-based yellow pigment. Furthermore, it is interesting to note that this pigment was possibly also used to paint the figure's hair, after being mixed with cinnabar, which was identified through a strong Hg signal in the same area.

3.2.3.4. Green pigments. The green colour widely used in Gothic miniatures has been achieved using a copper-based pigment (Fig. 11). However, the existence of multiple copper-based green pigments in the time period the manuscript was elaborated in does not permit its identification [37]. Furthermore, this matter appears to be quite complicated, as it seems that at least two different green pigments were used for the decoration of this group of illustrations. Whereas all miniatures are painted with a copper-based pigment that also contains Cl, there is one miniature where chloride is not present in any of the green areas analysed, while furthermore presenting a yellowish hue.

This fact could be an indication of the use of two different pigments, which could be a voluntary choice or not. Scott et al. mention that in the preparation of *viride salsum* following the recipe in Theophilus's *De diversis artibus*, the product can be different depending on whether the reaction vessel it is prepared in is sealed or not, yielding the copper chloride atacamite in the first case and verdigris in the second [38]. An alternative hypothesis would be that the presence of chloride is an indication of different conservation conditions and it is associated to the atmosphere each folio was exposed to. Such degradation processes have previously been described for azurite and malachite [39].

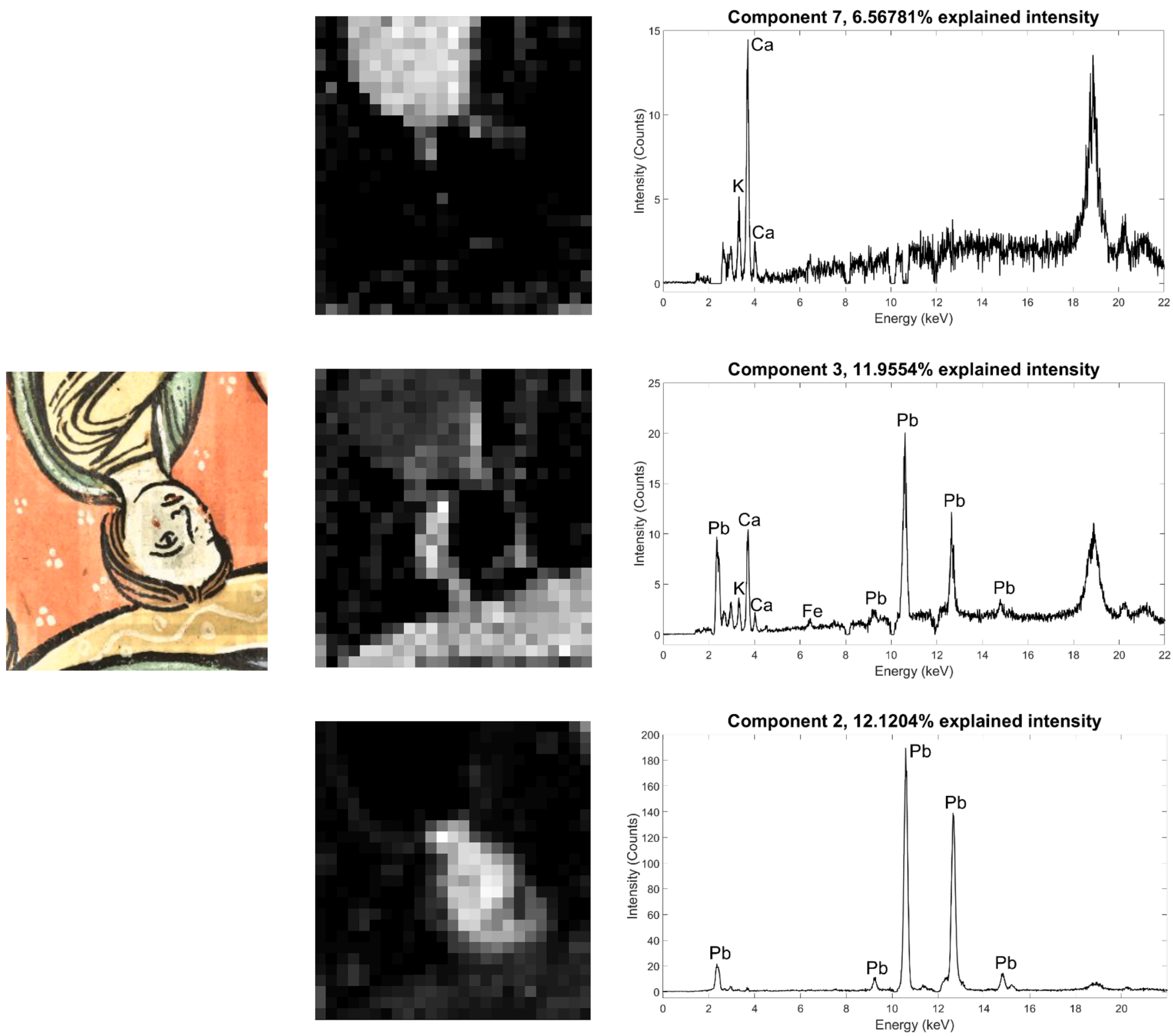

Fig. 10. NMF maps corresponding to the yellow zones of the miniature on folio 93r.

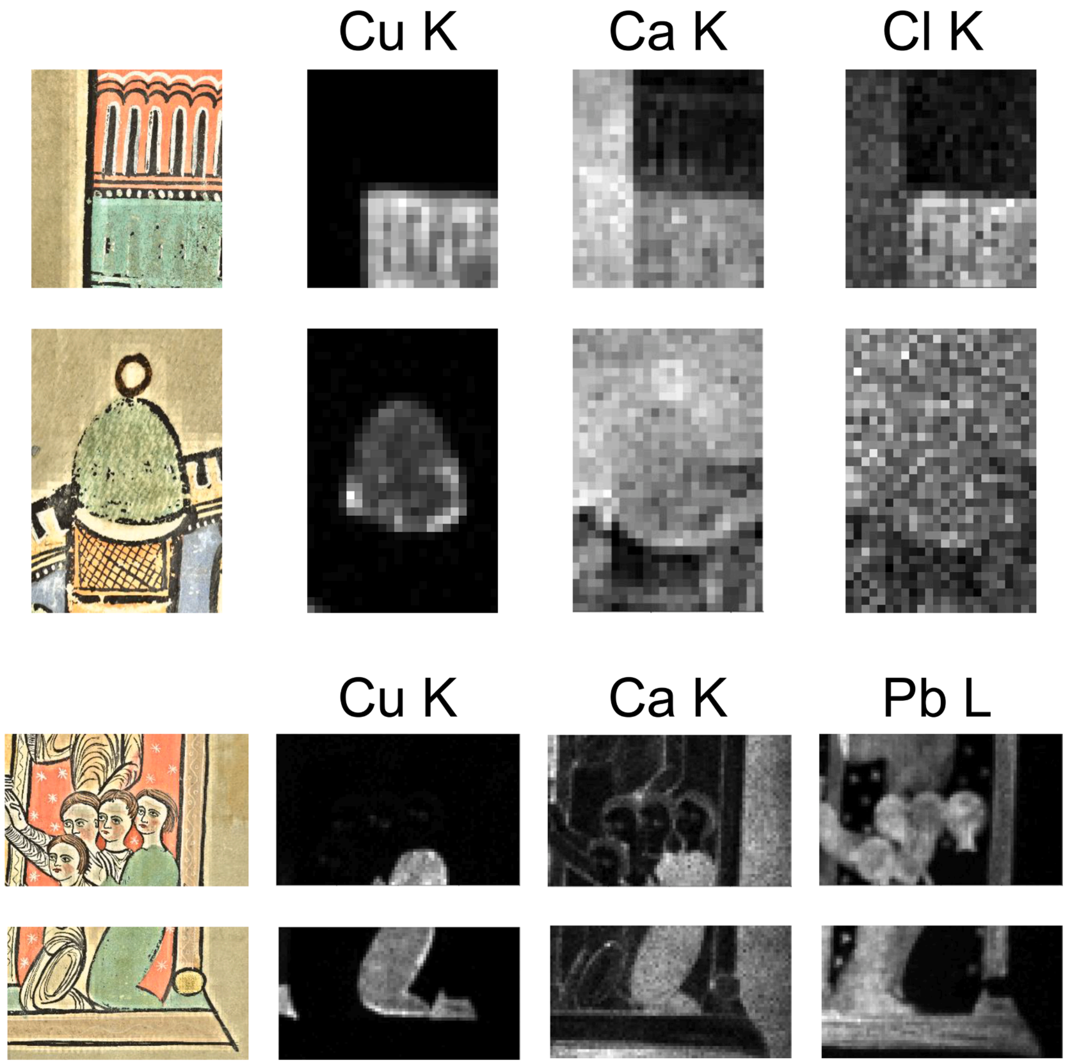

Fig. 11. NMF maps corresponding to the green zones of the miniatures on folios 94r (top), 1r (middle) and 82v (bottom two).

An additional inconsistency in the green pigments found in the Gothic miniatures can be seen in the one in folio 82v. The usual correlation between Ca and Cu can be seen in nearly all areas of the vassal's clothes, towers and the background, but there are certain zones, such as the bases and capitals of the column where no Ca can be found. Instead, these zones are characterized by a strong Pb signal, of the same intensity as the one coming from the yellow columns. The lead-based pigment seems to be situated under the green layer, as the Pb M signal is relatively lower. This would mean that lead does not form part of a third green pigment.

3.2.3.5. Black pigments / inks. Similar to the Romanesque miniatures, the determination of the nature of the black pigment or ink used to make the forms of the Gothic miniatures is a difficult task (Fig. 12). In these miniatures, the pigment has a darker and more intense hue and its presence can be correlated with the detection of Ca and K. These two elements, as has been seen in other occasions, could form part of the pigment's composition, but could also originate from the parchment. This would make sense if an organic carbon-based pigment was used to accomplish the lines.

In some miniatures, some details have been painted using what seems to be an iron-based ink. In this case, contrary to the Romanesque miniatures, the Fe signal is strong and corresponds exactly to the miniature's design, indicating that it is an iron-gall ink similar to the one used to write the text in the manuscript. Due to the scarcity of this ink's presence in the Gothic miniatures, it may be possible that these small details had been made after the completion of the miniature, by a person that was not the original illustrator.

3.2.3.6. Gothic exclusive pigments and materials. Apart from a wider range of pigments to achieve basic colours, gothic miniatures are also characterised by the introduction of new colours and hues, such as orange and brown and the use of other ornamental materials such as silver.

The detection of lead in orange areas (Figs. 8 and 11) is indicative of the use of an inorganic pigment, however its presence alone is not enough to determine the pigment. The signal could originate from either minium or a mixture of white lead with a red colourant and additional techniques, such as MA-FTIR could help clarify the matter. (Legrand 2018).

Brown is another colour that has been added to the colour palette of the Gothic illustrators. Similarly to the orange pigment, its identification using only XRF data is impossible, as in most cases the only element that can be detected is lead, which cannot be associated directly with any commonly used pigments. The presence of Cu in the brown-coloured area of one miniature, however, could indicate the mixing of a green copper-based pigment with a red or orange lead-based one, which would give the desired colour tone.

Finally, silver leaves were also used to decorate the miniatures. These leaves have been applied to the parchment using the same techniques that were used for the golden leaves. Both lead and calcium

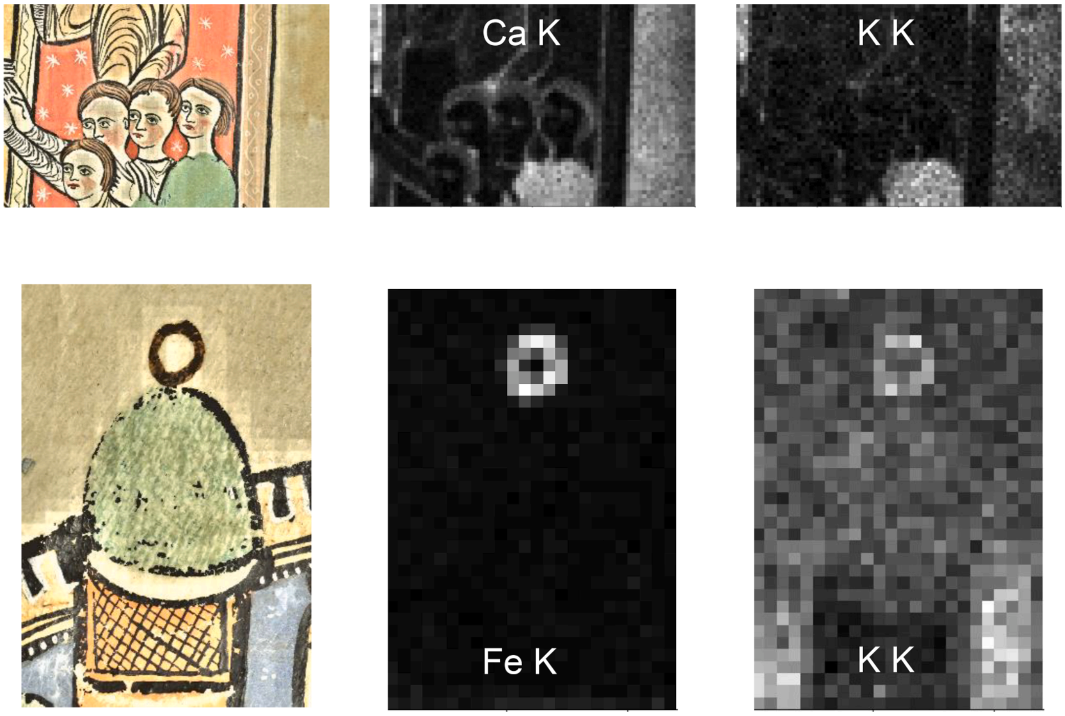

Fig. 12. The presence of two different types of black pigment in the Gothic miniatures found in folios 82v (top) and 1r (bottom).

preparation layers have been detected, visible with the naked eye and corresponding to red and white underlying layers.

To sum up, the Gothic miniatures are painted using the standard colour palette of the time period they were created in (Table 2). The variety of yellow and green pigments demonstrates the artists' need to achieve different colour effects, whereas the presence of two different preparation layers found under the golden leaves could be indicative of the participation of multiple artists, with different training backgrounds.

3.2.4. Comparison of the two styles

The palettes used to decorate the Romanesque and Gothic miniatures found in the manuscript are similar, with the second one presenting a larger variety of materials. This variety answers to the needs of the stylistic evolution between the two miniature types, which asks for a chromatic expansion. Multiple pigments of the same colour are used to achieve different hues, whereas certain pigments are mixed to achieve new colours. The pigments used in the Romanesque miniatures remain stable in practically all the illustrations, whereas the artists responsible for the Gothic miniatures show a greater adaptability, using colours according to the content of each miniature and what they want to portray. Furthermore, the idea established through the study of the golden leaves that at least two artists are responsible for the Gothic miniatures, could also explain the variety of colour choices among illustrations, as personal aesthetic criteria and working capacities of each artist could also influence the result.

The co-existence of the two palettes can be seen in the two mixed miniatures found in the manuscript's surviving folios, where Gothic-styled vassals have been added onto the basic Romanesque miniature, painting directly on top of the original kneeling vassal. In the two mixed miniatures, the composition of the pigments used is the same as that of the ones used for the rest of the manuscript's illustrations, with the artists involved in the elaboration of each miniature section remaining true to the palettes used in the corresponding style.

3.3. Determination of ink composition

The final part of the compositional study of the LFM involves the analysis of the inks used by the scribes to write the text in the manuscript. Two different coloured inks are found in the LFM: black and red.

Most of the manuscript's text is written in black and has faded into lighter brown tones, due to the passage of time. Not all letters have the same hue, but instead have faded to different extents, or they already had different aspects from the moment they were written. This was one of the characteristics that influenced the selection of letters analysed with XRF, as has already been mentioned in the Materials & Methods section, together with a focus on text areas with different calligraphy styles.

The analysis of the single point spectra and the comparison of the deconvoluted maps of the letter areas revealed that not all the text included in the manuscript is written with the same type of ink, but instead multiple inks can be identified, thanks to small changes in their composition (Fig. 13). All of the inks include Fe and K, and all but one ink category also include S, meaning that they can all be identified as iron gall inks, as these elements correspond to the three basic ingredients of the inks: iron sulphate, gallic acid and Arabic gum [40,41]. The letters can then be sorted into six different categories based on some minor ink composition components, such as Zn, Cu and Ca. These elements can be traced back to the different recipes that may have been used for the ink elaboration, or impurities in the materials added to the ink. However, it could also be possible that the Ca seen in some of the letters' compositions originates from the parchment under the letters. The ink's composition can be established through all the aforementioned methodologies. The presence of multiple compositions could be an indication of the participation of multiple scribes, using different recipes to prepare their inks.

The red ink is not as prevalent as the black ink, appearing in miniature captions and in parts of text where a special emphasis is given. The analysis of the ink through single point spectra and deconvoluted maps shows that it is cinnabar, the same pigment that was used to give the red colour to the miniatures decorating the manuscript. The pigment was determined through the detection of Hg. Sulphur was also detected in some cases, however, its presence was identified with more difficulty, as the signal it emits is minor in comparison to that of mercury.

Table 2
Elements and materials detected in the Gothic miniatures. (● Major signal ◍ Minor signal ○ No signal).

Colour	Si	S	Cl	K	Ca	Fe	Cu	As	Au	Hg	Pb	Ag	Pigment
Blue	●	◍	○	◍	◍	◍	○	○	○	○	○	○	Ultramarine Blue
Red	○	◍	○	○	○	○	○	○	○	●	○	○	Cinnabar
White	○	○	○	○	○	○	○	○	○	○	●	○	Lead White
Gold A	○	○	○	○	○	○	○	○	●	○	◍	○	Golden leaves – Lead preparation layer
Gold B	○	○	○	○	◍	○	○	○	●	○	○	○	Golden leaves – Calcium preparation layer
Yellow I	○	●	○	○	○	○	○	●	○	○	○	○	Orpiment
Yellow II	○	○	○	●	●	○	○	○	○	○	○	○	Organic yellow pigment
Yellow III	○	○	○	◍	◍	○	○	○	○	○	●	○	Lead-based yellow pigment or lead white mixed with yellow colourant
Green I	○	○	◍	◍	◍	○	●	○	○	○	○	○	Unidentified copper-based pigment (with chloride)
Green II	○	○	○	◍	◍	○	●	○	○	○	○	○	Unidentified copper-based pigment (no chloride)
Orange	○	○	○	○	○	○	○	○	○	○	●	○	Minium or lead white mixed with red pigment
Brown	○	○	○	○	○	○	○	○	○	○	●	○	Unidentified lead-based pigment mixture
Silver I	○	○	○	○	○	○	○	○	○	○	◍	●	Silver leaves – Lead preparation layer
Silver II	○	○	○	○	◍	○	○	○	○	○	○	●	Silver leaves – Calcium preparation layer
Black I	○	○	○	◍	◍	○	○	○	○	○	○	○	Organic carbon based ink / pigment
Black II	○	○	○	◍	○	●	○	○	○	○	○	○	Iron gall ink

4. Conclusions

The proposed methodology presented in this work aims to provide a thorough elemental analysis of manuscripts using XRF. The methodology consists of successive procedures that require different levels of expertise and it is important that it is adapted to the needs of every case. The combination of the retrieved information offers a better understanding of the results and helps overcome problems such as interpretations of minor signals, minor components or minor differences between signals.

Single point measurements offer a first general understanding of the manuscript, which is then enhanced by elemental distribution maps. ROI imaging can be a useful tool for a quick and in-situ interpretation of the maps, but the generation of deconvoluted maps ensures that signals from different elements are not misinterpreted. Furthermore, NMF has proven to be an adequate multivariate technique for this type of analysis, providing information about associations between different materials.

The methodology has been applied successfully to an important manuscript, the *Liber Feudorum Maior*, whose composition had never been studied prior to this work. A large part of the manuscript's palette has been determined through the information retrieved from the various types of analysis. The elemental distribution maps obtained and used to identify the constituents of the manuscript can be found in the Supplementary Material. The composition of the pigments used for the two styles of illustrations shows that the palette evolved from a simple Romanesque one composed of cinnabar, ultramarine blue, lead white, golden leaves and an organic yellow colourant to a more complex Gothic

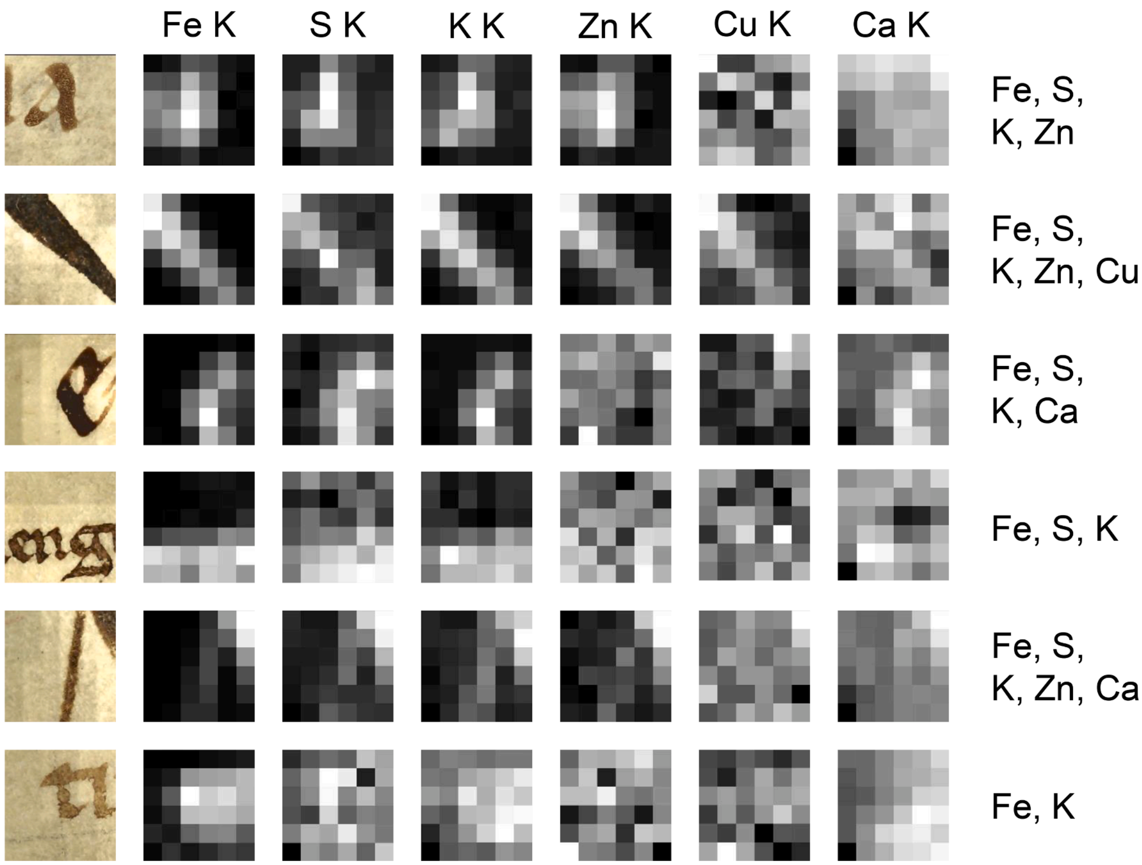

Fig. 13. Six types of ink have been identified due to small changes in their composition.

one, including, in addition to the Romanesque pigments, two different types of gold preparations, more yellow pigments, the ample use of green and the inclusion of new colours and materials, such as brown, orange and silver. The determination of materials and techniques, such as the differences in the gilding method, which could be indicative of the participation of two illustrators and the identification of different types of ink to write the text, which could indicate the involvement of multiple scribes, shows the necessity of material analysis using the CSM approach, as it enriches stylistic and historic studies that have already been made.

These differences could be an indication that with a more in-depth comparison of the composition of miniatures of the same style or the inks used for the text, combined with the application of chemometric techniques, groups of miniatures or inks with similar characteristics could be formed, providing information regarding authorship, as they would correspond to the work of different illustrators or scribes.

CRediT authorship contribution statement

G. Magkanas: Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **H. Bagán:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing - review & editing, Supervision, Project administration. **M.C. Sistach:** Conceptualisation, Investigation, Resources, Writing - review & editing, Supervision. **J.F. García:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquistion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2021.106112.

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