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Manuscript Details

Manuscript number	JASREP_2018_289_R1
Title	The Messale Rosselli: scientific investigation on an outstanding 14th century illuminated manuscript from Avignon
Short title	Scientific investigation on the Messale Rosselli
Article type	Research Paper

Abstract

The manuscript D.I.21 kept at Biblioteca Nazionale Universitaria in Torino, better known as Messale Rosselli, is one of the richest fully illustrated missals surviving from the mid-14th century. It was produced in Avignon for the Aragonese Cardinal Nicolas Rossell (1314-1362) but after the patron's death, it passed from hand to hand until it reached its final destination in Torino. The Messale Rosselli has recently been the object of a thorough interdisciplinary study, involving full characterisation of the colourants with non-invasive techniques (FORS, fluorimetry, XRF spectrometry, optical microscopy, IR photography). The full set of colourants was identified, highlighting the systematic use of precious pigments such as lapis lazuli, cinnabar and gold, a feature reinforcing the symbolic value of the manuscript; in addition, less valuable but interesting dyes such as brazilwood and folium were also identified, used either pure or in a mixture with pigments in order to obtain a wide range of hues. The palettes used by the various artists have been evaluated according to the availability of raw materials in the geographic area around Avignon, finding that most of the colourants could be at easy disposal of the artists. Information has also been obtained concerning the preparation of the parchment. The systematic measurement of the width of folios allowed hypothesising the number of the animals slaughtered to produce parchment, and the way of using skins. XRF analysis on the folios suggested that different preparations were used. Finally, ZooMS, a non-invasive technique able to provide information on the animal species from which parchment was produced, evidenced that calf and goat, but not sheep, were used to produce the parchment of the Messale Rosselli.

Keywords Manuscripts; Avignon; FORS; XRF; non-invasive; eZooMS; folium.

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Suggested reviewers Marcello Picollo, Pietro Baraldi, Paola Ricciardi, Abigail Quandt, Cheryl Porter

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There are no linked research data sets for this submission. The following reason is given:
Data will be made available on request



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to the attention of
Archaeological

Editorial Board of Journal of
Science: Reports

Alessandria, 10/23/2018

Object: *Submission of revised paper to Journal of Archaeological Science: Reports*

Dear Sir,

The paper “The *Messale Rosselli*: scientific investigation on an outstanding 14th century illuminated manuscript from Avignon” by Elisa Calà, Angelo Agostino, Gaia Fenoglio, Valerio Capra, Franca Porticelli, Francesca Manzari, Sarah Fiddymment and Maurizio Aceto has been revised following strictly the indication of the two referees. All issues have been addressed; in the main text, corrections have been highlighted in yellow. We believe that the present version is suitable for publication.

Looking forward to hear news from you

Best wishes

Prof. Maurizio Aceto

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Comments from the editors and reviewers:

- Reviewer 1

This paper presents the results of the non-destructive diagnostic campaign, without any sampling, carried out on the Messale Rosselli. The paper presents itself as a case study aimed at the characterization of palette and decoration technique of the whole masterpiece.

Moreover, the study has its peculiarity in the fact that a new technique as the EZooMS one has been applied to provide information on the animal species used for the parchment production. The work is well written; the division into paragraphs is very clear and the contents are explained.

However, for the palette characterization important information are missing (see below).

The English is correct.

Some modifications need to be performed before publication. Namely:

Q1. The acronym of the Electrostatic Zooarchaeology by Mass Spectrometry must always be written in the same way (ZooMS in the abstract; zooms in the keywords; eZooMS in the introduction...).

A1. We changed to eZooMS for all instances.

Q2. In the paragraph 3a there is a relevant discussion about the depth of the foils, but in the text no information about how this measurement has been performed. Please add all the information about it.

A2. The information on the measurement of parchment thickness has been added.

For the palette:

Q3. Blue: how you individuate the woad? Please specify

A3. The identification of woad instead of indigo is only based on practical considerations, not on diagnostic evidences. Due to the well-established trade of woad in the region of Toulouse, it is reasonable thinking that the artists used the local pigment and not a pigment – such as indigo – coming from Far Eastern Asia. At any rate we added the phrase “even in the lack of diagnostic evidences”.

Q4. Gold: what means “assiso”? Please add in the text. How you deduce the Armenian bole presence? How you distinguish yellow bole from the Armenian one?

A4. “Assiso” is the Italian term for the material used as basis for gold leaf involving chalk; I think the same term can be used in English. We added this definition in the text. The distinction of yellow bole from Armenian one by means of FORS is very simple: the first shows the spectrum of yellow ochre, while the second shows the spectrum of red ochre. Of course, they can be identified - and distinguished – only if small gaps are present in the gold leaf.

Q5. Green. You mention the use of indigo, but in the table 1 woad has been reported. Why?

A5. See answer A3.

Q6. Pink: in the text you mention cinnabar, but not in the Table 1, why?

A6. The use of cinnabar in incarnate tones was erroneously cited, we cancelled it from Pink.

Q7. Violet: please add the FORS spectra of folium and ultramarine as reference in the fig. 5. Please add the spectrum of parchment in the fig. 6.

A7. Figg. 5 and 6 have been changed following the indications of the referee; captions have been changed accordingly.

Q8. Inks: from the data shown in fig.7, you deduce that Fe/Cu ratio is 20:1: please add the equation of the interpolated straight line and add the units on the axes.

A8. The equation of the interpolated straight line and the units on the axes have been added to Fig. 7.

Q9. The different palettes: for the pigments mentioned in table 1, please provide the techniques used to determine their presence and which is the element, or emission band or... peculiar for each pigment identification (e.g. EDXRF detects the Hg in the red pigment and you can deduce that there is cinnabar...).

A9. This information was added for every colourant identified.

Q10 - Details from FT-IR photography: are you sure that the technique used is FT-IR photography?

A10. It is, indeed, IR photography, we changed the term.

Q11 - Reading the bibliography it is easy to understand the identity of the authors because 7 references out of 17 are from the same research group; please, delete / replace some references.

A11. This comment is not clear to us, please specify.

The paper can be published on JASREP after a major revision

- Reviewer 2

The paper presents the results of an interdisciplinary study performed on a 14th Century illuminated manuscript, which was deeply examined with a multi-analytical approach with the occasion of the restoration. A notable amount of data was acquired thus leading to new findings about the case-study considered. Some of these results supported some of the scholars' hypothesis about the manuscript. Since an increased knowledge has been gained with this research on the examined case-study, the work deserves attention and is worthy to be published. However, in my opinion, a main flaw of the manuscript is a weakness of rationale and organization of contents. Indeed, being the scientific approach adopted in this research well-established and based on consolidated analytical techniques, the novelty of the work mainly lies in the findings about the specific case-study examined, which is reported as an outstanding example of the 14th Century illuminated manuscript production from the Avignon area.

Q1. However, if this is the case, the Introduction should better focus this aspect, and a discussion of the results of under the broader perspective of the interdisciplinary approach should be introduced in the Results section.

A1. A brief discussion on this argument has been added in the Introduction section, and the discussion of results has been improved.

Q2. I would recommend adding in the Introduction a paragraph illustrating the specific aim of the investigations, and clearly stating the open questions raised by scholars about this manuscript, illustrating the wider historical and artistic context, etc.

A2. A short paragraph has been added in the Introduction, specifying the main aims of the scientific investigation.

Q3. In addition, since the use of non-invasive analytical techniques applied to the study of illuminated manuscripts has greatly grown in recent years, authors should dedicate a brief paragraph to this topic, with a short state of the art of other relevant studies published in the field.

A3. A brief paragraph has been added with references to the works lately published.

That said as general comment, I also found several specific issues which should be addressed to reach the standards required for publication, as reported in the detailed list below.

In conclusion I would recommend to resubmit the paper after major revisions.

Detailed list of comments and recommended changes.

1) Introduction: see comments above.

Q4. 2) P.4 l. 97, "many of the questions...". Please add further details about these questions, at least by mentioning those addressed by the scientific analysis

A4. The sentence has been improved.

3) Materials and methods.

Q5. P. 4 l. 106 and following. Please indicate the set-up adopted for the FORS measurements. Include a description of the probe head used. Rather than (or in addition to) the detector spectral range, the overall operational range of the device should be indicated (combination of lamps + detector).

A5. This information has been added in the experimental section.

Q6. P. 5 l. 150. Please include the number of samples extracted per each folium, their location and their dimension /weight.

A6. The information on samples for eZooMS analysis has been added to the text.

4) Results

Q7. P. 6, l. 205. A bibliographic reference or the source of Figure 2 has to be included, here or in the caption of figure 2.

A7. A reference has been included in the caption of Figure 2.

Q8. P. 8 from l. 227 to l. 229. Authors concede that data and samples they acquired are not sufficient to draw general conclusions about the constituting materials of all the folios. However, this motivation is not sufficient to justify a lack of conclusions in a scientific paper. If data are not enough to answer the question tackled, the data-set could be enriched. Alternatively I would suggest to omit this paragraph and present the data as preliminary result, or publish more complete results in a future publication.

A8. The knowledge on the animal source of parchment is only in its infancy at present; therefore we reputed that the result provided by eZooMS could be nevertheless of interest for scholars, despite being partial. At any rate we recognize that the data-set could be enriched in a future publication.

Q9. P. 8 l. 241. "several" is not informative for a scientific paper. The number of points acquired should be indicated P. 8 l. 241. Some" see above.

A9. The total number of XRF measurements on parchment has been added to the text.

Q10. P. 12. Fig 5 x-axis and y-axis scales are not optimised for readability. Minor ticks are uselessly too dense.

A10. We think that the readability of the figure is good as it is now.

Q11. P.15 l. 428. "The order is the following". The reasons and observations which lead to hypothesize this sequence should be reported.

A11. The rationale on the sequence has been added to the text.

Q12. P. 16 l. 447, and l. 453 "FT-IR Photography". This is strongly incorrect! IR Reflectography is the right name for the technique used. FT-IR is a different working principle, not used in this context.

A12. The referee is definitely right, it was a big mistake of ours.

- A precious 14th century manuscript has been analysed with different complementary techniques
- Measurements yielded information on all colourants used by ancient artists
- Different hands at work in the decoration were identified, confirming the hypothesis of scholars
- Many colourants were available in the area surrounding Avignon

1 **The *Messale Rosselli*: scientific investigation on an outstanding 14th century illuminated**
2 **manuscript from Avignon**

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21

22 **Abstract**

23 The manuscript D.I.21 kept at Biblioteca Nazionale Universitaria in Torino, better known as
24 *Messale Rosselli*, is one of the richest fully illustrated missals surviving from the mid-14th
25 century. It was produced in Avignon for the Aragonese Cardinal Nicolas Rossell (1314-1362)
26 but after the patron's death, it passed from hand to hand until it reached its final destination in
27 Torino.

28 The *Messale Rosselli* has recently been the object of a thorough interdisciplinary study,
29 involving full characterisation of the colourants with non-invasive techniques (FORS,
30 fluorimetry, XRF spectrometry, optical microscopy, IR photography). The full set of
31 colourants was identified, highlighting the systematic use of precious pigments such as lapis
32 lazuli, cinnabar and gold, a feature reinforcing the symbolic value of the manuscript; in
33 addition, less valuable but interesting dyes such as brazilwood and folium were also
34 identified, used either pure or in a mixture with pigments in order to obtain a wide range of
35 hues. The palettes used by the various artists have been evaluated according to the availability
36 of raw materials in the geographic area around Avignon, finding that most of the colourants
37 could be at easy disposal of the artists.

38 Information has also been obtained concerning the preparation of the parchment. The
39 systematic measurement of the width of folios allowed hypothesising the number of the
40 animals slaughtered to produce parchment, and the way of using skins. XRF analysis on the
41 folios suggested that different preparations were used. Finally, **eZooMS**, a non-invasive
42 technique able to provide information on the animal species from which parchment was
43 produced, evidenced that calf and goat, but not sheep, were used to produce the parchment of
44 the *Messale Rosselli*.

45
46
47 **Keywords (3-7)**

48 Manuscripts; Avignon; FORS; XRF; non-invasive; eZooMS; folium.
49
50

51 1) Introduction

52 a) *The history of Messale Rosselli*

53 The *Messale Rosselli* or *Rossell Missal* (*Messale* thereafter) is one of the richest fully
54 illustrated Missals surviving from the mid-14th century (Ragusa, 1975). It was produced most
55 probably in Avignon for the Aragonese Cardinal Nicolas Rossell (1314-1362), as indicated
56 both by the *colophon* at the end of the manuscript (f. 423v) where the scribe Alamannus, with
57 a riddle, indicates that the book was completed in 1361, and by a beautifully decorated note
58 (f. Iv), at the beginning of the book (Manzari, 2006). This note was drawn in coloured inks by
59 a gifted pen-flourisher, recognisable throughout the *Messale* and in other manuscripts
60 produced in Avignon, identified with the illuminator Bernard de Toulouse (Manzari, 2014).

61 The vast illustrative programme, comprising hundreds of historiated initials at the beginning
62 of the Masses throughout the liturgical year and fully illuminated borders highlighting the
63 most important festivities, was painted in *tempera* by a different workshop. This was led by
64 an artist whose style combined a basically Southern French culture – especially recognisable
65 in the type of foliage used in the decorated letters and borders – with Catalan components,
66 visible for example in the expressionistic elements in the full-page Crucifixion. The first quire
67 of the body of the *Messale* (ff. 19r-26v) was illuminated by a different artist, possibly later
68 and in an equally elegant style (Manzari, 2006).

69 The *Messale* stayed in the Avignon curia after Cardinal Rossell's death, which occurred in
70 Spain in March 1362, then passing into the hands of Cardinal Guillaume de Bragose. The
71 arms of Cardinal Bragose have been added on ff. 286r and 287v, showing that the *Messale*
72 must have been acquired by the prelate between Rossell's death in 1362 and his own in 1367.
73 As the other arms, present on the *incipit* page (f. 19r), are surmounted by a crozier topped
74 with a cross, a third owner can be identified with the Archbishop Pierre II de Cros, who must
75 have bought the manuscript between 1370, when he was named Archbishop of Bourges, and
76 1383, when he became a Cardinal (Manzari, 2006). After that, it was reported in a Franciscan
77 monastery in Pinerolo (northern Italy) in 17th century and eventually in the Savoy ducal
78 library in Torino, from where it reached the Regia Biblioteca Universitaria (now Biblioteca
79 Nazionale Universitaria) after the foundation of this library by Duke Vittorio Amedeo II di
80 Savoia.

81 The arms of the original owner, Cardinal Rossell, have been overpainted in many borders,
82 usually with decorative elements and by the same workshop responsible for the illustrative
83 programme, perhaps in preparation for its sale on the market, after the patron's sudden death.
84 Cardinal Rossell's arms survive, however, in certain cases, such as an initial with St. John the
85 Evangelist (f. 34r), or in some of the illuminated borders, where they were frequently
86 accompanied by the arms of the Crown of Aragon (Manzari, 2006).

87

88 b) *The interdisciplinary study*

89 It was opinion of the authors of this study that some open questions raised by scholars about
90 the manuscript could be addressed by means of analytical investigations, with particular
91 concern to the identification of the different hands at work in it and to the chemical nature and
92 geographic provenance of the colourants used. Therefore, taking the opportunity given by its
93 restoration, the *Messale* has recently been the object of a thorough interdisciplinary study,
94 involving full characterisation of colourants, inks and parchment with non-invasive

95 techniques. The multi-techniques approach applied to the study of illuminated manuscripts
96 has greatly grown in recent years. Elemental, molecular and imaging techniques are combined
97 in order to yield as most complete information as possible concerning the materials and the
98 techniques used by ancient artists. Considering only the last two years, good examples are the
99 studies by Cucci et al. (2018), Fruhmann et al. (2018), Legrand et al. (2018), Mounier &
100 Daniel (2017) and de Viguerie et al. (2018). In this study, a combination of molecular (UV-
101 visible diffuse reflectance spectrophotometry with optic fibres and Spectrofluorimetry),
102 elemental (X-Ray Fluorescence spectrometry) and visual (optical microscopy) techniques
103 yielded a vast amount of information; in addition, the application of mass spectrometry using
104 the eZooMS (electrostatic Zooarchaeology by Mass Spectrometry) method provided
105 information on the preparation of parchment.

106 The combination of the cited techniques allowed addressing many of the questions raised by
107 scholars, in particular those concerning the story of the *Messale* and its changes of ownership
108 , its manufacture and its geographic provenance in relation with the raw matters used, its
109 symbolic value and more generally its role inside the production of precious books in
110 Avignon.

113 2) Materials and Methods

114 a) UV-visible diffuse reflectance spectrophotometry with optic fibres (FORS)

115 FORS analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-
116 ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten
117 halogen light source; detector and light source were connected with fibre optic cables to an
118 FCR-7UV200-2-1,5x100 probe. In this configuration, both the incident and detecting angles
119 were 45° from the surface normal, in order not to include specular reflectance. The spectral
120 range of the detector was 200-1160 nm; the overall operational range of the device
121 (combination of lamp + detector) was 375-1100 nm. Depending on the features of the
122 monochromator (slit width 50 µm, grating of UA type with 300 lines/mm) and of the detector
123 (2048 pixels), the best spectra resolution was 2,4 nm calculated as FWHM. Diffuse
124 reflectance spectra of the samples were referenced against the WS-2 reference tile provided
125 by Avantes and guaranteed to be reflective at 98% or more in the spectral range investigated.
126 The investigated area on the sample had a 1 mm diameter. The probe was inserted into an
127 aluminum block, in order to exclude external light and to hold firmly the probe in place.
128 During analysis, the block is laid on the sheet; therefore the side in contact with the
129 manuscript was covered in Tyvek®, a soft tissue. In all measurements the distance between
130 probe and sample was kept constant to 2 mm. To visualise the investigated area on the
131 sample, the probe contained a USB endoscope inserted as well in the block. The instrumental
132 parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of
133 1.0 s for each spectrum. The whole system was managed by means of AvaSoft v. 8 dedicated
134 software, running under Windows 7™.

136 b) X-Ray Fluorescence spectrometry (XRF)

137 XRF measurements were performed with an EDXRF Thermo (Waltham, USA) NITON
138 spectrometer XL3T-900 GOLDD model, equipped with an Ag tube (max. 50 kV, 100 µA, 2
139 W), a large area SDD detector, energy resolution of about 136 eV at 5.9 keV. Analysed spot
140 had an average diameter of 3 mm and was focused by a CCD camera, with a working distance
141 of 2 mm. Total time of analysis was 240s. The instrument is held in position with a moving

142 stage allowing micrometric shifts, in order to reach the desired probe-to-sample distance; the
143 stage is laid on a tripod. The obtained spectra have been processed with the commercial
144 software WinAxil, derived by the academic software QXAS from IAEA.

145 146 *c) Spectrofluorimetry*

147 An Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was employed to
148 record molecular fluorescence spectra. The instrument is equipped with a 365 nm Jaz-LED
149 internal light source; a QF600-8-VIS/NIR fibre fluorescence probe is used to drive excitation
150 light on the sample and to recover the emitted light. The spectrophotometer works in the
151 range 191-886 nm; according to the features of the monochromator (200 μm slit width) and
152 detector (2048 elements), the spectral resolution available is 7.6 nm calculated as FWHM.
153 The investigated area on the sample is 1 mm in diameter. In all measurements the distance
154 between probe and sample was kept constant to 12 mm, corresponding to the focal length of
155 the probe. To visualise the investigated area on the sample, the probe contained a USB
156 endoscope. Instrumental parameters were as follows: 2 s integration time, 3 scans for a total
157 acquisition time of 6 s for every spectrum. The system is managed with SpectraSuite™
158 software under Windows 7™.

159 160 *d) Optical Microscopy*

161 A USB Dino-Lite (New Taipei City, Taiwan) AM4113T-FV2W model microscope was used
162 to acquire digital images at 50x and 200x magnification ratios. The instrument is equipped
163 with 375 nm and visible LED lights and a digital camera with 1.3 Megapixel resolution.

164 165 *e) electrostatic Zooarchaeology by Mass Spectrometry (eZooMS)*

166 Seventeen folios of the *Messale* were sampled using the dry non-invasive eraser-based
167 sampling technique of Fiddyment *et al.* (2015) for protein analysis. One eraser sample per
168 folio was taken from the border of the page over an area of approximately 2 cm^2 . Samples
169 were analysed using the eZooMS methodology following the protocol of Fiddyment *et al.*
170 (2015). Briefly, samples were incubated in 75 μL of 0.05 M NH_4HCO_3 (AmBic) buffer (pH
171 8) with 1 μL of trypsin (0.4 $\mu\text{g}/\mu\text{L}$) at 37 $^\circ\text{C}$ for 4 h. Samples were desalted and concentrated
172 using Pierce™ (Thermo Fisher Scientific, Waltham, USA) C18 resin, following the
173 manufacturer's instructions. Peptides were eluted in a final volume of 50 μL of 50%
174 acetonitrile/0.1% trifluoroacetic acid (vol/vol). Samples were spotted in triplicate and
175 analysed using a calibrated Bruker Daltonics (Bremen, Germany) Ultraflex III NLD1 model
176 MALDI-TOF-MS instrument in reflector mode. Spectral analysis was performed using the
177 open-source cross-platform software mMass (www.mmass.org) (Strohalm *et al.*, 2010).

178 179 *f) IR photography*

180 IR pictures were taken with a Canon (Tokyo, Japan) EOS 20D camera equipped with an
181 infrared filter blocking light below 750 nm. Lighting was obtained by means of 2 Profoto
182 (Sundbyberg, Sweden) flashes free from UV components.

183 184 *g) Thickness measurements*

185 Thickness measurements on parchment were taken with a Vogel (Leno, Italy) Käfer model
186 analogue thickness gauge with reading 0.01.

187 188 3) Results

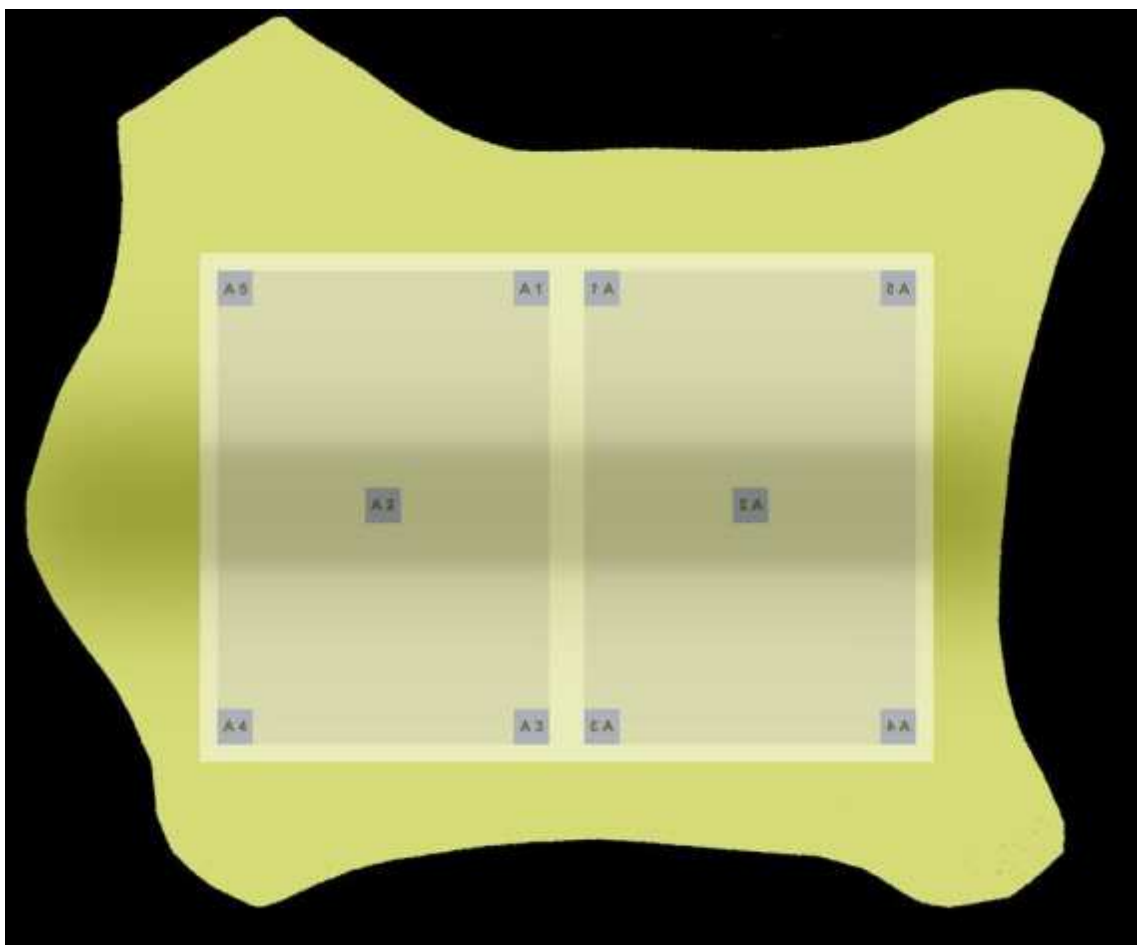
189 a) *The structure of Messale Rosselli*

190 The *Messale* is composed of 425 leaves with size 383x278 mm, divided into 57 quires: 51
191 quaternions, 3 ternions, 1 binions, 1 bifolium, 1 single leaf for a total of 216 bifolia. It is
192 divided into two main sections: (1) a Calendar with the most important liturgical feasts,
193 containing illustrations of the labours of the months and signs of the zodiac (ff. 1r-VIIv); (2)
194 the main part containing the texts necessary for the performance of the mass (ff. 1r-425v). The
195 true beginning of the main part is actually the quire at ff. 19r-26v, containing the liturgies for
196 First Sunday of Advent; this quire was apparently decorated by an artist different from the
197 others, particularly accomplished and possibly later.

198 The parchment is very smooth and was apparently prepared according to the transalpine style
199 (Maniaci, 1996) which, after a fine and accurate working, rendered the hair and the flesh sides
200 indistinguishable.

201 In order to evaluate the building sequence of the manuscript, **thickness** measurements were
202 taken into 5 points of every leaf: 4 at the corners and 1 in the centre of the leaf. The 4 corner
203 points gave average values comprised between 0.1644 and 0.1695 mm, while the central
204 points yielded an average value of 0.1709 mm, slightly but systematically higher than the
205 corner points: this means that the two central points of a bifolium (Fig. 1) corresponded to the
206 back part of a beast, and suggests that one skin, after trimming, provided one bifolium;
207 therefore the building of the *Messale* required not less than 216 beasts to be slaughtered.

208



209

210

Fig. 1 - Reconstruction of the making of a bifolium from a skin

211

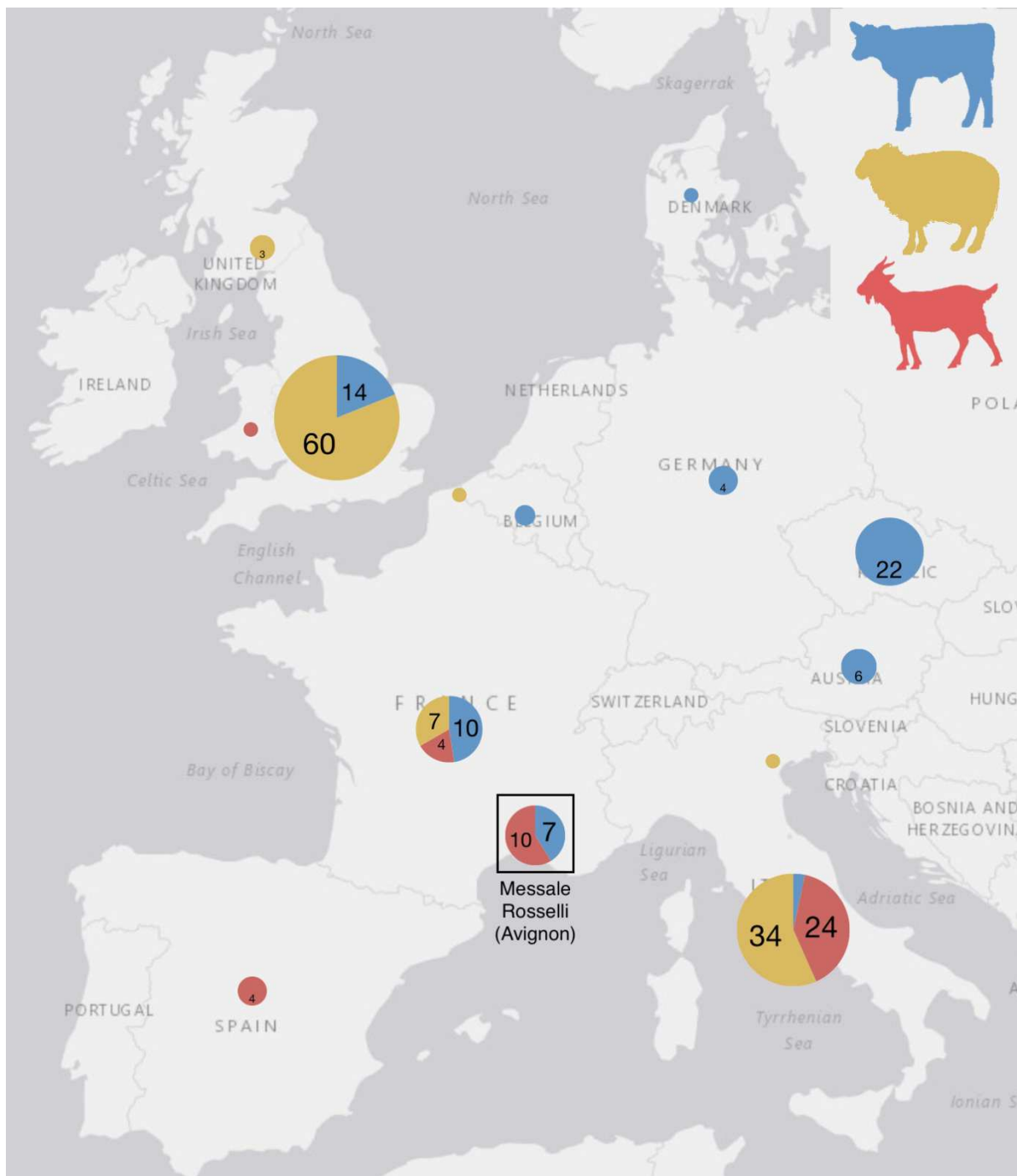
212 A different situation was found in the bifolium containing ff. 206-207, located at the very
213 centre of the manuscript: in this case the **thickness** ranged between 0.22 mm and 0.35 mm.
214 This must be regarded, however, as a particular bifolium as it contains the most important
215 miniatures of the whole manuscripts, most probably realised by the main artist.

216

217 *b) Analysis of the parchment with identification of the animal source*

218 In the study on the *Messale* the previously developed non-invasive **eZooMS** technique was
219 used to analyse a small collection of samples (n = 17). From this analysis we have identified 7
220 folios to be made from calf parchment (41%) and 10 folios to be made from goat parchment
221 (59%). The presence of both goat and calf, although intriguing, fits well into our geographic
222 distribution as the *Messale* is thought to be produced in Avignon, a location with influences
223 from both France (predominance of calf parchment) and Italy (predominance of goat
224 parchment) (Fiddyment et al., 2015). When comparing specifically to contemporary
225 documents (14th century) we can see that these trends are still observable (Fig. 2).

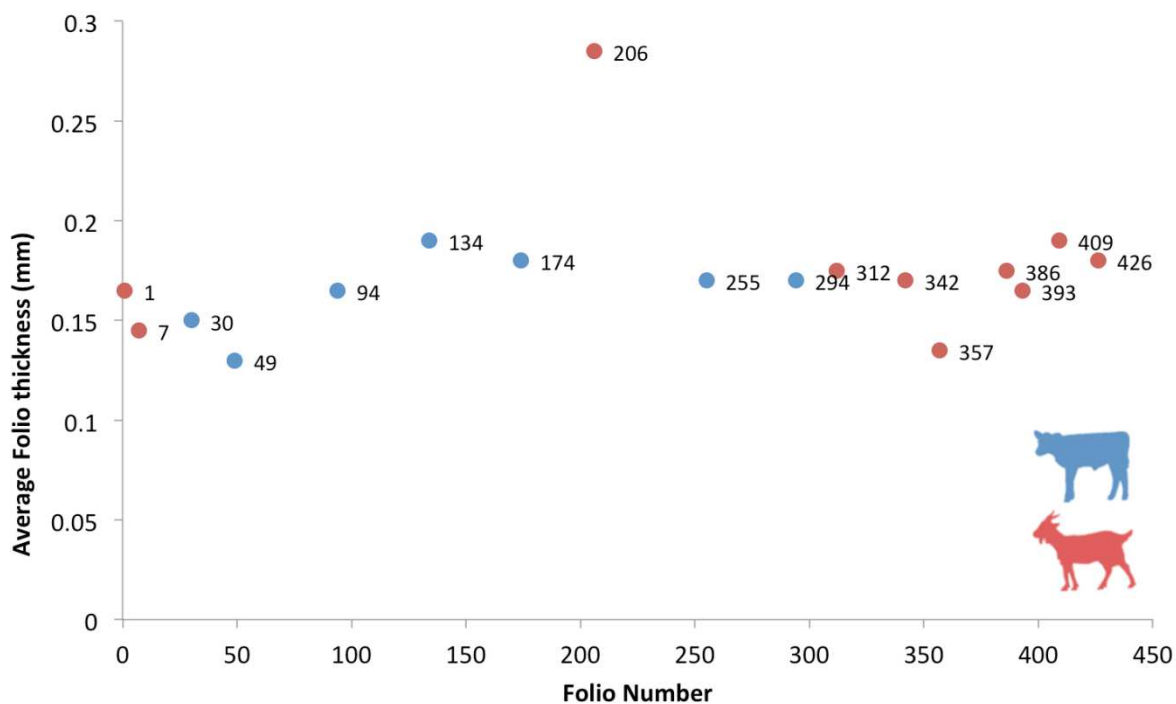
226



227
 228 Fig. 2 - Geographic distribution of 14th century European parchment samples including 17
 229 folios sampled from the *Messale Rosselli*. Map is based on data published in Fiddyment et al.
 230 (2015).
 231

232 The absence of sheep is not unexpected due to the nature of the document, a missal, which is
 233 considered to be a more prestigious and personal object, and a manuscript usually made with
 234 the most precious material as it was to be used on the altar, together with the chalice and
 235 paten, and would therefore be made from finer quality materials. We know from accounts at
 236 Beaulieu Abbey (Gullick, 1991) that even the best prepared sheep parchment was cheaper

237 (and presumably considered inferior) to even the worst prepared calfskin parchment,
 238 highlighting the prestige attached to the latter. It is interesting to note that the distribution of
 239 the animal species is mixed through the document (Fig. 3), with the first folios sampled (1 and
 240 7) being made from goat, followed by a section predominantly made from calf (with the
 241 exception of bifolium 206-207 which is also goat) and finally the second half of the
 242 manuscript seems to be exclusively goat once more.
 243



244
 245 Fig. 3 - Species identification and average thickness of 17 folios sampled from the *Messale*
 246 *Rosselli*
 247

248 However, as we have not sampled all the folios in the *Messale*, we cannot say whether this is
 249 definitely the case or if there is a more structured pattern of alternation that we cannot
 250 currently observe with this limited number of samples; the data-set will be enriched in a
 251 future publication. Regarding the thickness of the parchment, there doesn't seem to be a
 252 notable difference between the calf and goat parchment with the exception of bifolium 206-
 253 207 which is significantly thicker than any other folio sampled, as stated before. Although it
 254 is identified as goat this is not reason enough to warrant this thickness as the other folios
 255 identified as goat are much thinner and present similar thicknesses to the calfskin folios. This
 256 might indicate a problem with manufacturing where the skin was not shaved enough or could
 257 possibly indicate a problem with the skin itself. However, given that this is also the folio
 258 which contains the most important miniatures, it is likely that it may have been a deliberate
 259 choice to use a thicker parchment to provide a more stable substrate on which to paint.
 260

261 *c) Elemental analysis of the parchment*

262 40 XRF measurements were taken on the parchment folios in order to obtain information on
 263 the preparation of parchment itself. The presence of specific elements, in fact, could suggest
 264 that particular compounds or treatments had been applied for rendering the surface smooth
 265 and ready for writing/painting. The results of this survey highlighted that the parchment

266 makers did not use one single treatment but rather different kinds of treatments. Apart from
267 Ca which is ubiquitous and is due to the traditional use of lime, significant amounts of Pb
268 suggested the use of *lead white* – $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ - generally employed as white pigment
269 but in this case used to compact collagen fibres; the combined presence of Si, Al and K,
270 instead, suggested the use of clay materials, possibly to remove the residual greasiness of
271 parchment. The different treatments, however, are not related to the different animal source
272 (cow vs. goat). It is apparent, then, that the makers of the *Messale* purchased different sets of
273 parchment folios, maybe from different *pergamenarii*, e.g. parchment makers.

274

275 *d) The miniatures*

276 The restoration of the *Messale* was a very good opportunity for carrying out non-invasive
277 measurements, due to the fact that it was completely unbound into quires and therefore all
278 interesting features (miniatures, inks, pen-work decoration, etc.) were much more available
279 for probing. The decorative apparatus of the *Messale* is breath-taking for its richness: it is
280 composed of 2 full-page miniatures (at ff. 206v and 207r), 15 historiated frames, 285
281 historiated initials and 144 initials decorated with pen-work. In the following, the colourants
282 identified with non-invasive measurements will be discussed, trying to highlight the
283 differences among the different hands who worked at the decoration.

284

285 *i) Black*

286 Carbon-based pigments were used for black hues all through the *Messale*. It was not possible
287 to define the exact type of pigment; only *bone black* can be excluded, according to the lack of
288 phosphorus evidenced by XRF analysis.

289

290 *ii) Blue*

291 One of the most striking features of the *Messale* is the wide use of *ultramarine blue*, the
292 precious pigment made from lapis lazuli stone, identified according to the absorption band at
293 600 nm in FORS spectrum. According to Delamare (2013) in the late Middle Ages the price
294 of lapis lazuli on the Paris market was equivalent to its weight in gold. There was only one
295 known source, the mines of Badakshan (modern north-western Afghanistan), from which the
296 stone after a long trip, through the harbours of the near-eastern Asia coast, reached Venice
297 and eventually Europe.

298 Another blue pigment used on the *Messale*, identified according to the absorption band at ca.
299 660 nm in FORS spectrum, was *indigo*, the organic colourant extracted from *Indigofera*
300 *tinctoria*, a plant native to south-eastern Asia, or from *Isatis tinctoria*, a plant native to Asia
301 but widely cultivated in Europe; in this case the colourant is termed *woad*. In the *Messale* it is
302 obviously pointing to the use of woad rather than indigo (even in the lack of diagnostic
303 evidences), considering that the cultivation of *Isatis tinctoria* represented in Middle Ages the
304 richness of the area called *Pays de cocagne*, the triangle between Toulouse, Albi and
305 Carcassonne, very close to Avignon. Woad was used in the *Messale* mostly in mixtures: with
306 yellow ochre for obtaining greens, with brazilwood for obtaining violet-purplish backgrounds.

307

308 *iii) Brown*

309 All brown hues were obtained with *red ochre*, identified according to the absorption band at
310 ca. 850 nm and the inflection point at ca. 580 nm in FORS spectrum. The use of iron oxide
311 pigments is absolutely common in painting; nevertheless it is worth noting the availability of
312 high quality ochres at Roussillon (Vaucluse department), less than 50 Km from Avignon.

313

314 *iv) Gold*

315 To assess the value of the *Messale*, it would be sufficient to evaluate the huge number of
316 features decorated with gold, which account to almost 700. Gold was identified according to
317 the inflection point at ca. 510 nm in FORS spectrum and characterised with XRF analysis.
318 Some features are made with gold shell, such as clothes of important characters and the
319 beautiful interweaving on the background of several historiated initials. Most of gold features
320 are made in leaf and particularly relevant is the fact that gilding was carried out using
321 different preparations. Rather than to the action of various artists, this variety of preparation
322 could be due to the desire of the main artist to obtain different final hues of gold or to adapt
323 the preparation to the morphology of the parchment. The combination of XRF, yielding
324 information on the elements present below gold leaf, and FORS analysis carried out on leaf
325 losses, was suitable in elucidating this aspect. All the preparations were of the *assiso* type,
326 that is involving the use of a small layer of chalk. The following preparations could be
327 identified:

328 - *assiso* with gypsum: the presence of gypsum below gold is suggested by XRF analysis
329 which evidences Ca, S and Sr; the last element has been recently suggested (Franceschi &
330 Locardi, 2013) as a marker for natural gypsum;

331 - *assiso* with gypsum and Armenian bole;

332 - *assiso* with gypsum, lead white and Armenian bole;

333 - *assiso* with gypsum, Armenian bole and cinnabar;

334 - *assiso* with yellow bole, cinnabar and lead white;

335

336 *v) Green*

337 Three different green paints were identified, which characterised three different hands
338 working on the *Messale*. In the Calendar part, the painter used a mixture of ultramarine blue
339 and yellow ochre; this last can be hypothesised according to the detection of iron by means of
340 XRF. In the main part, instead, the artists used indigo/woad (in FORS spectrum the
341 absorption band at ca. 660 nm is well detectable) mixed with yellow ochre. Finally, only in
342 the central bifolium (ff. 206v and 207r) which is assigned to the main artist, all greens are
343 made with *verdigris*, a synthetic pigment largely used in miniature painting; *verdigris* was
344 identified according to the absorption band at ca. 720 nm and the detection of copper by
345 means of XRF. Rather than indicating three different hands, this variety could mean that the
346 main artist wanted to give different symbolic value to the different features depicted.

347

348 *vi) Grey*

349 Grey parts were mostly painted with a mixture of lead white, suggested by the detection of Pb
350 by means of XRF, and a carbon pigment. Some features, however, were painted with silver,
351 identified by XRF. In some cases, such as for the helmets of soldiers at f. 206v (Fig. 4), small
352 Ag leaves were probably used, perhaps applied on a yellow bole, lead white and cinnabar
353 according to the underlying presence of yellow ochre (identified according to the absorption
354 band at ca. 900 nm in FORS spectrum), Pb, Hg and S as detected by means of XRF.

355



356 Fig. 4 - Exploded view of the miniature at f. 206v (left) and 200x image of a grey helmet
357 (right)
358

359 In other cases Ag was used powdered, similarly to shell gold. A particular feature is the shield
360 with grey bands at f. 19r which shows an unusually high amount of Pb: most probably the
361 shield is a later addition painted by another artist.
362

363 *vii) Orange*

364 In the Calendar, *red lead* or *minium* – Pb_3O_4 – a very common and cheap synthetic pigment,
365 identified according to the inflection point at ca. 560 nm in FORS spectrum, was used for
366 orange hues. In the main part, red lead was used either pure and in mixture of red ochre.
367

368 *viii) Pink*

369 For rendering pink hues, i.e. for incarnates, the artists used only red pigments such as *red lead*
370 diluted with lead white (this last suggested by the detection of Pb by means of XRF); no dyes
371 or lakes were identified on such instances.
372

373 *ix) Purple*

374 For a wide range of hues, from dark red to purple and violet, the painters used *brazilwood*, the
375 dye extracted from different tree species native of South-eastern Asia such as *Caesalpinia*
376 *sappan*. Brazilwood was identified according to the absorption band at ca. 560 nm in FORS
377 spectrum. This dye was traded in Europe from Asia since at least 12th century (Roger et al.,
378 2003), so its use was all but usual in late Middle Ages. The dye was used for several
379 decorative features, but mostly initials and backgrounds of inhabited initials. In the Calendar,
380 pure brazilwood was used, while in the main part the painters used also brazilwood mixed
381 with cinnabar (suggested by the detection of Hg by means of XRF) for dark red tones and
382 brazilwood mixed with indigo, according to two absorption bands at ca. 560 and 660 nm in
383 FORS spectrum, for violet tones.
384

385 *x) Red*

386 In the Calendar, the only red pigment was *cinnabar*, identified according to the inflection
387 point at ca. 600 nm in FORS spectrum and confirmed by the detection of Hg by means of
388 XRF. In the main part, instead, the various artists used cinnabar but also red lead, red ochres
389 and cinnabar mixed (or adulterated!) with red lead; the mixture cinnabar/red lead was

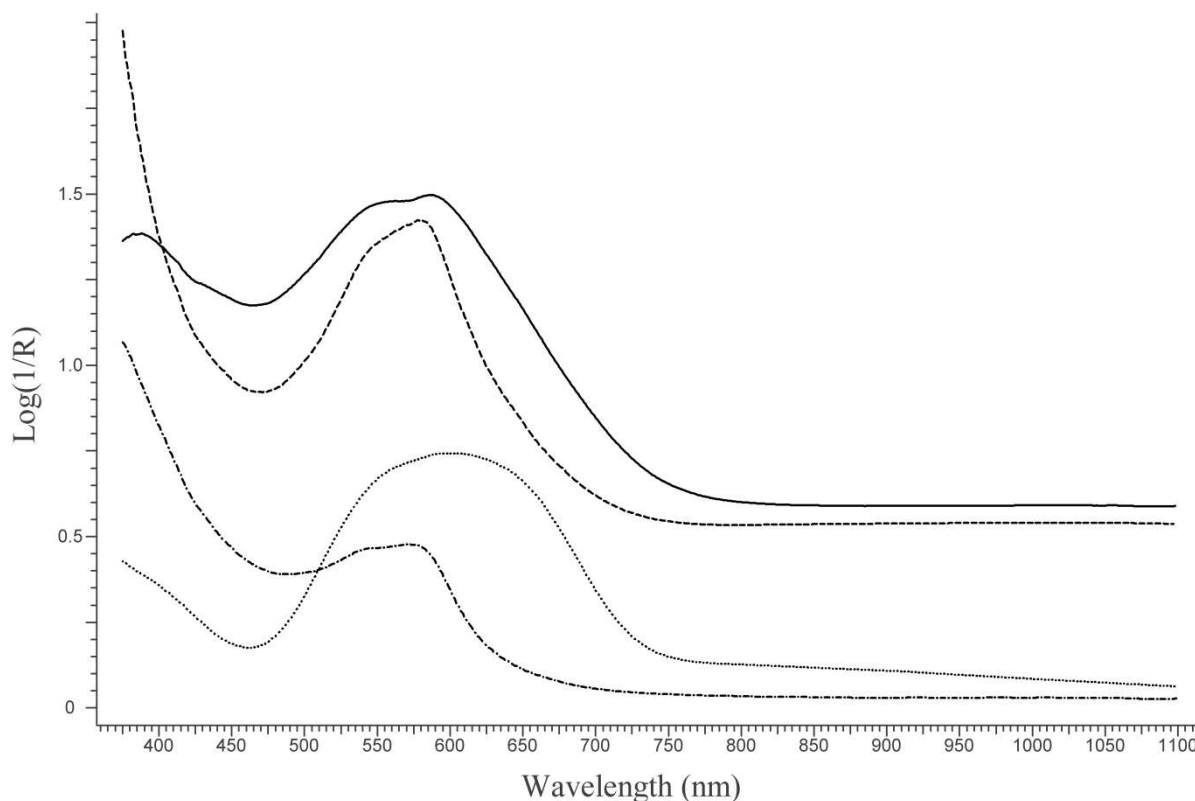
390 identified according to two inflection points at 560 and 600 nm in FORS spectrum and
391 confirmed by the detection of Hg and Pb by means of XRF.

392
393 *xi) Violet*

394 One remarkable feature of the *Messale* is the extensive use of delicate pen-work decorating
395 small red and blue initials. While the pen-flourishes decorating blue initials were made with
396 cinnabar, the pen-work decorating red initials was made with *folium*, the dye extracted from
397 *Chrozophora tinctoria* plant; *folium* was identified according to its typical absorption bands at
398 550 and 580 nm in FORS spectrum. Though the composition of this dye is largely unknown
399 (Aceto et al., 2015), its use in miniature painting was documented in many instances (Aceto et
400 al., 2017a; Aceto et al., 2017b) and above all in 14th and 15th centuries manuscripts of Italian
401 and French production. The wide use of *folium* on the *Messale* is not surprising considering
402 that Avignon is only 60 Km far from Grand-Gallargues (present day Gallargues-le-
403 Montueux), a small hamlet in the Gard department which was in Middle Ages the European
404 centre of cultivation of *Chrozophora tinctoria* and of production of the dye.

405 In many instances, *folium* was added with ultramarine blue as evidenced by FORS analysis
406 (Fig. 5) in which the spectral features of ultramarine blue (absorption band at 600 nm) overlap
407 to those of *folium* (absorption bands at 550/580 nm); XRF analysis confirmed the presence of
408 ultramarine blue according to a higher amount of Si, S and K. The mixture *folium*/ultramarine
409 blue was perhaps done by the artists in order to obtain a more intense blue hue.

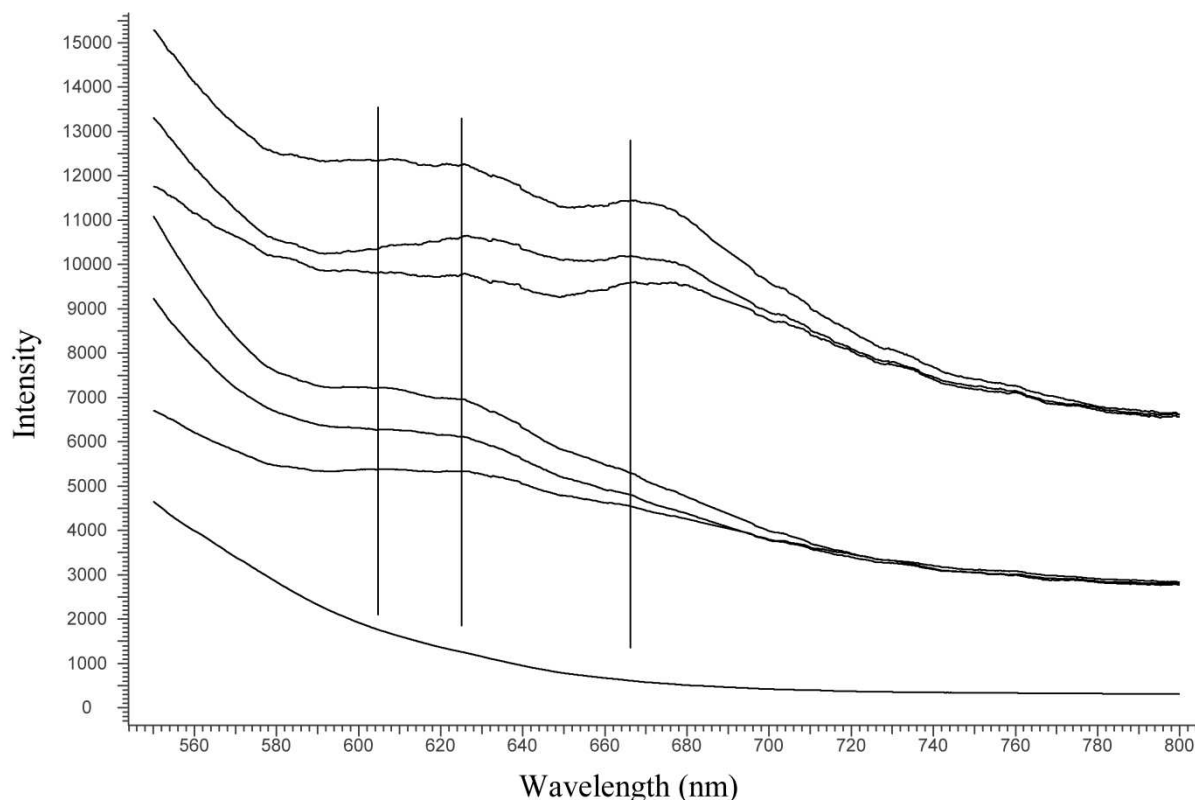
410



411
412 Fig. 5 - FORS spectra in Log(1/R) coordinates of a violet pen-flourished decoration filigree
413 (dashed line) and an intensely blue pen-flourished decoration (solid line) compared with a
414 standard paint of *folium* (dashed-dotted line) and a standard paint of ultramarine blue (dotted
415 line)

416

417 Under the stylistic point of view, at least two different pen-flourishers can be recognised in
 418 the making of red and violet pen-work: one more gifted artist, who can be identified as the
 419 illuminator Bernard de Toulouse (Manzari, 2014) and one more conventional craftsman.
 420 Indeed, the analysis of violet pen-work – which in France is specifically restricted to
 421 manuscripts produced in the South (Manzari 2006) – by means of spectrofluorimetry (Fig. 6)
 422 evidenced two slightly different preparations corresponding to the two different styles of
 423 drawing, according to spectral features at 605/625 nm (Aceto et al., 2015) in the pen-work
 424 attributed to Bernard de Toulouse and at 605/625/665 nm in the pen-work attributed to a
 425 second hand. Apparently, the second illuminator used a recipe which contained a compound
 426 with a further fluorophore in addition to folium.
 427



428
 429 Fig. 6 - Fluorimetry spectra of violet pen-work made by Bernard de Toulouse (center lines)
 430 and by another illuminator (top lines); the spectrum of parchment (bottom line) is given for
 431 reference

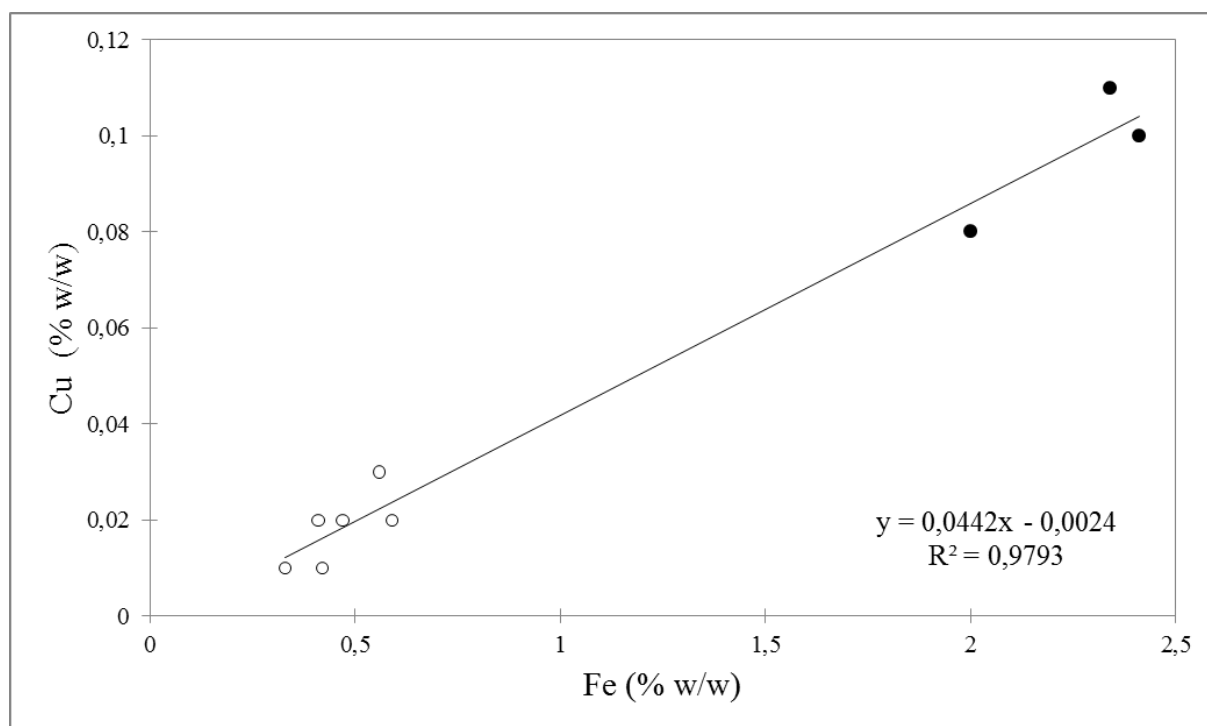
432
 433 *xii) White*
 434 The only white pigment used throughout the manuscript was *lead white*, suggested by the
 435 detection of Pb by means of XRF.

436
 437 *xiii) Yellow*
 438 The yellow hue is rare, probably due to the wide use of gold. The main use of yellow seems to
 439 be as preparatory ground for gold and silver leaf, as described before; in this case, as in the
 440 rare cases of miniature details, the pigment used was *yellow ochre*, identified according to the
 441 absorption band at ca. 900 nm in FORS spectrum and confirmed by the detection of Fe by
 442 means of XRF.

443

444 *xiv) Inks*

445 The coloured inks were made with the same pigments used for miniatures, that is cinnabar for
 446 red inks and ultramarine blue for blue inks. For the main text and musical notations, iron gall
 447 inks (IGI) were used, as identified by means of FORS analysis (Aceto & Calà, 2017c). The
 448 composition of IGI, as it results from XRF analysis, seems to be homogeneous all through the
 449 manuscript, as if it had been written by a single scribe. In addition, there is no apparent
 450 difference between the ink used for text and that used for musical notations: both show a
 451 Fe/Cu ratio of ca. 20:1 (Fig. 7) with a small amount of Zn. The absolute amounts of Fe and
 452 Cu in musical notations are higher only because the spots analysed with XRF (3 mm) were in
 453 those cases completely filled with ink, while the text lines were thinner (1-1.5 mm).
 454



455 Fig. 7 - Fe vs Cu plot as determined by XRF analysis on text (white circles) and on musical
 456 notations (black circles)
 457

458 The overall condition of inks is very good all through the *Messale*, so it seems like the scribes
 459 used a well-balanced recipe for IGI.
 460

461 *xv) The different palettes*

462 According to the results of non-invasive measurements, it is possible to define the palettes
 463 used in the different sections in which different artists were at work. The sections seem to be
 464 at least four: (1) the Calendar; (2) the main part; (3) the starting quire of the main part at ff.
 465 19r-26v; (4) the bifolium 206v-207r. The main colourants used are listed in Table 1.
 466

Colours	Calendar	Main	ff. 19r-26v	ff. 206v-207r
black	carbon	carbon	carbon	carbon
blue	ultramarine blue	ultramarine blue, woad	ultramarine blue, woad	ultramarine blue, woad
brown	red ochre	red ochre	red ochre	red ochre

gold	shell gold, gold leaf	shell gold, gold leaf	shell gold, gold leaf	shell gold, gold leaf
green	ultramarine blue/yellow ochre	woad/yellow ochre	woad/yellow ochre	verdigris
grey	shell silver	shell silver	shell silver	silver leaf
orange	red lead	red lead/red ochre	red lead/red ochre	red lead/red ochre
pink	red lead/lead white	red lead/lead white	red lead/lead white	red lead/lead white
purple	brazilwood	brazilwood	brazilwood	brazilwood
red	cinnabar	cinnabar, cinnabar/red lead, brazilwood/cinnabar	cinnabar, cinnabar/red lead, brazilwood/cinnabar	cinnabar, cinnabar/red lead, brazilwood/cinnabar
violet	folium, folium/ultramarine blue	folium, folium/ultramarine blue, brazilwood/indigo	folium, folium/ultramarine blue, brazilwood/indigo	folium, folium/ultramarine blue, brazilwood/indigo
white	lead white	lead white	lead white	lead white
yellow	yellow ochre	yellow ochre	yellow ochre	yellow ochre

468 Table 1 - Palettes used in the different parts of the *Messale*

469

470 *e) Sequence of manufacture of the Messale*

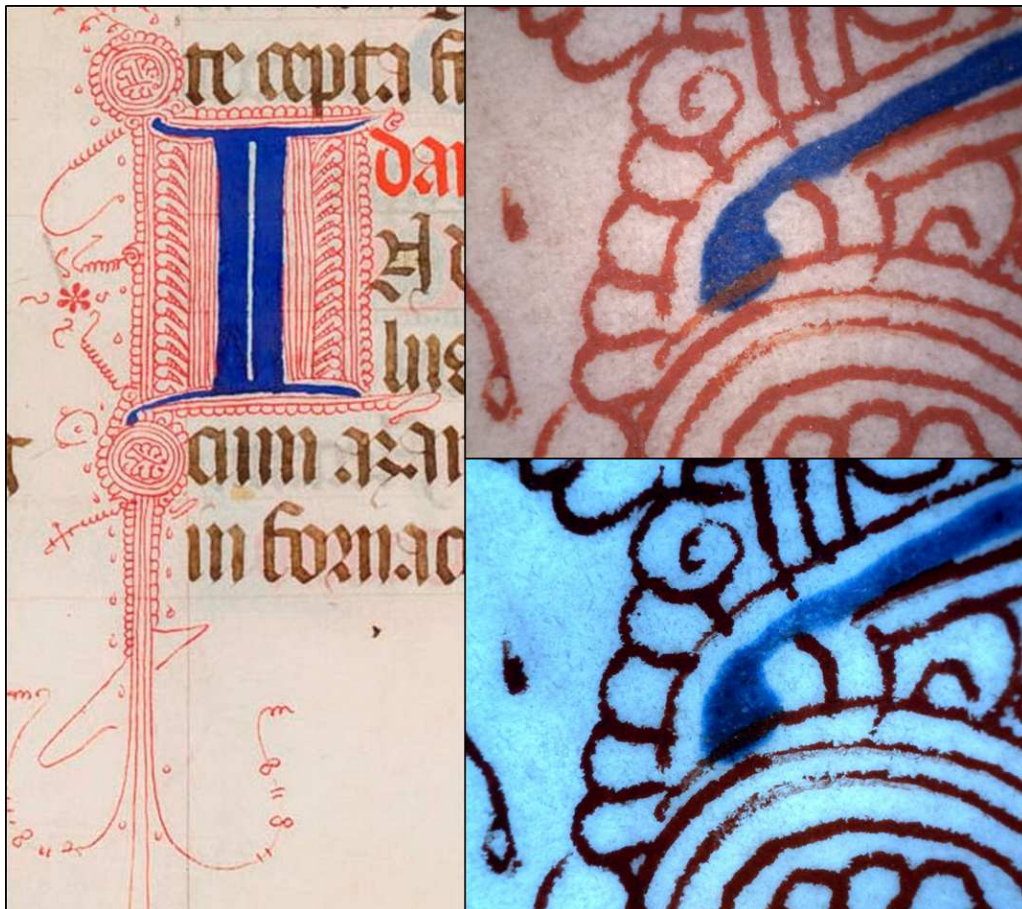
471 The results of the different analyses, including micro images taken on particular features,
472 **complemented the technical-artistic knowledge on miniature painting and** allowed
473 hypothesising a sequence of operations in the manufacture of the manuscript, from the point
474 of view of the materials involved. The order, **outlined after discussion involving different**
475 **competences**, is the following:

476 1) First at all, the ruling, that is the lines used to delimit the written surface, are traced; in the
477 Calendar part ruling was traced either with cinnabar (red) and with folium (violet), while in
478 the main part they it was traced with IGI;

479 2) Then text and musical notations were written by the scribes with IGI;

480 3) Then comes the decoration of the text with red and blue initials, ornamented by,
481 respectively, violet and red pen-flourished decoration: this sequence can be appreciated in
482 Fig. 8, where the red pen-work apparently overlaps the blue initial previously laid.

483

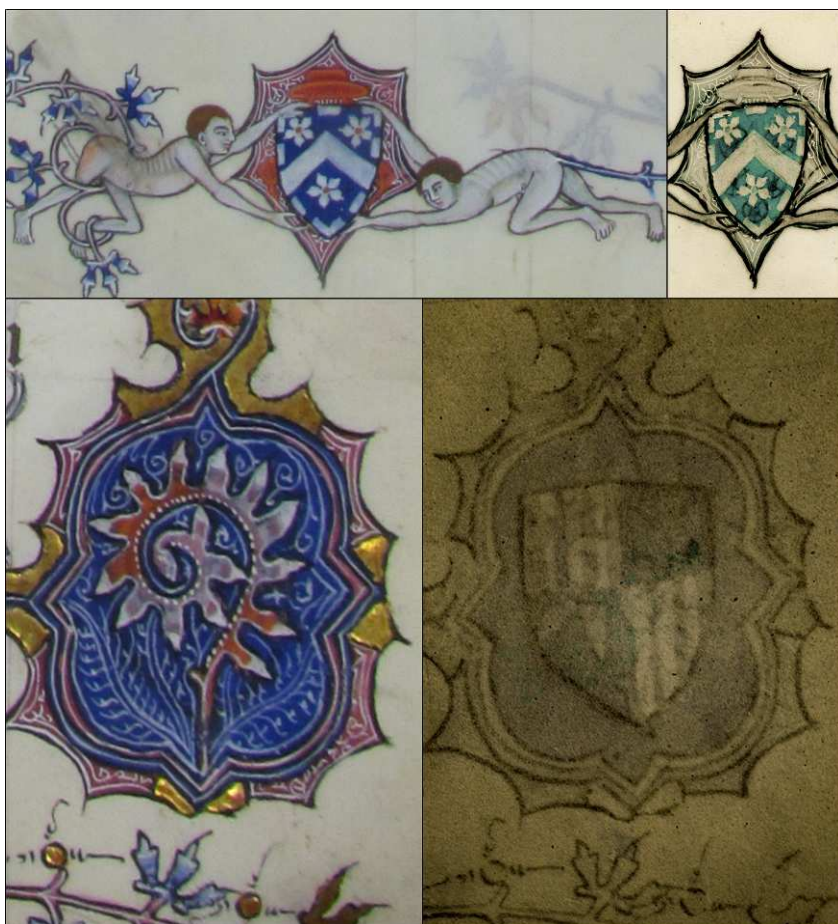


484
 485 Fig. 8 - Decorated blue initial with red pen-work at f. 66v (left), 50x image (top right) and 50x
 486 UV image (bottom right)

- 487
 488 4) gold leaves are laid and contours are defined.
 489 5) Miniatures are then painted in the fields specifically left by scribes; usually the leading
 490 artist carried out the preparatory drawings, while less-experienced artists painted the first
 491 layers and the main artist finished hands and faces (Alexander, 1992);
 492 6) In the Calendar part, the zodiac signs were the last features painted.

493
 494 *f) Details from IR photography*

495 In the Introduction paragraph, the various changes in ownership of the *Messale* have been
 496 described. The arms of Cardinal Rossell, the original owner, still appear in few instances: the
 497 five roses, the red and yellow *Barras de Aragón* (the coat of arms of the Crown of Aragon)
 498 and the red Cardinal's hat. Many others, though, were hidden by the artists who changed some
 499 decorative features in order to adapt the manuscript to the needs of the new owners. By means
 500 of IR photography it was possible to confirm this sequence. Some examples can be
 501 appreciated in Fig. 9. At f. 287v the three roses of Cardinal Guillaume de Bragose, owner
 502 from 1361 to 1367, were overpainted on the five roses of Cardinal Rossell, adding two
 503 animals supporting the shield. At f. 252r the *Barras de Aragón* appear below a generic
 504 decorative feature when the image is seen under IR light: in this case, after the patron's
 505 sudden death, the artists overpainted his arms perhaps in preparation for the sale of the
 506 *Messale* to a new, but still unknown, purchaser.



508
 509 Fig. 9 - The three roses of Cardinal Guillaume de Bragose (top left) over the five roses of
 510 Cardinal Rossell (top right) at f. 287v; a decorative feature at f. 252r (bottom left) and the
 511 same photographed under IR light (bottom right)

512
 513

514 4) Conclusions

515 The combined use of non-invasive techniques, and the opportunity of applying them with ease
 516 due to the restoration of the artwork, offered the perfect situation to obtain a very considerable
 517 amount of information on the history of the *Messale Rosselli*, its manufacture and the raw
 518 materials used. The different artists who contributed in its decoration employed the most
 519 precious pigments known at the age: lapis lazuli, cinnabar, gold, silver. These and other
 520 colourants were used both pure and in mixture, in order to obtain a wide range of hues.
 521 Chemical analysis provided the characterisation of the palettes used by the different artists,
 522 reinforcing the hypotheses raised by scholars. In addition, the overall palettes have been
 523 evaluated according to the availability of raw materials in the geographic area around
 524 Avignon, finding that most of the colourants could be at easy disposal of the artists.
 525 Information has also been obtained concerning the preparation of the parchment and the
 526 volume itself. The systematic measurement of the width of folios allowed hypothesising the
 527 number of the animals slaughtered to produce parchment, and the way of using skins. XRF
 528 analysis on the folios suggested that different preparations were used. Finally, **eZooMS**
 529 analysis evidenced that calf and goat, but not sheep, were used to produce the parchment of
 530 the *Messale Rosselli*.

531 By means of IR photography, it was also possible to obtain information on the sequence of
532 owners of the manuscript, identifying the materials used in the coats of arms of each ones.

533

534

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542

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