

1 **Characterisation of the different hands in the composition of a 14th century breviary by means**
2 **of portable XRF analysis and complementary techniques**

3 Maurizio Aceto^a, Angelo Agostino^{b*}, Gaia Fenoglio^b, Valerio Capra^d, Enrico Demaria^e and Patrizia
4 Cancian^f

5 ^a Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università degli Studi del Piemonte
6 Orientale, viale Teresa Michel, 11 - 15121 Alessandria, Italy & Centro Interdisciplinare per lo
7 Studio e la Conservazione dei Beni Culturali (CenISCo), Università degli Studi del Piemonte
8 Orientale, via Manzoni, 8 - 13100 Vercelli, Italy. Tel.: +39 0131 360265; Fax: +39 0131 360250; E-
9 mail: maurizio.aceto@uniupo.it.

10 ^b Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria, 7 - 10125 Torino, Italy.
11 Tel.: +39 011 6707585; Fax: +39 011 6707590; E-mail: angelo.agostino@unito.it.

12 ^c Nanostructured Interfaces and Surfaces Center of Excellence (NIS), via Giuria, 7 - 10125 Torino,
13 Italy.

14 ^d Laboratorio di restauro del libro, Abbazia benedettina dei S.S. Pietro e Andrea, Borgata San
15 Pietro, 4 - 10050 Novalesa (TO), Italy.

16 ^e Astra Media s.r.l., via al Cerrone, 12 - 10040 Villar Dora (TO), Italy. Tel. +39 011 9351333; Fax
17 +39 011 9351703; E-mail: enrico.demaria@astramedia.it.

18 ^f Dipartimento di Studi Storici, Università degli Studi di Torino, via Verdi, 8 - 10124 Torino, Italy.
19 E-mail: cancianpatrizia@gmail.com.

20 * corresponding author

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22 **Abstract:** A 14th century breviary known as *Breviario di San Michele della Chiusa*, produced at the
23 disposal of the monks of Sacra di San Michele abbey (near Turin, Italy) has been analysed in order
24 to identify the different authors who contributed in its making. The study aimed at revealing how
25 many scribes composed the text and the musical notations and how many artists worked for
26 miniatures and for the decorations of initials. All inks and decorative features have been analysed
27 by means of portable XRF spectrometry for determining elemental distribution and by means of
28 UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS) and spectrofluorimetry
29 for identifying colourants. The results on non-invasive measurements highlighted that at least 11
30 persons (6 scribes for the text, 2 scribes for the musical notations, 2 artists for initials and filigrees,
31 1 artist for the full-page miniature at f. 208v) were at work at the *Breviario*. Moreover, the black
32 inks used for text and notes have an anomalous composition, being iron-gall inks with a larger than
33 usual amount of zinc, possibly as a consequence of the use of vitriols made from goslarite; this
34 suggests that the scribes could come from Northern Europe.

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36 **Keywords:** manuscript; inks; non-invasive; XRF; goslarite

37

38 **1 Introduction**

39 The contributions of analytical chemistry to cultural heritage can be highly variegated,
40 ranging from authenticating artworks or archaeological remains to identifying the geographic
41 provenance of an item. One fascinating aspect is the identification of different hands in an artwork,
42 i.e. the different authors who contributed in its creation. This can be revealed if authors used
43 materials that can be somehow distinguished: an example is the palette used in a painting.^[1,2] The
44 identification of different hands provides useful information for a thorough comprehension of the
45 artwork, such its meaning and symbolic value, its conservation and restoration history, etc.

1 Items that may be created from different contributions are typically the manuscripts. In the
2 Middle Ages, in the creation of a manuscript inside a scriptorium it was common practice dividing
3 the whole of the writing among different scribes,^[3] in order to speed up the procedure; all sections
4 were then unified by another artisan specialised in bookbinding. Usually, scribes were designated
5 for writing only, while other artisans, more skilful in painting or drawing, were designated for
6 miniatures, decorated initials and other artistic features. In the case of musical texts such as
7 antiphonaries or breviaries, it was possible that some scribes contributed for text while other scribes
8 contributed for the musical notation.^[1]

9 While it is not generally difficult to identify different contributions in a painting, according
10 to the different palettes present, it may be harder to distinguish among different scribes in a
11 manuscript because it is highly probable that the same kind of ink had been used, especially if
12 scribes worked inside the same scriptorium. With concern to black inks, in the Middle Ages
13 manuscripts in Europe were mostly composed with the so-called iron-gall inks (IGI in the
14 following) obtained from gallnuts.^[1] The preparation of IGI involved milling gallnuts, extraction
15 with water and addition of FeSO₄, known as *vitriolum romanum* (Roman vitriol), and of other
16 vitriols (CuSO₄, ZnSO₄), to form a soluble Fe²⁺-tannins complex. Oxidation of Fe²⁺ to Fe³⁺ by air
17 caused precipitation of the insoluble Fe³⁺-tannins complex which, dispersed into gum Arabic or
18 other ligand media, generated a brown-black substrate suitable for writing, with a much higher
19 durability than carbon-based inks. Despite IGI could be prepared with innumerable variations with
20 concern to ligand media and/or additives,^[6] it is usually not possible distinguishing different
21 recipes, especially when only non-invasive measurements are involved. Moreover, when texts from
22 the same scriptorium or even from the same geographic or cultural area are considered, it is possible
23 that the same recipe had been used for preparation of black ink. At the same time, though, it must be
24 considered that scribes were used to prepare small amounts of inks, covering few days of writing;
25 preparations were not done on industrial scale, so that from one batch of ink to the following there
26 could be slight differences in the raw matters, depending on their availability. This statement is
27 even truer when considering different scribes, each one preparing his own ink. In the end, therefore,
28 one possibility of distinguishing different preparations of ink can/must rely on the distribution of
29 metals contained in the raw matters, such as vitriols or additives, which can be present as main
30 components (usually iron or copper) or as impurities (manganese, zinc, lead, nickel, etc.). It is
31 obvious that such a task can be fulfilled only with elemental analysis; therefore, techniques such as
32 XRF spectrometry have a key role in studies on inks.

33 Similar considerations can be drawn on inks of other colours, i.e. red, blue, etc. which are
34 made from pigments: cinnabar, red ochre or red lead in the case of red inks, azurite or lapis lazuli
35 for blue inks. Again, different preparations could involve different impurities and therefore
36 characteristic metal distributions.

37 In the past, some works were carried out in the analysis of manuscripts that involved
38 characterisation of the elemental distribution in inks. Particularly interesting were the studies of
39 Giuntini *et al.* on Galileo's writings,^[7] which allowed to reconstruct a time sequence in their
40 making. Hahn *et al.*^[8] analysed historical manuscripts and music compositions, again identifying
41 time sequences in the writings. Aceto *et al.*^[9] distinguished inks in the black and red text of the
42 Vercelli Gospels, a 4th century manuscript reputed to be the oldest Gospels in Latin. Similar studies
43 were performed on printing inks^[10] that allowed identifying different artisans at work on
44 Gutenberg bibles.

45 In this study, a 14th century breviary written on parchment and known as *Breviario di San*
46 *Michele della Chiusa* has been analysed in order to identify the different authors who contributed in
47 its making. The study aimed at revealing how many scribes composed the text and the musical
48 notations and how many artists worked for miniatures and for the decorations of initials. All inks
49 and decorative features have been analysed by means of portable XRF spectrometry for determining

1 elemental distribution and by means of UV-Visible diffuse reflectance spectrophotometry with
2 optic fibres (FORS) and spectrofluorimetry for identifying colourants.

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4 **2 Materials and methods**

5 *2.1 X-Ray Fluorescence spectrometry (XRF).*

6 XRF measurements were performed with an EDXRF Thermo (Waltham, USA) NITON
7 spectrometer XL3T-900 GOLDD model, equipped with an Ag tube (max. 50 kV, 100 μ A, 2 W), a
8 large area SDD detector, energy resolution of about 136 eV at 5.9 keV. Analysed spot had an
9 average diameter of 3 mm and was focused by a CCD camera, with a working distance of 2 mm.
10 Total time of analysis was 240s. The instrument is held in position with a moving stage allowing
11 micrometric shifts, in order to reach the desired probe-to-sample distance; the stage is laid on a
12 tripod. The obtained spectra have been processed with the commercial software WinAxil, derived
13 by the academic software QXAS from IAEA.

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15 *2.2 UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS).*

16 FORS analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-
17 ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light
18 source; detector and light source were connected with fibre optic cables to an FCR-7UV200-2-
19 1,5x100 probe. In this configuration, light is sent and retrieved with a single fibre bundle positioned
20 at 45° with respect to the surface normal, in order not to include specular reflectance. The spectral
21 range of the detector was 200-1160 nm; depending on the features of the monochromator (slit width
22 50 μ m, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra
23 resolution was 2.4 nm calculated as FWHM (Full Width at Half Maximum). Diffuse reflectance
24 spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and
25 guaranteed to be reflective at 98% or more in the investigated spectral range. Blank correction was
26 not efficient on both the extremes of the spectral range, therefore the regions 200-250 and 900-1160
27 were not considered in the discussion. The diameter of the investigated area on the sample was 1
28 mm. In all measurements the distance between the probe and the sample was kept constant at 1 mm.
29 In order to visualise the investigated area on the sample, the probe contained a USB endoscope. The
30 instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition
31 time of 1.0 s for each spectrum. The system was managed by means of AvaSoft v. 8TM dedicated
32 software, running under Windows 7TM.

33

34 *2.3 Spectrofluorimetry.*

35 An Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was employed to
36 record molecular fluorescence spectra. The instrument is equipped with a 365 nm Jaz-LED internal
37 light source; a QF600-8-VIS/NIR fibre fluorescence probe is used to drive excitation light on the
38 sample and to recover the emitted light. The spectrophotometer works in the range 191-886 nm;
39 according to the features of the monochromator (200 μ m slit width) and detector (2048 elements),
40 the spectral resolution available is 7.6 nm calculated as FWHM. The investigated area on the
41 sample is 1 mm in diameter. In all measurements the sample-to-probe distance was kept constant to
42 1 mm (corresponding to the focal length of the probe) with aid of a small black cylinder inserted on
43 top of the probe, which also shields external light. Instrumental parameters were as follows: 2 s
44 integration time, 3 scans for a total acquisition time of 6 s for every spectrum. The system is
45 managed with SpectraSuiteTM software under Windows 7TM.

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47 *2.4 Optical microscopy*

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

4 5 2.4 Multivariate analysis

6 Principal Component Analysis (PCA) was performed on XRF elemental data using
7 XLSTAT (Addinsoft, Paris) v. 2012.2.02 software.

8 9 3 Results and discussion

10 The *Breviario* is datable to 1315 according to a precise notation inside it, and was composed
11 in Northern Italy at the disposal of the monks of San Michele della Chiusa abbey, a well-known
12 centre of spirituality still active at present, located in a mountain zone near Turin (Piedmont, Italy).
13 It is composed by two books: the *Temporale*, i.e. a cycle of Sunday celebrations and of *Tempi Forti*
14 of the year, and the *Santorale*, i.e. a calendar of Saints' feast days. Alongside the text, red and blue
15 small initials are present, some simpler and some with much more elaborated filigrees. These last
16 occur in red colour on blue initials, and in purple colour on red initials. A single, though highly
17 relevant from the artistic point of view, full-page miniature is present at f. 208v, depicting Saint
18 Michael fighting against a dragon.

19 The construction of the page architecture was done, as commonly in medieval manuscripts,
20 by means of *rubricatura*, i.e. by tracing straight lines at definite intervals in order to mark the
21 succession of writing lines. These lines, though very light, are still visible in the *Breviario* and were
22 done with a tip lead (Pb) as demonstrated by XRF analysis at various points.

23 In the following discussion, results will be shown for the analysis of the black inks used for
24 text and for notes, of the red, blue and purple pigments used for initials and decorations, and of the
25 palette used for the miniature at f. 208v.

26 It is well known that x-ray sources can easily penetrate parchment (or paper as well) and
27 cause fluorescence emission from the back side of the folio under analysis and from one or more
28 underlying folios also, if they contain written/painted areas. Therefore, all XRF measurements were
29 performed choosing areas that were free from ink or paint on the corresponding back side of the
30 folio; moreover, to avoid contribution from the underlying folios, 10 cellulose acetate sheets were
31 put below the folio under analysis in order to create thickness. Cellulose acetate was chosen as a
32 material free from metals after checking it with a blank measurement. Finally, care was taken in
33 avoiding areas that could have contributions from the opposite folio in case of loss of colour.

34 35 3.1 Black inks

36 All the black inks used for the *Breviario* for the writing, the musical notations and the text
37 accompanying music, are of the IGI type as suggested by their FORS spectra (Figure 1). As all
38 these inks appeared very dark, while usually IGIs appear brown or dark brown, a Raman analysis
39 was performed *in situ* to verify the possible presence of carbon as an additive to IGI, but the
40 hypothesis of an IGI/carbon mixed ink proved wrong as no trace of carbon was identified. Inks with
41 a similar dark tone were noted on the text of the 8th century Insular manuscript *Lindisfarne Gospels*^[12]
42 but in that case also, no clear addition of carbon to IGI was highlighted. Therefore, Raman
43 analysis confirmed that the black texts of the *Breviario* were written with a peculiar recipe made of
44 pure IGI. Additionally, as it will be discussed later on, these inks are very peculiar in that they
45 contain an unusually high amount of copper and zinc with respect to iron, while it is known from
46 traditional sources that these inks were mostly prepared using mostly iron sulfate.^[13,17]

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3.1.1 Recognition of different hands in the text

According to the palaeographic studies by Notarrigo,^[18, 19] at least six different scribes worked at the *Breviario*, despite the fact that both volumes are graphically homogeneous, being written with a uniform gothic style known as *littera textualis*. This type of writing was developed in 13th and 14th century in France and England but later spread all over Western Europe.^[20] The six scribes can be distinguished as follows, on a stylistic basis:

- Scribe A - *Temporale* volume;
- Scribe B - *Temporale* volume, text accompanying musical notations;
- Scribe C - *Santorale* volume, first 20 *folia*
- Scribe D - *Santorale* volume, *folio* 20 recto and verso, documentary lowercase cursive writing
- Scribe E - *Santorale* volume, from 21 recto to the end of the volume
- Scribe F - *Santorale* volume, text accompanying musical notations.

Scribes can in turn be divided into three groups, according to the variety of style:

- 1 - C, E and F hands: these scribes used a gothic librarian style of international effort;
- 2 - A and B hands: these scribes used a librarian writing very similar to *rotunda*;
- 3 - D hand: this scribe used a lowercase cursive writing.

Examples of letters from the six scribes may be seen in Figure 2. For each of the different sections, at least 6 points of analysis were executed by means of XRF spectrometry, determining the following elements: Al, Cu, Fe, K, Pb, S, Si and Zn; in addition, Ca, Cl, P, Sr and Ti were also identified but their signals were comparable to the signal arising from parchment, therefore they were not used in the comparison among different hands. All data, expressed as **weight percent (% w/w)**, were normalised to iron. A Principal Component Analysis (PCA) was performed on the dataset composed by 7 elements: Al, Cu, K, Pb, S, Si and Zn. The results of this investigation are shown in Figure 3 which reports the PC1 vs PC2 plot, accounting for 75.48% of the overall information. The classification is only partially coherent with the one proposed on palaeographic basis: it appears that hands E and F used similar inks, but hand C is very different from them. Hands A and B used inks not correlated as well, with A more similar to C and B more similar to D. The differences among inks in the various hands arise from raw sources, of course, with a major role given to vitriols, as it appears from the loadings plot superimposed to PC1 vs PC2 plot (Figure 3): the inks used by hands E and F have a higher content of Cu and Zn, while the inks used by hands B and D are poorer in vitriols other than Fe. A biplot showing the content of Cu and Zn normalised to iron (Figure 4) reinforces this classification.

The consequence of these results is the following: if, according to the palaeographic analysis, six different scribes were at work on the *Breviario*, it is reasonable to think that every scribe used his own ink, prepared according to a personal recipe; the alternative hypothesis of a common ink can be done only for scribes E and F.

It must be noted that a marked difference in the appearance of inks exists between the hair side (the side originally facing the animal's hair, generally recognisable by traces of hair follicles) and the flesh side (the side originally facing the animal's flesh) of folios: on the former side the text is darker and more clean, while on the latter side it is more faded (Figure 5). This difference, though, must not be attributed to different hands in the writing, but rather to the preparation of the parchment which was made according to the subalpine style;^[1] this caused a stronger “hooking” of the ink to parchment on the hair side. XRF measurements confirmed that inks of the opposite sides of the same folio were absolutely identical in all instances.

1 3.1.2 Musical notations

2 Musical notations were made with IGIs appearing darker than those used for text. As for
3 text, musical notations were not made by a single scribe: according to a palaeographic study,^[22] at
4 least two hands wrote them:

5 Scribe 1 - *Temporale* volume, ff. 86r – 93v, 244v-263r; *Santorale* volume, ff. 139r-145r, 191r-
6 194v, 245v-254r, 265r-266v, 267r-279v;

7 Scribe 2 - *Santorale* volume, ff. 145v-151v, 254v-259v, 266v-267r, 288v-305r.

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9 XRF analysis on notes highlighted again a significant difference between the two styles, as can be
10 appreciated in Figure 6 (top) which shows the PC1 vs PC2 plot, accounting for 66.76% of the
11 overall information; the same elements identified in text analysis, i.e. Al, Cu, K, Pb, S, Si and Zn,
12 were used after normalisation to Fe. In this case the difference between the two hands seems more
13 related to accompanying elements, such as Al, Si, K, than to the elements associated to vitriols, that
14 is Cu and Zn; it is therefore probable that the two scribes assigned to the writing of music used
15 similar recipes for what concerns the amount of vitriols, but with a difference in the additives.

16 Interestingly, the ink used for musical notations shows slight differences with respect both to
17 the ink used for the main text and to that used for the text accompanying music. Using again PCA
18 analysis on XRF dataset, from PC1 vs PC2 plot (Figure 6, bottom), accounting for 66.29% of the
19 overall information, it seems like the inks used for music (scribes 1 and 2) have intermediate
20 features between those of scribes A, B, C and D and those of scribes E and F. It is particularly
21 noteworthy that the inks used by scribes B and F, respectively at work for the text accompanying
22 music in the *Temporale* and the *Santorale* volume, are different from the inks used for the musical
23 notations.

24 One can therefore hypothesise that different scribes were at work, a group writing text
25 (scribes A, B, C, D, E and F), another smaller group writing music (scribes 1 and 2).

26 27 3.1.3 Comparison with other inks

28 The high contents of Zn and Cu in the black IGIs of the *Breviario* are somewhat unusual
29 with respect to known data obtained on medieval manuscripts. In Middle Ages different kinds of
30 vitriols were used, among which the so-called *vitriolum goslarensis* or German vitriol^[23] which,
31 apart from iron, was rich in zinc, being obtained mainly from the mineral goslarite, an eptahydrate
32 zinc sulfate with formula $ZnSO_4 \cdot 7(H_2O)$ originally found in Rammelsberg mine, near Goslar
33 (Niedersachsen, Germany). According to the scientific literature, IGIs rich in zinc could be more
34 popular in Northern Europe, and perhaps archival research in the documentary sources of Hanseatic
35 League could confirm this in terms of metals and vitriols marketed in the towns of Northern
36 Europe. It is a fact that some analytical studies performed on manuscripts created beyond the Alps
37 highlighted a significant amount of zinc besides iron in IGIs. Van Bos and Watteuw^[23] carried out
38 a survey on illuminated manuscripts produced in the Low Countries in the range 11th-16th centuries,
39 finding mostly Zn-rich IGIs. Similar results were found by Klockenkämper *et al.*^[24] on a Flemish
40 late 15th century manuscript and by Čechák *et al.* on documents of the Kingdom of Bohemia
41 between 14th and 19th century.^[25] Recently Wachowiak *et al.*^[26] reported on the occurrence of inks
42 with a percentage of zinc higher than iron in the 14th-century *Graduale de Tempore de Sanctis* held
43 at Diocese Library in Pelplin (Poland); authors suggested that among the raw sources for these inks,
44 a major role could be played by goslarite.

45 In rare cases the presence of goslarite has been signalled in Italian mines (Friuli Venezia
46 Giulia, Sardinia, Trentino Alto Adige and Tuscany) but not in large amounts. Consequently, it is not
47 surprising that most of the diagnostic information pertaining manuscripts produced in medieval
48 Italy report only classical Fe-rich IGIs. In a work by Lucarelli and Mandò^[27] on a group of
49 documents written in Central Italy between 12th and 15th century, the trend of Cu/Fe ratio showed a

1 raising of copper amount in the inks of later documents, as it was S/Fe ratio, so suggesting that
2 other vitriols could be used in addition to FeSO₄; zinc was found at trace level on most documents
3 except for a small series of manuscripts datable to the start of 15th century, whose Zn/Fe ratio was
4 similar to the one found in the *Breviario*. Verri *et al.*^[28] found high levels of zinc in the inks used
5 for Italian drawings; these artworks, though, were datable to the Renaissance.

6 In order to evaluate the anomaly of the inks of the *Breviario*, a comparison was made with
7 coeval manuscripts produced in the same abbey or in the same geographic area. It is known from
8 literary sources that an active scriptorium was present at the San Michele della Chiusa abbey, which
9 importance was acknowledged in particular in 11th century and later on in 14th century under the
10 regency of abbot Guglielmo III di Savoia (1310-1325).^[29] Unfortunately very few manuscripts from
11 that scriptorium still remain to us, located at Biblioteca Nazionale Universitaria and other
12 institutions in Turin, and most of them being just fragments used as bindings for more recent books.
13 These remains could be identified thanks to stylistic features and/or to the lettering "secundum
14 consuetudinem monasterii Sancti Michaelis de Clusa" ("according to the tradition of San Michele
15 della Chiusa abbey"). Much richer is the heritage of documents on parchment, mostly kept at
16 Archivio Arcivescovile in Turin. The comparison has been carried out against three categories:

- 17 1. manuscripts coeval to the *Breviario*, produced at the San Michele della Chiusa
18 scriptorium: ms. RARI XIX.3 kept at Biblioteca Diocesana in Susa (Italy) and some
19 fragments of liturgical books used as bindings of notarial files presently kept at
20 Archivio di Stato in Turin; in addition, later manuscripts produced at the San Michele
21 della Chiusa scriptorium (mss. D.VI.11 and E.VI.39, Biblioteca Nazionale Universitaria
22 in Turin, 15th century) have been included in the comparison;
- 23 2. manuscripts coeval to the *Breviario*, produced in scriptoria located in Northwestern
24 Italy (i.e. close to San Michele della Chiusa abbey) and presently kept at Biblioteca
25 Nazionale Universitaria in Turin;
- 26 3. documents produced at San Michele della Chiusa abbey datable in a range of ± 16 years
27 with respect to the *Breviario*, nowadays kept at Archivio Arcivescovile in Turin.

28 The black inks of all the books and documents involved in the study were analysed with
29 XRF after verifying their nature as IGIs with FORS analysis. At least 5 points of analysis were
30 determined on each item, verifying the homogeneity of inks along the whole text. The results of the
31 comparison highlight the apparent anomaly of the black inks of the *Breviario*, as it is shown in
32 Figure 7 which reports the PC1 vs PC2 plot, accounting for 74.45% of the overall information. The
33 inks corresponding to A, C, E and F hands have elemental compositions far different from the other
34 samples analysed; the discrimination is supported mostly by higher amounts of Cu, Pb and Zn as
35 suggested by the loadings plot superimposed to PC1 vs PC2 plot (Figure 7). A biplot showing the
36 content of Cu and Zn normalised to iron (Figure 8) confirms the clear distinction. As to the inks of
37 B and D hands, these appear to follow more conventional recipes, being the amounts of vitriols
38 similar to the other samples analysed.

39 The information arising from XRF analysis of the black inks of the *Breviario* allows us to
40 formulate the following hypothesis: combining the palaeographic features of the writing and the
41 differences in ink composition, it is possible not only that in the writing of the *Breviario* six
42 different scribes were at work, but also that at least four of them (hands A, C, E and F) were
43 external to the scriptorium of San Michele della Chiusa abbey, in agreement with the use of IGIs
44 prepared largely from goslarite; the same holds true for the scribes who worked on musical
45 notations. The hypothesis of foreign scribes was already cited by Notarrigo^[19] with concern to A
46 and B hands who could be related to scribes coming from Southern Italy, called at the abbey to
47 offer their services; from XRF results it seems like this hypothesis should be extended to a larger
48 number of scribes, if not to all of them. Alternatively, we must think of local scribes who were
49 aware of the recipes used in Northern European scriptoria and were able to get themselves specific
50 raw sources such as goslarite to produce their black inks. Finally, it must be considered that the

1 abbey was placed inside a cross-border region with frequent contacts with French kingdoms (such
2 as Burgundy), therefore with a high degree of exchange of techniques, materials and people.

3 To reinforce the above cited hypothesis about an external source or knowledge for black
4 inks, it must be noted that the internal differences between A, C, E and F hands (and 1 and 2 hands
5 for what concerns musical notations) are irrelevant if compared with the difference among the inks
6 of the *Breviario* and the inks of all other manuscripts and documents taken into consideration in this
7 study.

8 The use of a higher amount of zinc vitriol in ink could be explained with the role of Zn^{2+} ion
9 as protective agent. Some studies^[8, 30] demonstrated that IGIs containing zinc were better preserved
10 and had a darker tone, while IGIs rich in copper were more brownish and subject to alteration, most
11 probably due to the catalytic effect of Cu^{2+} ion on the degradation of paper or parchment.^[31]

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13 3.2 Red initials and decorations

14 All red rubrics, initials and filigrees in the *Breviario* were made with cinnabar/vermillion
15 (natural or synthetic HgS). As for the text, for decorated initials and filigrees also at least two
16 different styles can be identified, the first one due to a hand elegant and attentive to details, while
17 the second one due to a less expert and neat hand (examples in Figure 9 - a and b). This difference
18 is confirmed by XRF analysis. At least 5 points were determined on red initials for each style, that
19 yielded the results shown in Table 1; data are normalised to sulphur, being it a key element of
20 cinnabar. For the comparison, the elements Cl, K, P, Pb, Si and Zn were taken into consideration,
21 while Al, Sr, Cu and Fe, though determined, were discarded as their amounts were comparable to
22 parchment. Apparently, the red pigment used by the less expert hand is richer in chlorine, lead and
23 potassium, possibly as a result of the addition of a higher amount of white lead to cinnabar; in this
24 case, the difference could arise from a different source of raw matters (e.g. lead and mercury
25 minerals from different mines). Similar results were obtained from XRF analysis of the red filigrees
26 that were used to decorate blue initials: the two different filigrees styles corresponded to two
27 slightly different compositions of the pigment.

28

29 3.3 Blue initials

30 The case of blue initials is totally similar to red initials, i.e. two styles can be recognised
31 suggesting different expertise (examples in Figure 9 - c and d). Both artists used azurite -
32 $2CuCO_3 \cdot Cu(OH)_2$ - but XRF analysis highlighted (data in Table 1) that the less expert hand used
33 the blue pigment more diluted with white lead; in this case elemental data were normalised to Cu,
34 the key element for azurite. The elements used for the comparison were in this case Al, Fe, K, Pb
35 and Si.

36

37 3.4 Purple filigrees

38 A large number of red initials were decorated with thin purple filigrees, which, according
39 resulted to FORS and spectrofluorimetric analysis, resulted to be composed by folium, the dye
40 extracted from *Chrozophora tinctoria* (L.) A. Juss. plant belonging to *Euphorbiaceae* family. The
41 identification of folium is notable because this dye has been found on artworks in very rare
42 instances.^[32, 33] Though *Chrozophora tinctoria* be a plant growing in warm and dry climates (e.g.
43 Sardinia, Turkey, Southern France), the use of folium in a scriptorium set in a mountain zone is not
44 surprising as this dye, like many others, was preserved in Middle Ages with the *pezzuola* method,^[34]
45 that is by soaking a linen clothlet into dye juice in order to make it absorb a relevant amount of dye,
46 which could be later leached out with an alkaline treatment; in this way the clothlet would act as a

1 portable reservoir for the dye. Also, it must be considered that the Sacra di San Michele abbey had
2 properties in Southern France, so that *Chrozophora tinctoria* or folium itself could be easily
3 recovered; in addition, being placed along the path between Mont Saint-Michel (Normandy, France)
4 and San Michele Arcangelo (Puglia, Italy), the abbey could take advantage of cultural exchanges.

5 Upon visual inspection once again it is not difficult identifying two different hands in the
6 making of purple filigrees: one less elaborate, characterised by wider strokes, and one highly
7 sophisticated with thinner strokes and more evolved drawings (Figure 9 - e and f). In this case also,
8 results of XRF analysis confirmed this distinction on the basis of the elemental composition of the
9 inks used for the purple filigrees. It was not easy to decide how to normalise elemental data,
10 because no apparent key element could be single out (folium is a dye, so it contains only light
11 elements); therefore, it was decided to use raw data. K, P, Pb, S, Si, Sr and Zn were the elements
12 used for the comparison. The results, shown in Table 1, once again confirm the hypothesis of two
13 artists at work, each of which using his own folium solution; the ink used by the less elaborate hand
14 is richer in lead, as if that ink was more diluted with white lead.

15

16 3.3 The miniature at f. 208v

17 It is interesting to evaluate whether the beautiful miniature at f. 208v, representing Saint
18 Michael and a dragon (Figure 10), was composed by the same artists who worked at the initials or
19 by another artist. According to analysis carried out by means of FORS, spectrofluorimetry and XRF
20 spectrometry, the palette involved was composed by the following colourants:

- 21 • *red lead* for details depicted in orange such as the dragon's tail, vegetal shots, etc. (the
22 same pigment is present in some tetragram lines mixed with cinnabar);
- 23 • *azurite* and *indigo* for blue details;
- 24 • *weld* for few yellow details (e.g. Saint Michael's shield); the presence of this dye was
25 hypothesised on the basis of FORS and spectrofluorimetry analysis and of the fact that
26 XRF analysis identified no key elements;
- 27 • *folium* for Saint Michael's dress and for details in the vegetation

28

29 Apart from the stylistic features, the whole palette suggests that another artist was at work in
30 the miniature at f. 208v: the use of red lead in place of cinnabar can hardly be justified, considering
31 that the latter pigment was widely used for rubrics, initials and filigrees all along the manuscript.
32 XRF analysis of purple areas painted with folium highlighted a higher Pb amount with respect of
33 the folium ink used for filigrees, but the comparison is in this case somewhat incorrect: it is logical
34 to think that the purple paint in the miniature should have more hiding power than an ink, so more
35 white lead could be needed.

36

37 4 Conclusions

38 The results on non-invasive measurements carried out on the *Breviario di San Michele della*
39 *Chiusa* by means of XRF spectrometry, FORS and spectrofluorimetry, highlighted that at least 11
40 persons (6 scribes for the text, 2 scribes for the musical notations, 2 artists for initials and filigrees,
41 1 artist for the full-page miniature at f. 208v) were at work for writing and decorating it. Particularly
42 relevant are the black inks used for text and notes which have an anomalous composition, being
43 iron-gall inks with a larger than usual amount of zinc, possibly as a consequence of the use of
44 vitriols made from goslarite; this suggests that the scribes could come from Northern Europe. As to
45 the red/blue/purple colourants used for decoration, in all cases it was possible to distinguish
46 between two artists according to the elemental distribution; this clear distinction allows us
47 hypothesising that two scribes only were at work for both painting in miniatures and in filigrees,

1 one more expert and the other less expert, as if a teacher and a student alternated in the decoration
2 of the *Breviario*.

3

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Colour	Artist	Al	Cl	Cu	Fe	K	P	Pb	S	Si	Sr	Zn
Red initials	student	-	0,14	-	-	0,06	0,29	0,044	1	0,09	-	0,009
	master	-	0,02	-	-	0,01	0,39	0,003	1	0,05	-	0,010
Blue initials	student	0,03	-	1	0,037	0,01	-	0,010		0,953	-	-
	master	0,03	-	1	0,034	0,01	-	0,002		0,889	-	-
Red filigrees	student	-	0,18	-	-	0,05	0,25	0,040	1	0,08	-	0,008
	master	-	0,02	-	-	0,01	0,37	0,003	1	0,04	-	0,011
Purple filigrees	student	-	-	-	-	0,36	0,56	0,114	1,13	0,75	0,01	-
	master	-	-	-	-	0,29	0,97	0,022	1,66	0,54	0,005	-

1 Table 1 – Elemental compositions (% w/w) of red and blue initials and of red and purple filigrees in
2 the *Breviario*

3

- 1 **Figure captions**
- 2 Figure 1. FORS spectra of black inks from the *Breviario*
- 3 Figure 2. Examples of letters from the six scribes of the *Breviario*
- 4 Figure 3. PC1 vs PC2 plot from elemental analysis of the black inks of the *Breviario*
- 5 Figure 4. Cu/Fe vs. Zn/Fe in the black inks of the *Breviario*
- 6 Figure 5. Text on the hair side (a) and on the flesh side (b) of a folio
- 7 Figure 6. PC1 vs PC2 plot from elemental analysis of the black inks of the musical notations of the
- 8 *Breviario* (top); PC1 vs PC2 plot from elemental analysis of all black inks of the
- 9 *Breviario* (bottom)
- 10 Figure 7. PC1 vs PC2 plot from elemental analysis of the black inks of the *Breviario* and of other
- 11 manuscripts and documents
- 12 Figure 8. Cu/Fe vs. Zn/Fe in black inks of different manuscripts and documents
- 13 Figure 9. Different styles in red (a and b) and blue (c and d) initials and in purple (e and f) filigrees
- 14 Figure 10. The miniature at f. 208v, representing Saint Michael and the dragon