

## Resumo

A fluorescência de raios-X por radiação de sincrotrão é uma técnica eficaz de análise elemental, *in situ* e não-invasiva. O uso de novos detectores permite operar com fluxos elevados sem perda de resolução. Apresentamos um estudo onde a SR-XRF é utilizada, com um sensor CCD (*thick fully-depleted*), no estudo dos pigmentos utilizados numa iluminura de um manuscrito produzido no círculo de Fra Angelico, em torno a 1450. Os dados obtidos são utilizados conjuntamente com a análise estilística e a pesquisa em arquivos para a interpretação do processo de decoração de manuscritos no séc. XV em Florença. ●

## Abstract

*Synchrotron-radiation induced X-ray fluorescence is an effective technique for non-invasive, in-situ, elemental analysis. The use of new detectors enables operation at large fluxes without loss of resolution. We present a case-study application of SR-XRF with a thick, fully-depleted CCD sensor to the analysis of the pigments on the illumination of a manuscript decorated in the circle of Fra Angelico around 1450. Physical data are integrated with stylistic analysis and archive research in the interpretation of the process of manuscript decoration in XV century Florence. ●*

## palavras-chave

SINCROTRÃO  
FLUORESCÊNCIA DE RAIOS-X  
DISPERSIVA DE ENERGIAS  
ILUMINURAS  
FRA ANGELICO

## key-words

SYNCHROTRON  
X-RAY FLUORESCENCE  
MANUSCRIPT ILLUMINATIONS  
FRA ANGELICO

# THE APPLICATION OF SR-XRF TO THE ANALYSIS OF MANUSCRIPT ILLUMINATION *A CASE STUDY*<sup>1</sup>

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## Introduction

The use of synchrotron radiation induced X-ray fluorescence (SR-XRF) is well suited for the elemental analysis of pigments in artworks since the analysis is fast and non-destructive, the beam can be made monochromatic and its energy changed to fit the analysis requirements. The small spot size probes tiny regions and disentangles individual pigments and small pitch scans can be performed to acquire detailed pigment maps.

XRF<sup>2</sup> and PIXE<sup>3</sup> analyses have already provided us with fundamental data for the study of the pigments used in the decoration of Medieval and Renaissance manuscripts. Here we discuss pigment analysis by SR-XRF to clarify the methods of work and sharing of responsibilities among artists of the circle of Fra Angelico in mid-XV century Florence. This case study is based on the analysis of the illuminated opening page of a manuscript decorated by Battista di Biagio Sanguigni and another artist, around 1450. The physical data are integrated with stylistic analysis and archive research in the interpretation of manuscript illumination. This analysis introduces also a novel detector for XRF. We employ a thick, high-resistivity, front-illuminated Charge Coupled Device (CCD). CCD sensors offer several advantages over a conventional Si(Li) detectors. Their active surface is large and the high pixellisation allows us to operate with large X-ray fluxes without pile-up effects.

This paper is organized as follows. First we discuss some aspects of the organisation of manuscript decoration in Florence around 1450 as it emerges from archival sources. Then we present the manuscript under study, the experimental set-up and the CCD performance. Finally we discuss the results of the analysis of the red pigment composition, in areas which appear to be due to different artists, and of the

1. In this article LAB has been responsible for the sections on art history and archive research, the other authors for the XRF analysis.

2. M Picollo et al., these proceedings and references therein.

3. M Bernasconi et al., Analyse des couleurs dans un groupe de manuscrits enluminés du XII au XV siècle avec l'emploi de la technique PIXE, in Ancient and Medieval Book Materials and Techniques, Citta' del Vaticano, 1993, pp. 57-101.

rendering of the «incarnato», comparing it with that by other artists active in Florence in the same decade.

## «Ad faciendum storias» and «ad miniandum»: the Sharing of Illumination Roles and the circle of Fra Angelico

Fra Angelico and the artists of his immediate circle enjoy a privileged role in the landscape of manuscript decoration in XV century Florence, as they were responsible for some of the most prestigious cycles of service books. This small group of artists included Zanobi Strozzi and Battista di Biagio Sanguigni and they all worked both as panel painters and as illuminators, at least according to the recent identification of the so-called Maestro del 1419 with Battista di Biagio<sup>4</sup>. The profile of Battista di Biagio as illuminator, which still needs to be studied in detail, can be reconstructed from few documented commissions from the 1430s<sup>5</sup>. The choirbooks for San Gaggio, now at San Marco, are the centerpiece for the identification of his style. Starting from these works, a large corpus of illuminations has been assembled. Battista di Biagio emerges as one of leading illuminators in Florence in the second quarter of the XV century and his relationship to Fra Angelico and the other artists of his immediate circle appears of special importance. Not only did he collaborate with Fra Angelico and Zanobi Strozzi to the decoration of manuscripts, but he also developed close personal relations to these artists<sup>6</sup>. The analysis of documented commissions of manuscript decoration by these artists has clarified the difference of roles between «istoriatore» and «miniature», as it has recently been pointed out<sup>7</sup>. Three examples are particularly pointing. The first is the 1437 commission for an illumination for the monastery of San Pancrazio<sup>8</sup> to Zanobi Strozzi and Filippo di Matteo Torelli<sup>9</sup>. The second is the 1445 commission for the decoration of the antiphonaries of Santa Maria del Fiore<sup>10</sup> to Zanobi Strozzi, Filippo di Matteo Torelli, Battista di Niccolò da Padova and a not yet identified Bartolomeo<sup>11</sup>. Finally, the «Libro delle Ricordanze del Convento di San Marco, A» relates us details of the making of the choirbooks for the Dominican foundation by Zanobi Strozzi and other artists from 1446 to 1454<sup>12</sup>. In all these documents the sharing of roles is clearly defined. Specific artists are named as responsible for the «figure» in the main scene, or «storia», and others for the leafy marginal decoration, «fogliami e oro e altri adornamenti». These roles are generally respected: Filippo di Matteo Torelli is attributed almost exclusively the role of «miniature», while Zanobi Strozzi is documented to work on the same leaves as «istoriatore». In at least one instance the exchange of leaves from one artist to the next during the decoration process is documented<sup>13</sup>. We know from stylistics analysis that Battista di Biagio was similarly active as «miniature», responsible for the marginal decoration and the body of the letters, in the majority of the manuscripts for which Fra Angelico painted the historiated initials<sup>14</sup>. This collaboration may date

4. LB Kanter, Zanobi Strozzi miniatore and Battista di Biagio Sanguigni, *Arte Cristiana*, 90 (2002), pp. 321-331.

5. ASF, Conv. Soppr. 234, San Gaggio, n. 77, c. 13v (1432): note of a credit with the monastery of San Gaggio: «Batista miniatore dee avere per insino a di' primo di novembre 1432 per miniature d'uno ynnario grande notato e per miniature in uno salterio grande da coro e per miniature negli antifonari nuovi»; *ibid.* n. 78, c. 35r (1435) «Batista di ... miniatore de avere a di' 14 ottobre (1435) lb. 33 s. 14 d. 2 per resto di sua ragione per i libri miniati al munistero ...»; ASF, Catasto 1433, vol. 482, c. 264r (1433): note of a credit with Bardo de' Bardi «per un libricciuolo gli fe'»; published in W Cohn, *Il Beato Angelico e Battista di Biagio Sanguigni. Nuovi documenti*, *Rivista d'arte*, 30 (1955), pp. 207-216, in particular pp. 213, 215-216.

6. As it is well known, it was Battista di Biagio who introduced Guido di Pietro (Fra Angelico) to the Compagnia di San Niccolò di Bari in 1417 (ASF, *Compagnie Soppresse*, vol. 1549: Compagnia di San Niccolò di Bari in Santa Maria del Carmine, *Elenco dei Confratelli c-c 17*, n. 410 e a-c 18, n. 507) and lived near his house in S. Michele Visdomini. He later shared a house, located near San Domenico in Fiesole where Guido di Pietro moved after joining the Dominican order, with Zanobi Strozzi from around 1430 until 1438; Cohn 1955.

7. A Dillon Bussi, *Zanobi Strozzi istoriatore e non miniatore (Indagine nel mondo della miniatura muovendo dai quattro piu' importanti corali quattrocenteschi fiorentini)*, *Rara Volumina*, 13 (2006), 1, pp. 15-25.

8. A Dillon Bussi, *Una «glorificazione di San Pancrazio» di Zanobi Strozzi*, *Paragone Arte*, Anno 57, n. 69 (2006), pp 3-19.

9. ASF, *Corporazioni Religiosi Soppresse dal Governo Francese 88*, San Pancrazio, vol. 63, c. 34r, published in M Levi d'Ancona, *Miniatura e Miniatori a Firenze dal XIV al XVI secolo*, Firenze, Olschki, 1962, p 107: «nel qual libro abbiavamo speso insino nel 1437 in fare fare le figure del minio della messa di san pancrazio e piu' altri fogliami ed adorneza di detto minio. Il quale fece

Zanobi degli Strozzi cioè le figure et il resto Pippo di Matteo che dacordo ebbono insino a di' 17 di maggio 1437 L.20 s.-».

10. Mss. Edili 148-151 in the Biblioteca Medicea Laurenziana, see I libri del Duomo di Firenze: codici liturgici e biblioteca di Santa Maria del Fiore (secoli XI-XVI), L. Fabbri and M. Tacconi (eds.), Firenze 1997, pp. 79-96 (Dillon Bussi) and pp. 217-224 (Tacconi).

11. Archivio Opera del Duomo, I-1-4, c. 41t, 54 published in G. Poggi, Il Duomo di Firenze, vol. II (1988), p. 39, n.1630: «Nobiles viri ... operarii antedicti omni modo etc. locaverunt Zanobio Benedicti Carocii de Strozis ad faciendum storias de uno ex antifanariis locatis ad scribendum Goro, pro pretio, et remuneratione alias fiendis. Item locaverunt magistro Batiste... ad faciendum storias in alio antifanario predicto pro pretio alias fiendo. Item locaverunt ad miniandum unum de dictis antifanariis Filippo Mathei Torelli, miniatori, pretii (sic) alias fiendo. Item locaverunt ad miniandum alium antifanarium Bartolomeo minatori...».

12. Biblioteca Medicea Laurenziana, Libro delle Ricordanze di San Marco «A», San Marco 902, f. 26v: «Ricordo come Zenobio degli Strozzi miniature à auto da me frate costantino [da Nocera] de san marco per storie fan el primo graduale delle feste florin dodici in duo partite» and following entries published in S. Orlandi, Beato Angelico, Firenze, 1964, pp. 116-117 and 194-195.

13. On 23 May 1447 Zanobi receives from Filippo Matteo Torelli two letters to be decorated, San Marco 902 cit., f. 23r published in M. Levi D'Ancona, Miniatura e miniatori a Firenze dal XIV al XVI secolo, Firenze, 1962, p. 265.

14. LB Kanter, ad vocem Guido di Pietro, in Dizionario biografico dei miniatori italiani: secoli IX-XVI, M. Bollati (ed), Milano 2004, pp. 334-335.

15. See for example and references therein: A. Guidotti, Indagini su botteghe di cartolai e miniatori a Firenze nel XV secolo, in La miniature italiana tra Gotico e Rinascimento, Atti del II Congresso di Storia della Miniatura Italiana, E. Sesti (ed.), Firenze 1985, pp. 473-507; A. Guidotti, Nuovi documenti su Vespasiano da Bisticci la sua bottega e la sua famiglia, in Federico da Mon-

as early circa 1425 in the work for the choirbook Ms 558 for San Domenico, now in San Marco. It likely continued shortly afterwards in the decoration of Ms. Gerli 54 in Biblioteca Braidense of Milano. We recognize again his hand in the decoration of the two Psalters, Mss 530 and 531 of San Marco, which can be dated circa 1449 near the end of his life and are very close in style to the miniature analyzed here. This peculiar organisation of work, which sees two different artists working on the same initial is further confirmed by the analysis of Missal Ms 534 from San Marco where one artist, possibly Sanguigni himself, paints all the letters and their marginal decoration leaving the space for the work of the «istoriatore». As the decoration of the missal was left unfinished, today we see the spaces left for the «storie». Conversely, in the choirbooks for San Gaggio, the main illumination, by Sanguigni, was completed, but several foliated decorations were left unfinished. All these examples demonstrate that the decoration of the letters and their marginal extensions and those of the «storie» belonged to two distinct and possibly independent phases in the process of manuscript decoration, thus confirming the evidence from the archival sources.

The organisation of artist workshops has been studied in details,<sup>15</sup> including the relations between the workshop principal and his collaborators and the role of the «cartolaio» in the distribution of the work of manuscript production and decoration. Since the appearance of the finished manuscript does not reveal to us chromatic inconsistencies, we are faced with the question whether different artists did work side-by-side, sharing the same pigments, or the observed chromatic uniformity is the result of a high degree of organisation of this process, which ensured the constant quality of the final product<sup>16</sup>. While archival sources are generally scarce on such details of the process of manuscript production, in a few instances, documents confirm that single leaves were brought to the artist for being decorated. One of these is the case of a group of leaves for one of the antiphonaries being produced for Santa Maria del Fiore and brought to Filippo Maria Torelli in 1450<sup>17</sup>. Therefore, we know about the effective organisation of manuscript production, which followed the various stages of the work, from the acquisition of the parchment to the writing, decoration and binding, dispatching the parts through the work chain. Responsible for this was in general, probably, the «cartolaio» but in the specific case of the choirbooks of the Duomo this role was taken by the patron itself, i.e. the «Opera di Santa Maria del Fiore». It is suggestive to assume that the same form of organisation could also ensure the uniformity of the decorative work, even when «storie» and decorative borders were painted by different hands at different locations. The sources do not help us in clarifying this point. In fact, mentions of transactions of colours between patrons and artists, in the surviving documents for XV century Florence, are mostly limited to the gold and the «azzurro», possibly due to their high cost<sup>18</sup>, even though the quality of the colours to be employed is often mentioned in contracts<sup>19</sup>. Now, the identification of another manuscript where Battista di Biagio shares the decoration work with an artist of the immediate Fra Angelico circle, provides us with the opportunity to better understand their working practice and confirm the stylistic evidence with physical data.

## SR-XRF Analysis of a Miniature by Battista di Biagio Sanguigni and a Collaborator of Fra Angelico

The illumination analysed in this study is on the opening page of a manuscript containing works attributed to St. Jerome, now in a private collection, decorated around 1450<sup>20</sup>. The stylistic analysis indicates that its decoration is the work of two distinct artists. One is responsible for the body of the initial and its foliated extensions and can be doubtlessly identified with Battista di Biagio Sanguigni, while a second artist, who expresses a style very close to that of Fra Angelico himself, paints the figure of the St. Jerome in the initial.

This SR-XRF analysis was performed on beam line 5.3.1 at the Lawrence Berkeley National Laboratory Advanced Light Source (ALS). Synchrotron radiation is produced by the 1.9 GeV electron beam in one of the main ring bending magnets, which gives a continuum X-ray spectrum up to ~20 keV. Upstream from the sample a mono-chromator selects the beam energy. A collimator eliminates the white beam and defines the monochromatic beam geometry while a shutter controls the exposure time. For this study the beam energy was chosen to be 12 keV. The beam spot at the sample surface has a diameter of ~1 mm. The sample is mounted on a computer-controlled XY stage, which allows us to perform automated scans of the surface of the manuscript. X-rays are detected with a thick, front-illuminated CCD sensor developed at LBNL on high resistivity Si. The CCD has an active surface of 118 mm<sup>2</sup> with 1024x512 pixels arrayed on a 15 µm pitch and two output channels. Under the operating conditions adopted for this analysis the sensitive thickness is ~450 µm, which offers high spectral sensitivity up to energies well above the beam energy. Thick, high-resistivity CCDs offer high detection efficiency and an excellent energy resolution, matching or surpassing that of conventional solid-state X-ray detectors. The single pixel noise is measured to be  $(4.2 \pm 1.0) e^-$  ENC. The energy resolution measured for reconstructed clusters from a <sup>55</sup>Fe source is 155 eV FWHM at 5.9 keV. The CCD response is calibrated in the range 3-12 keV using thin metal foils in the same geometry used as for the manuscript analysis. Data are saved in the fits format and subsequently converted to the Icio format, while performing pixel-by-pixel pedestal subtraction and noise computation from CCD exposure taken without beam. The offline analysis is performed using custom clustering processors in the Marlin C++ analysis framework. Beam back-scattering from the sample is removed by subtracting a reference spectrum obtained with the beam aimed at a non-decorated part of the parchment. The spectrum is reweighted to correct for the effect of X-ray absorption in the kapton window and the inactive detector surface. The final spectrum analysis and peak search is performed in ROOT. Cluster shape analysis is helpful for rejecting spurious background signals, pile-up clusters and scattered photons striking the detector at large angles. This is particularly important when performing XRF on a high intensity primary beam, such as at a light source. The XRF analysis sampled a total of twenty-six points on the decorated

tefeltro: lo stato, le arti, la cultura, G Cerbeni Baiardi et al (eds.), Roma, 1986, pp. 97-111; L Indrio, Firenze nel Quattrocento: divisione e organizzazione del lavoro nelle botteghe, in *Il colore dell'antico, Ricerche di storia dell'arte*, 38 (1989), pp. 61-70; J.J.G. Alexander, *Medieval illuminators and their methods of work*, New Haven 1992; *Maestri e botteghe: pittura a Firenze alla fine del Quattrocento*, M Gregori et al. (eds), Firenze 1992, *Organizzazione, componenti e ruoli della bottega laica tra XIV e XV secolo*, A Guidotti (ed.), Firenze, 2006.

16. A Dillon Bussi, *Rara Volumina* (2006).

17. Archivio Opera del Duomo, VIII-4-1, Giornale H, c. 54 pubblicato in G Poggi, *Il Duomo di Firenze*, vol. II (1988), p. 47, n.1672: «A Filippo di Matteo Torelli, miniature, addi' 6 di luglio gli porto' a chasa Martino manovale cho' licenza di Pazino operai 2 asse d'albero nero entrovi... charte scritte e notate del primo antifanare si fanno di nuovo perche' lle minii ... Rimando' dette cose all'opera». Another case concerns the Olivetan convent of «S. Bartolomeo alle Sacca» in nearby Prato where leaves written in the convent scriptorium were sent to an outside workshop for being decorated, M Ciatti, *Appunti e documenti per la storia della miniature a Prato nel Quattrocento*, in *La miniatura italiana tra Gotico e Rinascimento*, Atti del II Congresso di Storia della Miniatura Italiana, E Sesti (ed.), Firenze, 1985, pp. 509-533, in particular p. 528.

18. For example, Battista di Biagio contracted a debt with the friars of Santa Maria degli Angeli for blue pigment in 1430 (ASF, Catasto 1430, vol. 389, c. 354). Filippo di Matteo Torelli is paid for blue pigment in 1437 «l. tre s. xi demo a Pippo miniature per oncia 1 dazuro de la magna e per ¼ oncia dazuro ultramarino», ASF, *Conventi Soppressi* 78, Badia vol. I, *Giornale* (1435-1441).

19. A Guidotti, *Il mestiere del «dipintore» nell'Italia Due-Trecentesca*, in *La Pittura in Italia. Il Duecento e il Trecento*, E Castelnuovo (ed.), Milano, 1986, pp. 529-540, in particular p. 535.

20. L Alidori Battaglia, *An unpublished miniature from the circle of Fra Angelico*, *The Burlington Magazine*, vol. CLI, n. 1277 (2009), pp. 518-525.

surface of the manuscript (see Figure 1). Ten different pigments have been analyzed. In some cases, the same pigment has been sampled at different locations to study the effect of possible local in-homogeneities. Here we discuss the pigment composition on those parts which appear to be due to two different artists and the technique for the rendering of the «incarnato» of St. Jerome face.



FIG.1 PAGE WITH THE INITIAL L WITH ST. JEROME FROM THE REGULA MONACHORUM, C. 1R, TEMPERA ON PARCHMENT, 19 BY 14 CM (PRIVATE COLLECTION).

First, we study the composition of the red pigment at various locations on the foliated decoration and on the book hold by the St. Jerome. The spectra are shown in Figure 2. The analysis reveals Pb and a small amount of Cu in the red pigment on the leaf protruding from the letter. This is consistent with what we would expect for minium. Instead, the red pigment on the book is characterized by a large quantity of Cu with Pb, Fe with traces of Zn and Ba. This composition indicates that the artist mixed minium with another pigment, possibly an «ocra rossa». We sampled three distinct spots on the leaf and two on the book. Results are consistent. Differences in the pigment composition, associated to the work of different artists in the same manuscripts have already been observed<sup>21</sup>. The different composition of the two pigments seems to support the indication from the stylistic analysis that there are two artists working independently on the miniature.

21. M Bagnoli, Amanuensi e miniatori in un Decretum Gratiani del Walters Art Museum di Baltimore, *Arte Medievale*, n.s. Anno VI (2007), 2, pp. 65-74 reports subsequent interventions on the same initials; M Bernasconi et al., 1993 identifies differences in pigment composition between Florentine-style and Lucca-style artists working on BML, Conv. Soppr. 298.

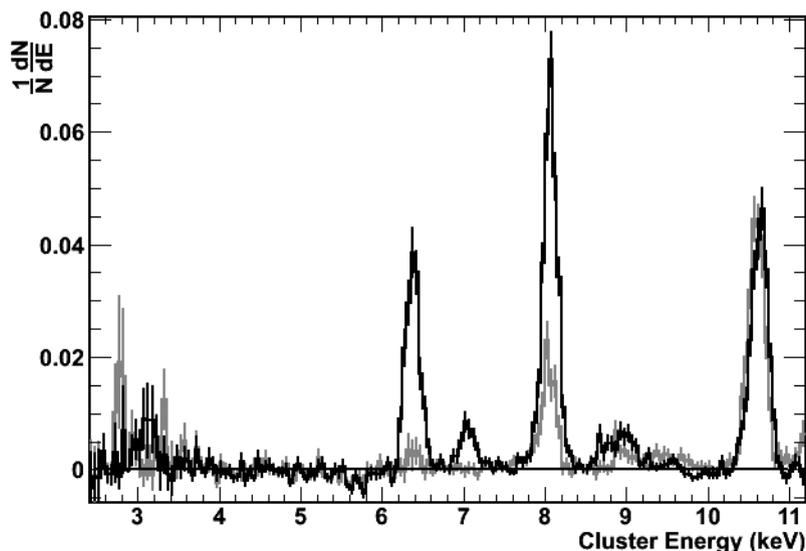


FIG.2 ABSORPTION- AND EFFICIENCY-CORRECTED XRF SPECTRA FOR THE RED PIGMENT ON THE BOOK HOLD BY THE SAINT (BLACK HISTOGRAM) AND ON THE MARGINAL LEAF (GRAY HISTOGRAM).

The second part of this study attempts to elucidate the technique employed for the rendering of the «incarnato». The deep shadows on the face of St. Jerome are obtained with brushstrokes in an olive colour, possibly a «terra verde» which follows the outline of the cheeks and the beard. The analysis of the beard shows that the pigment has Fe, Cu, Pb and traces of Ba. Instead, on the forehead there are larger brushstrokes beneath the final painted layer, revealed by infra-red photography. This technique is adopted by Fra Angelico as well as Zanobi Strozzi. The XRF analysis enables us to compare the pigment composition on the forehead, the breast and the hand. The four spectra are shown in Figure 3. The composition of the pigment used on the breast and on the hand appears to be identical. It is characterised by Fe and Pb, with traces of Cu, Zn and Ti. On the contrary, we observe a much larger Fe and

22. R Cambria et al, A PIXE analysis of Manuscripts Illuminated by Francesco di Antonio del Chierico, *Ancient and Medieval Book cit.*, pp. 103-119.

Cu content on the forehead, with traces of Mn and Cr. The rendering of deep shades on the face by underlying a Cu-based green pigment has already been observed in the PIXE analysis of ms. Plut. 66.22 of the Biblioteca Medicea Laurenziana<sup>22</sup>. This manuscript is dated 1455 in the colophon and was decorated by Francesco d'Antonio del Chierico. Other pigments differ significantly in the two manuscripts. For example, the analysis reveals only Ca, from the parchment preparation, in a pink-coloured area in the miniature of Francesco d'Antonio, which suggests the use of a pigment of organic origin. On the leaf by Battista di Biagio in our manuscript the pink is characterized by Sb, Pb, Cu and Fe. These comparisons are particularly interesting since they refer to two manuscripts decorated within a few years by two of the most prominent workshops in Florence and highlight the variety of techniques and pigments adopted by these artists.

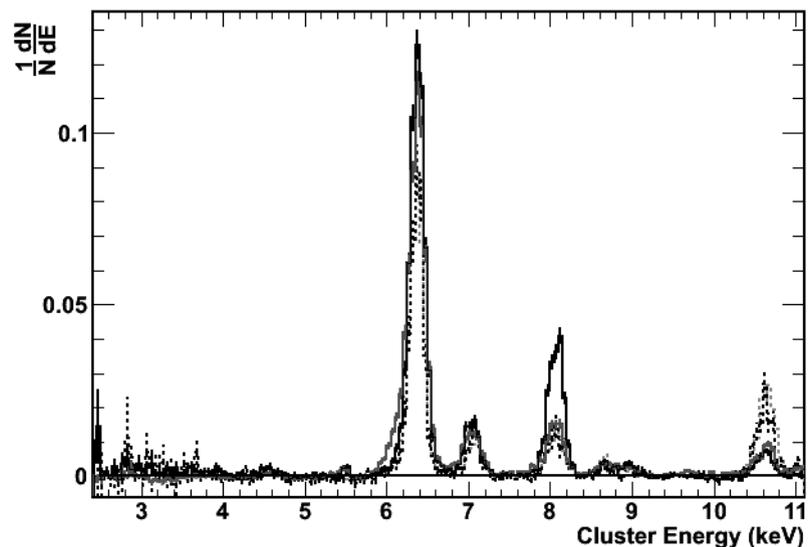


FIG.3 ABSORPTION- AND EFFICIENCY-CORRECTED XRF SPECTRA FOR THE PIGMENT ON THE FOREHEAD IN THE REGION OF THE DEEP SHADOW (CONTINUOUS BLACK HISTOGRAM) AND AWAY FROM IT (CONTINUOUS GRAY HISTOGRAM), ON THE BREAST OF THE SAINT (DASHED BLACK HISTOGRAM) AND ON THE HAND (DASHED GRAY HISTOGRAM).

## Conclusions and Perspectives

This case study offered us with the opportunity to address some issues in the practice of manuscript decoration in mid-fifteenth century Florence. We attempted to combine the results of SR-XRF analysis with stylistics analysis and archival research. Even within the limitations imposed by data collected from a single manuscript, the picture which emerges is very consistent and quite encouraging for the continuation of such studies. Manuscript decoration was a well-organized and structured process

with different artists contributing as «miniatori» and «istoriator». This seems to be the case not only in the decoration of major cycles, but also on minor commissions consisting of a single illuminated initial per manuscript. Results of physical elemental analysis confirm the evidence from stylistic analysis and documents. The results of this case study highlight the need to tightly integrate future campaigns of elemental analyses with well-defined art history problems which can be answered by the knowledge of pigment composition. At the same time it is apparent that more data on pigment analysis should be made available to support the work of art historians in the understanding of manuscript decoration practice and techniques across chronological and geographical boundaries.

The effect of the intense X-ray beam from a light source on the pigment and the parchment is an issue which is often raised by conservationists and curators and deserves further studies. Proton irradiation is known to induce the so-called «dark spot» phenomenon which appears to be related to the generation of colour centers<sup>23</sup>, but there is only limited understanding on the mechanisms responsible for pigment damage and on their reversibility<sup>24</sup>. Contrary to the case of protons, in SR-XRF, the X-ray energy is often below threshold for displacement damage. We carried out some observations on the pigments on a XV century bas-de-page after exposure to a 15 keV X-ray beam at the ALS. Observations were performed immediately after the irradiation, after several months and after more than a year. No effect was detectable. However, it would be important to further study the issue.

Finally the use of advanced pixellated sensors, as the high-resistivity CCDs adopted for this case study, offer new opportunities for high resolution spectroscopy with large photon fluxes, which will benefit the study of manuscript pigments both in terms of the exposure time and sensitivity to trace elements. ●

23. J Absil et al., Study of color centers induced by PIXE irradiation, *Nuclear Instruments and Methods in Physics Research*, B198 (2002), pp. 90-97.

24. E. Enguita et al., Damage induced by proton irradiation in carbonate based natural painting pigments, *Nuclear Instruments and Methods in Physics Research*, B219-220 (2004), pp. 53-56.

