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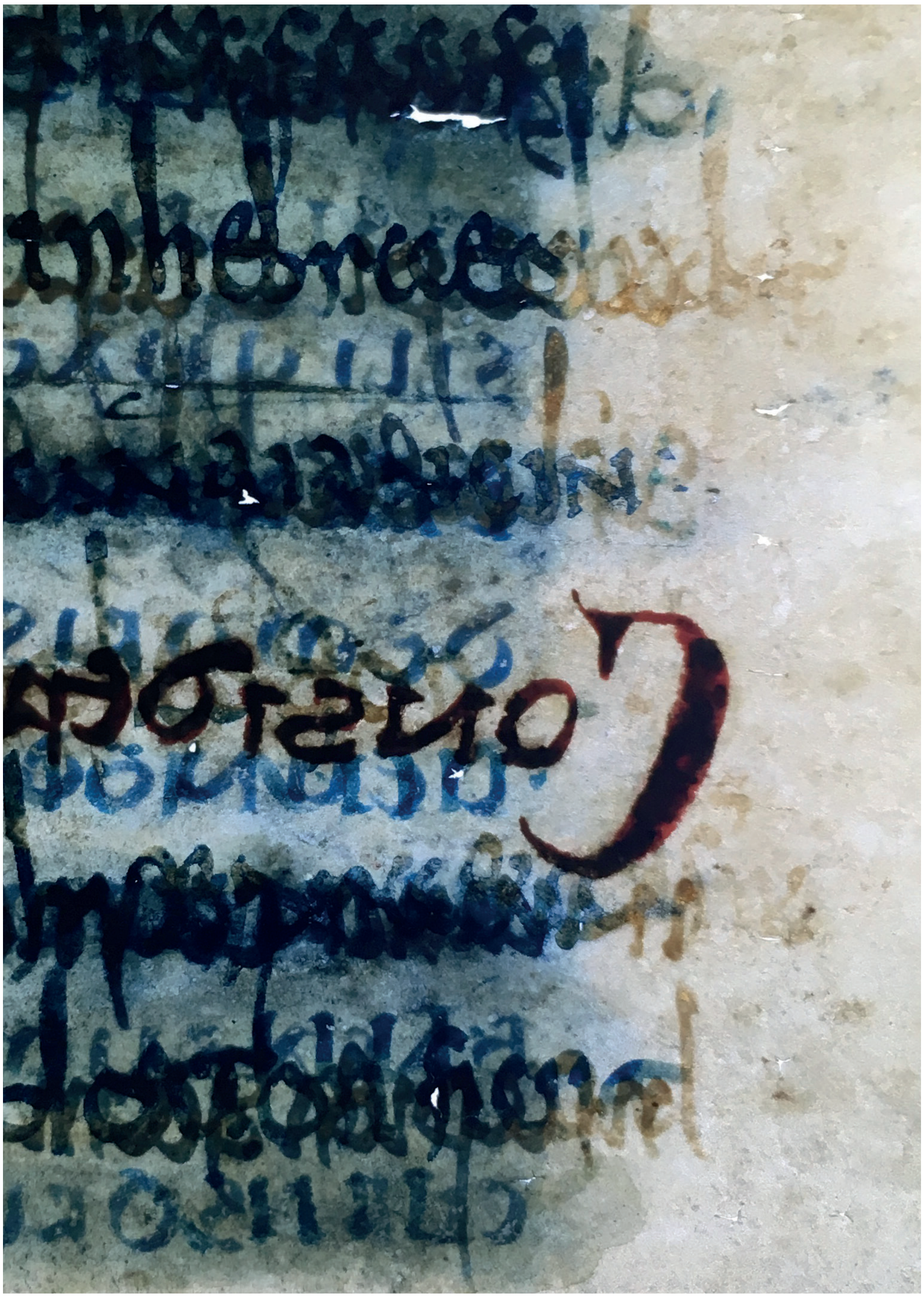

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Transmitted light image (detail) of Codex 3/1 (5th century Luxueil or 7th–8th century Italy), Benedictine Abbey St Paul in Lavant Valley, Austria. Hieronymus, *Commentarius in Ecclesiasten*; Plinius Secundus, *Historia naturalis.* Photography by Thomas Drechsler, Berlin.

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Article

Hard Science and History

Marina Bicchieri | Rome

1. Introduction

Books, archival documents and graphic works of art are amongst the most invaluable patrimony in human history. Each single document is an open window on our history, and its preservation is paramount.

The value of books is often evaluated merely on the basis of their content, either textual or graphic, neglecting the history of the physical support, the paper used, the kind of ink chosen, their provenience, what they are made of and the fabrication procedures. All of this information, stored between the pages and somehow hidden to the eye, tells us of the long travel of the paper used, the technological and scientific discoveries made at the time the book was written or drawn, and the genius of those who invented an ink or a specific paper treatment; it reveals the evolution of the aesthetics, morals, and costumes of the time.

In brief, it is a carrier of our story, of human history.

This entire incommensurable heritage is unfortunately destined to a slow death.

Supports, media and binding are subject to aging, and they lose their mechanical characteristics; inks can fade or induce acidity in the support, damaging it to the point of complete destruction.

Natural aging is a spontaneous and irreversible process, quite slow by itself in the absence of external interference such as storage in unsuitable places, when other degradation processes – physical, biological or chemical – can take place.

The function of scientists in the field of conservation of cultural heritage is manifold. On the one hand, by investigating the structure of materials, they can understand the nature and causes of degradation and find solutions to prevent further decay. On the other hand, they can solve problems or questions related to the manufacture of the object or to its past life, thus helping scholars in their historical studies. Moreover, each discovery also permits us to explore issues of the history of science.

In this paper, two case studies – a self-portrait by Leonardo da Vinci and the Purple *Codex Rossanensis* – will be presented to underline the positive or negative synergy between different expertises.

2. Instruments

Raman measurements were performed with a Renishaw In-Via Reflex Raman microscope equipped with a Renishaw diode laser at 785 nm. The laser spot measured about 20 $\mu m^{2;}$ the resolution was 3 cm^{-1}, and the laser power on the sample was 0.03–1 mW, depending on the characteristics of the sample investigated.

Micro-FTIR measurements were executed with a Nexus Nicolet interferometer and a Continuμm™ Microscope equipped with an Infinity Reflachromat™ 15X ∞/V objective. The measurements were performed on a surface of 100 x 100 μm^2 in the 4000–650 cm^{-1} range at a resolution of 8 cm^{-1}, averaging 200–400 acquisitions per sample. No ATR spectra were collected, in order to avoid any direct contact with the original documents.

XRF spectra were recorded by means of an Assing Lithos 3000 portable spectrometer, equipped with a Mo X-ray tube. The measurements were carried out with a 2-mm collimator and a Zr filter. The tube operated at 25 kV, 0.300 mA in the 0-25 keV range with a resolution of 160 eV at 5.9 keV, lasting 10–60 minutes for each acquisition. Long-time acquisitions were performed to obtain information on the elements present in minor amounts.

The AFM measurements were performed with the AFM easyScan 2 Nanosurf instrument with FLEX-AFM head and conical tip (thickness 7 μm, height 17 μm, radius <10 μM) covered with 'aluminium reflex'. The instrument was provided for the measures by Lot-Oriel-Nanosurf. The tip, inserted in the measuring head, vibrates with an oscillation frequency of 190 kHz and, when approaching the area to be analysed, is sensitive to short-range forces, due to the interaction with the surface of the sample (non-contact mode). When applied to 'soft' samples, such as paper, the non-contact mode is more suitable, because it avoids removing fibrils and modifying the surface, which would compromise the analysis. The non-contact method allows a completely non-destructive way of working, obtaining a real three-dimensional reconstruction of the roughness of the analysed surface and avoiding any contact with it.

3. Materials

Apart from the measurements performed directly on the original documents, for the study of the *Codex Rossanensis* some laboratory samples were prepared.

a. Historical samples of lake pigments, belonging to the collection of the Icrcpal chemistry laboratory (gift of Lorilleux, Milan, 1938) obtained from *Rubia Tinctorum* (red) and *Porphyrophora hamelii* (Armenian cochineal, red) were applied to the surface of a parchment following the indication of Bisulca.[1]

b. Aluminium lake pigments from *Crocus Sativus* (red) and *Sambucus Nigra* (pink-mauve) were prepared following ancient recipes reported in Carriera and in Caffaro.[2] Each pigment was then mixed with egg white, as reported in Caffaro[3] and in *De Arte Illuminandi*[4], and then applied to the parchment.

c. Two different kinds of purple-dyed parchment samples were prepared by treating the parchment with: a) an aqueous solution of *Roccella Tinctoria* prepared as described in the Stockholm papyrus,[5] recipe 131; and b) an aqueous solution of *Roccella Tinctoria* and sodium carbonate, as described in recipe 123 in the same manuscript.

4. Results and discussion

4.1 Leonardo da Vinci self-portrait

In 2012, the very famous self-portrait of Leonardo da Vinci, conserved in the Biblioteca Reale di Torino, was subjected to a completely non-destructive diagnostic campaign at Istituto Centrale Restauro e Conservazione del Patrimonio Archivistico e Librario (Icrcpal), Chemistry Laboratory. The purpose of the analyses was to assess the conservation status of the drawing, which presented an apparent fading of the graphic medium and diffuse foxing. To this end, surveys were accomplished in the chemistry laboratory using molecular (Raman and Infrared) and elemental (X-Ray Fluorescence) spectroscopies. At the same time, Atomic Force Microscopy (AFM) was applied to obtain a topographic description of the paper in damaged and less-damaged areas. The topography of the paper is, in fact, related to its state of preservation.[6] The other laboratories of the Institute performed microbiological studies, codicological investigation, measures in FORS and Multispectral Reflectance.

Only the comparative analysis of experimental results obtained with different techniques and methods can actually provide scientific information to correctly characterize the work and predict how time will alter its chemical-physical characteristics and what the life expectancy of the work of art is.

I summarize below the results obtained by the laboratories of the Institute before examining in depth the results from the chemical laboratory.

The codicological analyses consisted of the measurements of the portrait (33.2 cm high × 21.2 cm wide; average paper thickness: 230 µm) and the characteristics of the manufacturing wire. The latter were obtained by collecting images of the paper under grazing light. The wire used had 8–9 wire lines/cm and the distance between the chain lines was equal to 2.7 cm; no watermarks were present. These technological characteristics are compatible with the wires typically used in the sixteenth century. Moreover, it was possible to recognize – without any sampling – the pulp composition as a mixture of hemp and flax fibres with the addition of some coloured wool fibres, indicating a low quality of paper.[7]

The analysis under UV light evidenced a considerable presence of glue, leftover of a previous arrangement of the drawing, which had been glued directly to a piece of cardboard. Part of the glue had penetrated the paper; moreover, thick residues of glue were still present on the perimeter of the sheet, inducing undulation.[8]

Optical measurements in visible and ultraviolet light, followed by TDDFT (Time Dependant Density Functional Theory) analysis and interpretation evidenced the presence

[1] Bisulca et al. 2008

[2] Carriera 2005; Caffaro 2004.

[3] Caffaro 2004.

[4] *De Arte Illuminandi*, ed. Brunello 1976.

[5] Caley 2008.

[6] Piantanida et al. 2005.

[7] Pascalicchio 2014.

[8] Botti et al. 2014.

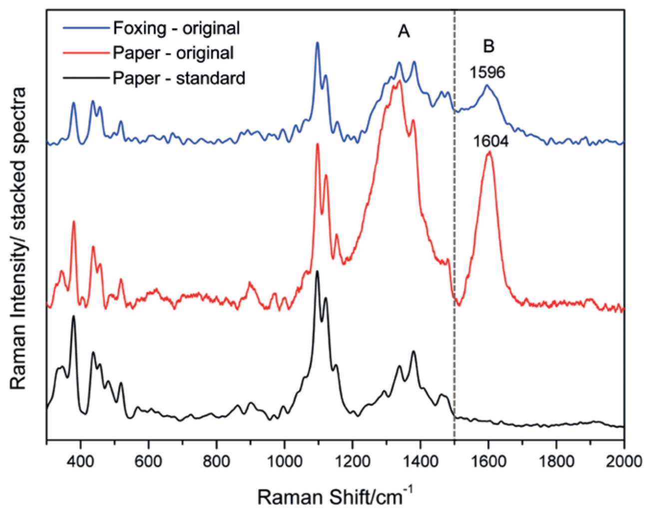

Fig. 1: Raman spectra collected from Leonardo's self-portrait. From top: foxed areas, not foxed paper, cellulose standard reported for comparison. In the figure, A indicates the spectral features related to superimposition of collagen and paper, and B to the formation of carbon-carbon double bonds; the dotted line indicates the separation between the signals characteristic of the pure cellulose (Raman shift lower than 1500 cm^{-1}) and those typical of oxidisation of the chain, at higher Raman shift.

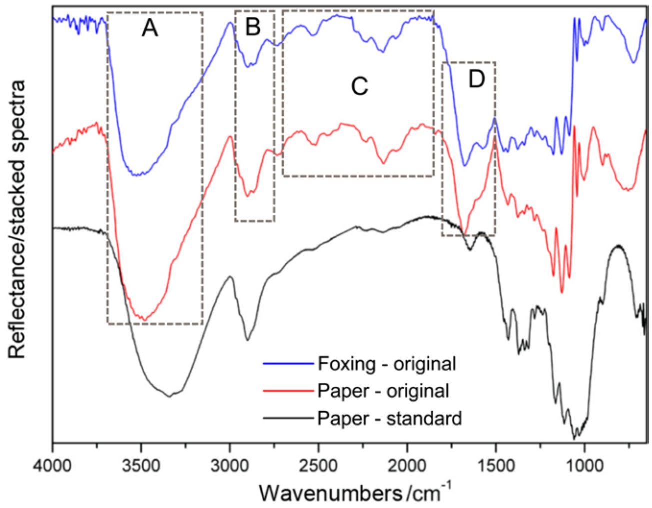

Fig. 2: FTIR reflectance spectra collected from Leonardo's self-portrait. From top: foxed areas, not foxed paper, cellulose standard reported for comparison. In the figure, A indicates the spectral features related to dehydration of the paper, B to gelatine size, C to the formation of carbon-carbon triple bonds, and D to carbon-carbon double bonds and carbonylic functions.

in the paper of a great amount of oxidised groups, indicating a serious degradation of the paper, compatible with storage in a closed and humid environment.[9]

Meanwhile, the microbiological analyses showed diffuse traces of fly's catabolites and the absence of active fungal attacks, but a massive presence of fungal remains – mostly *Eurotium Halophilicum* – on the back of the portrait and in the region with glue. A previous fungal attack could be hypothesised as causing the formation of oxidised function in the cellulose (chromophores), giving rise to spots and discolouration of the paper.[10]

The Chemistry Laboratory analysed the drawing using Raman, FTIR in reflectance, XRF and AFM.

Raman spectroscopy can identify the functional groups characterizing degradation, and previous researches allowed the evaluation of the modification induced in the spectra of cellulose after oxidative degradation.[11] The investigations of the self-portrait indicated a severe oxidation, both of the cellulosic support and of the areas affected by foxing. Double carbon-carbon bonds were, indeed, detected, and their amount was so great as to produce a very intense peak, normally absent in the Raman spectra of undamaged cellulose, at 1596 cm^{-1} and 1604 cm^{-1} in the foxed areas and in the paper support, respectively (Fig. 1).

This behaviour was confirmed by infrared analysis (Fig. 2), which, indeed, showed an even worse situation, highlighting the formation of carbon-carbon double bonds and carbonyl groups (1500–1700 cm^{-1} region) and even of triple carbon-carbon bonds (2100–2300 cm^{-1} region), which implies the breaking of the anhydroglucose ring. Moreover, the peak of the OH stretching, centred at around 3500 cm^{-1}, was not as broad as usual; this behaviour is typical of a severe dehydration of the support.

Very interesting results were obtained by applying, in a completely non-destructive way, atomic force microscopy (AFM) to the self-portrait.

Previous researches performed at the Chemistry Laboratory made it possible to correlate the morphological changes of the paper's surface to its aging,[12] the hydrolytical or oxidative degradation of cellulose[13] and the biological or chemical origin of foxing[14].

[9] Missori et al. 2014.

[10] Pinzari et al. 2014.

[11] Bicchieri et al. 2000.

[12] Piantanida et al. 2005.

[13] Coluzza et al. 2008.

[14] Piantanida et al. 2006.

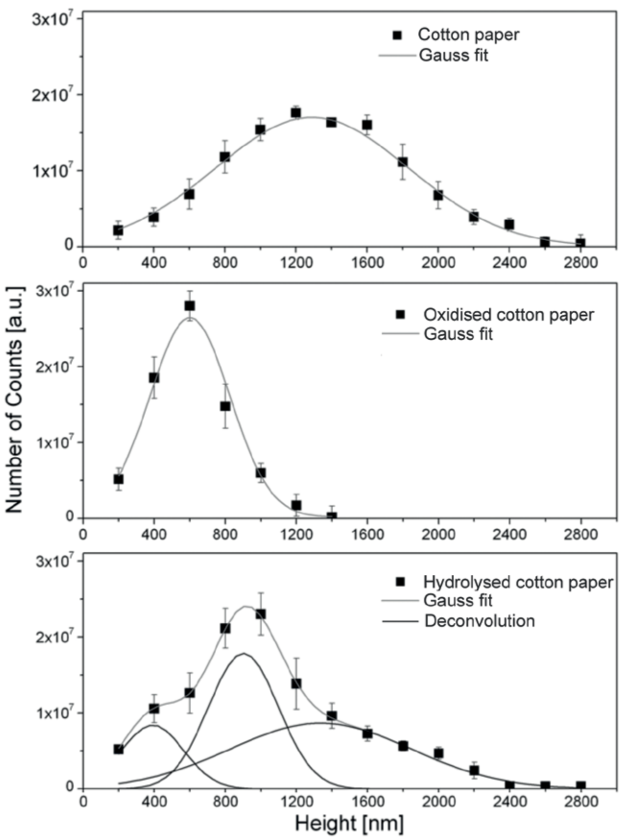

Fig. 3: AFM surface corrugation of (from top): not damaged, oxidised and hydrolysed papers. Oxidation produces a unique peak at lower dimension in respect to paper. The fragmentation of the cellulose, caused by hydrolysis, give rise to a superimposition of different surface distributions.

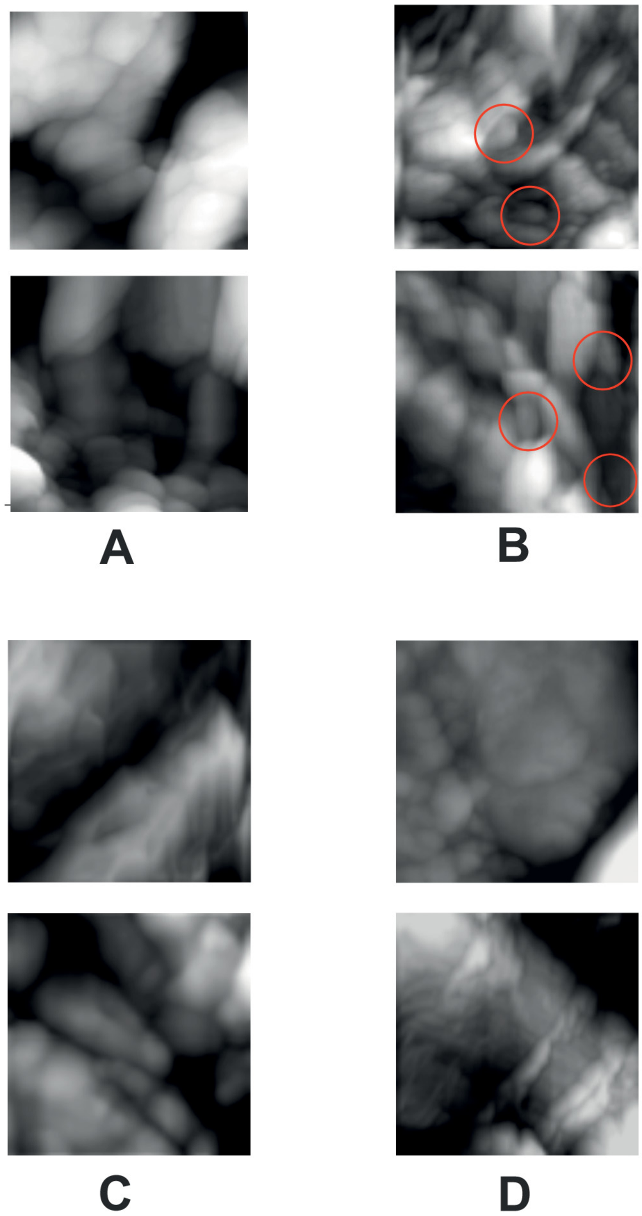

Fig. 4: AFM morphologies (15 μm x 15 μm) of A: paper in an original document (Original A in Fig. 5) at 3 mm distance from a foxing spot. B: foxing spot – induced in the same document by iron – in which repeated morphologies are evidenced by red circles. C: paper in an original document (Original B in Fig. 5) different from A at 3 mm distance from a foxing spot. D: foxing spot – induced by *Aspergillus terreus* in the same document – in which no repeated morphologies are visible.

A dominant oxidation causes a surface height distribution easily distinguishable from the one induced by a mainly hydrolytical degradation. Oxidative processes give rise to the formation of a single peak in dimensions lower than those observed in well-preserved paper. After hydrolysis, the fragmentation is an expected effect and causes, firstly, a random spread of the surface distribution and, eventually, an increase in the lower dimensions (Fig. 3).

When foxing spots are analysed by AFM, it is possible to distinguish whether they were produced by a biological or a chemical attack. In the case of chemical foxing, some morphologies are repeated regularly, whereas biological foxing produces morphologies randomly distributed on the surface of the stains and the paper (Fig. 4).

This behaviour reflects the distribution of the surface corrugation (Fig. 5).

In chemically induced foxing, the roughness of the spot does not increase, but decreases slightly. Paper and foxing stain surfaces are each described by a unique peak; moreover, stain and paper peaks are well separated. This is consistent with the strong oxidation usually found in foxed areas (Fig. 5, Original A).

In biological foxing, the roughness variation is caused by the presence of two peaks: one is consistent with the peak found in the paper; the other is well separated from this and is a marker of the stain, a completely independent colorimetric aspect of the foxing spot (Fig. 5, Original B).

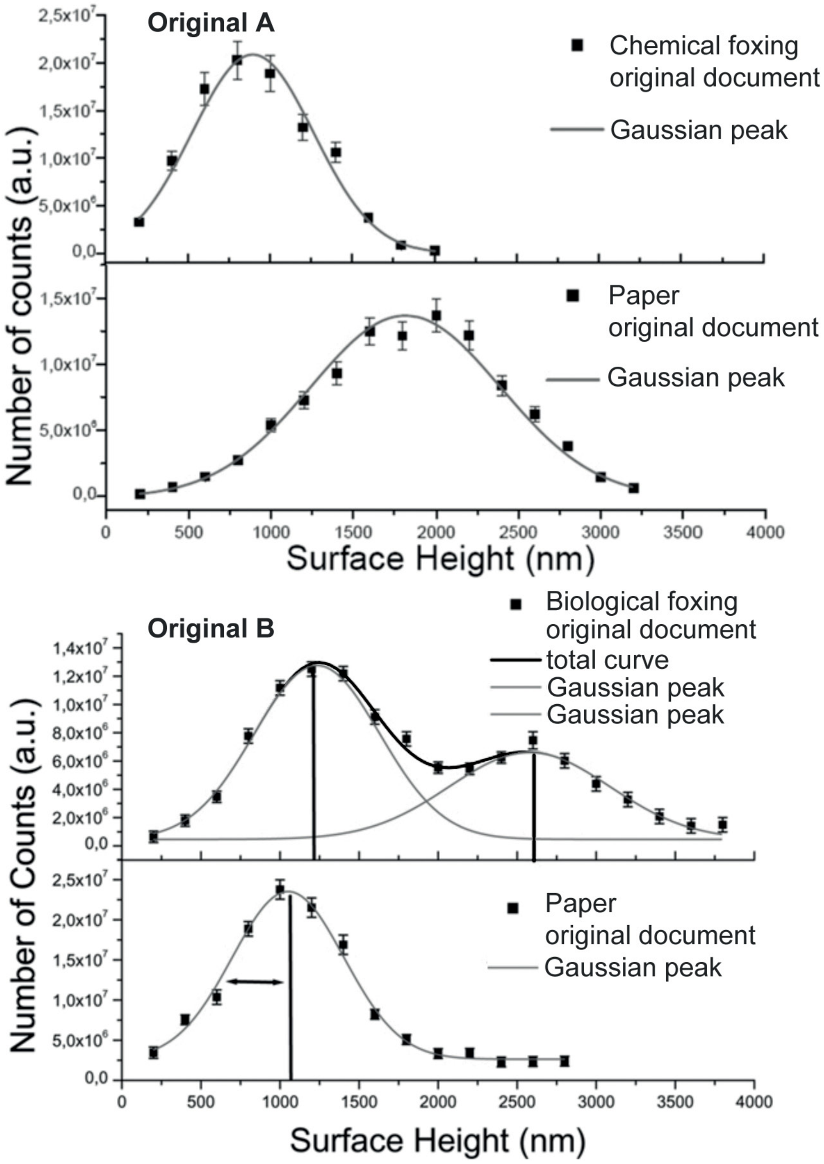

Fig. 5: AFM surface corrugation of (from top): chemical foxing spot on an original document, not-foxed paper of the same document; biological foxing spot on an original document, not-foxed paper of the same document.

A restoration project, including chemical treatment to stabilise the paper, was proposed, but the art historians rejected it for purely ‘philological’ reasons, in this way condemning the drawing to its destruction. In this case, the positive synergy between the different branches of science did not correspond to a positive synergy with the world of the humanities, thus leading to negative results.

4.2 The purple Codex Rossanensis

The *Codex Rossanensis* is a sixth-century illuminated manuscript written on purple parchment, conserved at the Museo Diocesano di Rossano (Cosenza, Italy).

In 1917–19, the codex was subjected to a restoration treatment, carried out by Nestore Leoni, a famous miniaturist active from the end of the nineteenth century to the mid-twentieth century. Leoni’s intervention irreversibly modified the aspect of the illuminated sheets. Nestore Leoni never wrote which materials he used for the restoration.

In June 2012, the Codex arrived at Icrcpal for a complete characterization of the pigments, support and materials Nestore Leoni used and to ascertain its state of conservation to determine the real restoration needs.

A scientific commission was established, including palaeographers, Bible scholars and historians specialized in the study of illumination.

In the analysis of Leonardo’s self-portrait, AFM topographies of the paper showed a very corrugated surface, indicating a coexistence of hydrolysis and oxidation. In the foxed spots, AFM topographies demonstrated a severe decrease in the thickness of the paper, ranging on average from 20% on the whole foxing spot to 60% in some parts of the spot, where the spectroscopic measures showed the presence of triple carbon-carbon bonds (Fig. 6).

All the techniques applied in the different laboratories of the Institute showed a very dramatic oxidation of the paper, caused by chemical, physical and biological attacks.

The challenge of the analysis of the *Codex Rossanensis* lies in the lack of analytical information on the pictorial media used in the Early Middle Ages (fourth–ninth centuries). Old-medieval illuminated manuscripts have been deeply studied from the historical standpoint, but their material composition has rarely been described.[15]

The results obtained at the Icrcpal Chemistry Laboratory are based on micro-Raman (378 spectra), micro-Fourier Transform Infrared (80 spectra) and X-Ray Fluorescence (35 spectra) spectroscopic analyses, performed on the

[15] Aceto et al. 2012.

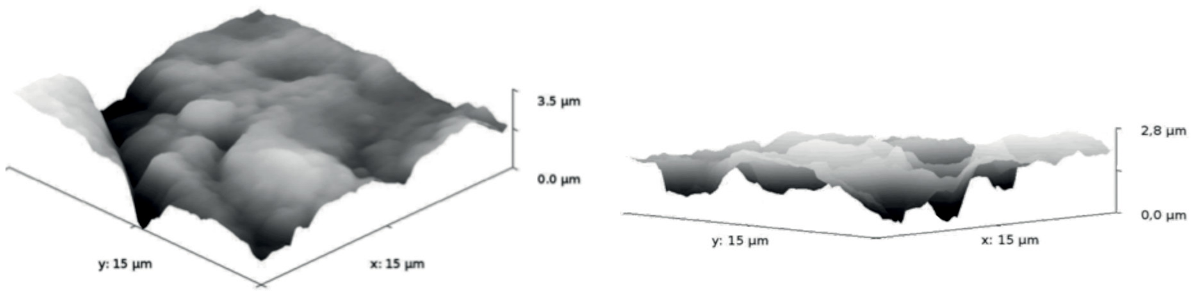

Fig. 6: Leonardo self-portrait. Left: AFM topography of the paper. Right: AFM topography of the paper in a foxing spot. In this case there is an evident decrease of the thickness of the paper as well as the formation of holes on the surface.

whole volume, the pigments, the support and the previous restoration. For a better understanding of some spectra acquired on red lakes, laboratory samples were prepared, using historical lake samples belonging to the collection of the Icrcpal chemistry laboratory or newly synthesized samples, on which spectroscopic analyses were performed. For the analysis of the purple substrate, FORS technique was also applied to originals and laboratory samples, in collaboration with the physics laboratory of the Institute.

Many questions were posed to the chemistry laboratory about the nature of the products applied by Leoni during the restoration, the composition of the pictorial palette used by the miniaturist(s) and the composition of the different inks present in the manuscript. The laboratory also had the task to provide scientific information that could help solve a problem of paramount historical importance. Some scholars[16] supposed that the illumination of Mark inspired by Sophia did not belong to the original manuscript, but could be dated to the twelfth century. The question needing an answer was whether the scientific tools could be useful to confirm or reject this hypothesis.

For clarity, each point will be discussed in a separate paragraph.

4.2.1 Materials used in the previous restoration (1917–19)

The first 20 pages of the codex show a clearly evident layer of an unknown material applied during the restoration performed by Nestore Leoni, who never revealed any details about the compounds he used, not even in the technical reports (conserved at the Archivio Centrale dello Stato, Rome, Italy) he had to present to the Ministry at the end of his work.

These materials deeply penetrated into the support, modifying its optical characteristics: the restored pages are now completely transparent and their colour is brown instead of purple. Sometimes the applied layer was partially detached.

When some regions of the applied layer were observed under the Raman microscope, some fibres were visible; from which spectra of cellulose were then collected. In the remaining part of the pellicle, both Raman and infrared analyses showed the spectrum of collagen. The analyses directly executed on other pages showed the presence of cellulose nitrate in some restricted areas, usually close to blue pigments. This lets us suppose that the first step of the restoration was an attempt to protect the more damaged pigments with cellulose nitrate.

The last 15 pages of the codex showed insect damage and extensive corrosion caused by the silver ink. Here the parchment pages were particularly fragile, and, instead of a gelatine layer, Leoni applied a fabric with a loose weave, crêpeline[17], made of silk, as confirmed by Raman. Results are shown in Fig. 7.

Between the end of the nineteenth century and the beginning of the twentieth century, three products were mainly used to reinforce damaged parchments:[18] gelatine mixed with formaldehyde, directly applied on the parchment or reinforced with Japanese paper; Archiv-Zapon (cellulose nitrate dissolved in amyl acetate with the addition of camphor or formaldehyde); and Cellit (cellulose acetate mixed with acetic ether, ethanol, acetic acid and camphor). No traces of cellulose acetate were found in the codex.

At that time, the mentioned methods were supposed to be safe and reversible, although many scholars had

[16] Kresten, Prato 1985.

[17] Anonymous 1900-1901.

[18] Schill 1899; Frederking 1910; Casanova 1928.

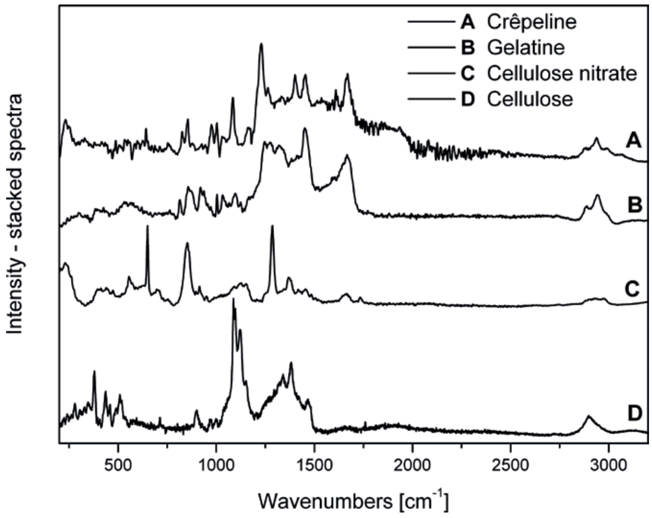

Fig. 7: Raman spectra collected from the materials applied in the previous restoration of the *Codex Rossanensis*. A: spectrum of silk (crêpeline) used in the last 15 pages of the codex; B: spectrum of gelatine applied as a thick layer to reinforce the parchment support; C: spectrum of cellulose nitrate found in restricted areas near the blue colours; D: spectrum of cellulose collected from fibres dispersed in the restoration layer.

already expressed doubts about their long-term effects. As an example of the debate, I have translated here the words of Eugenio Casanova,[19] concerning the use of gelatine. Casanova examines the restoration methods used in his time, which he was able to directly observe and record, thereby experiencing the underlying relative merits and defects of the various methodologies. In his description of the methods, Casanova expresses a strongly negative opinion about Marré gelatine, which gives documents a 'brilliant varnish', but in a short time leads to their total ruin:

> I am horrified at the thought that, if that bright patina is not removed soon, it will quickly destroy the manuscripts. It is, in fact, composed of siccative materials; under the influence of the temperature, this film cracks and detaches in pieces, at the same time removing fragments of the membrane to which it sticks. Using such gelatine simply adds more troubles to something that was already damaged.

Manifestly, Nestore Leoni, although aware of the debate, as evidenced by his preliminary reports (unpublished; conserved at the Archivio Centrale dello Stato, Rome, Italy), which he wrote to obtain the assignment of the restoration work, did not take into account the problem. The results are evident in

Table 1: Palette of the *Codex Rossanensis:* attribution to specific pigments/dye

Colour	Compound
Pictorial palette	
White	White lead [$2PbCO_3{\cdot}Pb(OH)_2$]
Black	Carbon black [amorphous C]
Red	Red lead [$2PbO{\cdot}PbO_2$] Cinnabar [HgS]
Orange	Red lead mixed with goethite
Yellow	Goethite [α-$Fe^{3+}O(OH)$] Orpiment [As_2S_3]
Green	Goethite mixed with lapis lazuli Goethite mixed with indigo Orpiment mixed with indigo
Blue	Lapis lazuli [$Na_3Ca(Al_3Si_3O_{12})S$]
Indigo	Indigo[$C_{16}H_{10}N_2O_2$]
Violet	Red lead mixed with lapis lazuli Pink lake mixed with lapis lazuli
Pink	Red lead mixed with white lead
Mauve	Pink lake from *Sambucus Nigra* *
Gold	Gold [Au], traces of iron [Fe]
Writing inks	
Original black inks	Carbon black [C]
Black inks added on top of silver inks	Carbon black [C]
Posterior inks	Iron-gall inks [$C_{14}H_6O_{10}Fe_2$]
Silvery inks	Silver [Ag] as main component
Golden inks	Gold [Au] as main component
Purple dye	
Purple support	Purple lake from *Roccella Tinctoria* [mainly orcein** $C_{28}H_{24}N_2O_7$]

* The composition of the lake is very complex. No single formula can be attributed to the lake (European Medicines Agency 2013).

** Orcein comprises a mixture of three major chromophores: 7-hydroxy-phenoxazone, 7-aminophenoxazone and 7-aminophenoxazine (Elix 1996). Being an extract from lichen, lake can also contain other organic compounds, such as erythrolitmin, lecanoric acid, erythrolein, α,β,γ-amino orcein, hydroxyl orcein.

[19] 1908, 'Report to the Interior Minister' published by Spadaccini 2013.

the codex: huge and irreversible damage to the pages treated with products that irreversibly penetrated into the support, which had become transparent and brittle by aging. The main problem in the use of gelatine and cellulose nitrate is the transparency of the parchment support. These products migrate into the porous parchment structure, causing transparency; furthermore, the brittleness of the support correlates with the penetration of the these products into the parchment. Filling the air cavities in the collagen structure with polymers able to link with the collagen reduces the softness of the parchment, making it brittle.

4.2.2 The pictorial palette

Many colours are present in the precious manuscript, from white to black and passing through all possible hues of visible light. Moreover, gold and silver were used for the text of the Gospels, as well as black inks in the title, the explanations of the miniatures and in the posterior notes. Some parts of the faded text in silver were rewritten in black ink at an unknown time.[20]

Fortunately for the scientist in charge of the analyses, the miniaturist(s) did not finely grind the pigments used for the illuminations. That made it possible to collect individual Raman spectra from each pigment, even when applied in a mixture, thus aiding in the identification of the colouring substances. In some cases, XRF spectra were recorded to confirm the Raman attribution. For the organic dyes, lakes and purple, infrared technique was employed, being complementary to Raman. The black inks were analysed using the three cited techniques. No preparatory layer for the pigments (Armenian bole or lead white or gypsum) was present in the manuscript, though this was common in the Byzantine area where the codex was written and decorated. Table 1 summarizes the results of the analyses.

White lead was the unique source of white in the manuscript and was also used as heightening; carbon black was applied both as black colour and as a darkener for other pigments; minium for all red hues or in mixture with other pigments (Table 1) to obtain orange, pink and some violet tones. Only one exception needs to be mentioned: on page 241 (Mark the Evangelist and Sophia), cinnabar, an expensive mineral, was used to write the name of the Evangelist.

Throughout the whole manuscript, yellow areas were drawn with goethite, which was also applied mixed with blue to obtain green shades. There are only two occurrences of the use of another yellow. On pages 3 (The cleansing of the Temple) and 241 (Mark the Evangelist and Sophia), a dark green was obtained by mixing orpiment and indigo. The presence of arsenic in the pigment was confirmed by XRF.

No *true* green pigments, such as malachite, verdigris, copper resinate or green earths, were found in the manuscript; all the different greens were obtained by mixing blue and yellow.

Raman analyses showed the use of lapis lazuli and indigo for the light and dark blue areas, respectively.

Violet was obtained by mixing minium with lapis lazuli, sometimes with an addition of carbon black. For a brown-violet colour, goethite was mixed with carbon black and lapis lazuli.

No silver areas were found in the miniatures, whereas very pure gold was used in all the illuminations.

The mauve colour needed more complex work to be characterised: identical Raman spectra of an unknown organic compound were collected from all the illuminations drawn in mauve. Manifestly, the dye used was a lake; in fact, in the false colour images the mauve pigment acquired a yellow hue, typical of organic red lakes (inset in Fig. 8).

Identification of lakes with infrared spectroscopy is usually almost impossible, due to the very low concentration of the dye: the spectral features of the support – parchment or paper – dominate in the collected data. For the same reason, the direct Raman analysis of dyes and lakes is particularly difficult; moreover, these colourants are poor Raman scatterers. Usually, when molecular spectroscopies are chosen, the lakes are analysed by using SERS (Surface Enhanced Raman Spectroscopy), but this involves direct contact with the original work of art, which should be avoided. A detailed discussion of the differences between Raman and SERS spectra of lakes can be found in Bicchieri, as well as an analysis of the composition of *Sambucus Nigra* extracts.[21]

Even though the spectra of the original miniatures presented features that could correspond to an anthocyanic compound, it was decided to compare the original spectra with those obtained from some red and red-violet lakes prepared in the laboratory with different chromophores.

The chosen lakes contain as principal compounds: alizarin (*Rubia Tinctorum*), carminic acid (*Porphyrophora hamelii*),

[20] Bicchieri 2014.

[21] Bicchieri 2014

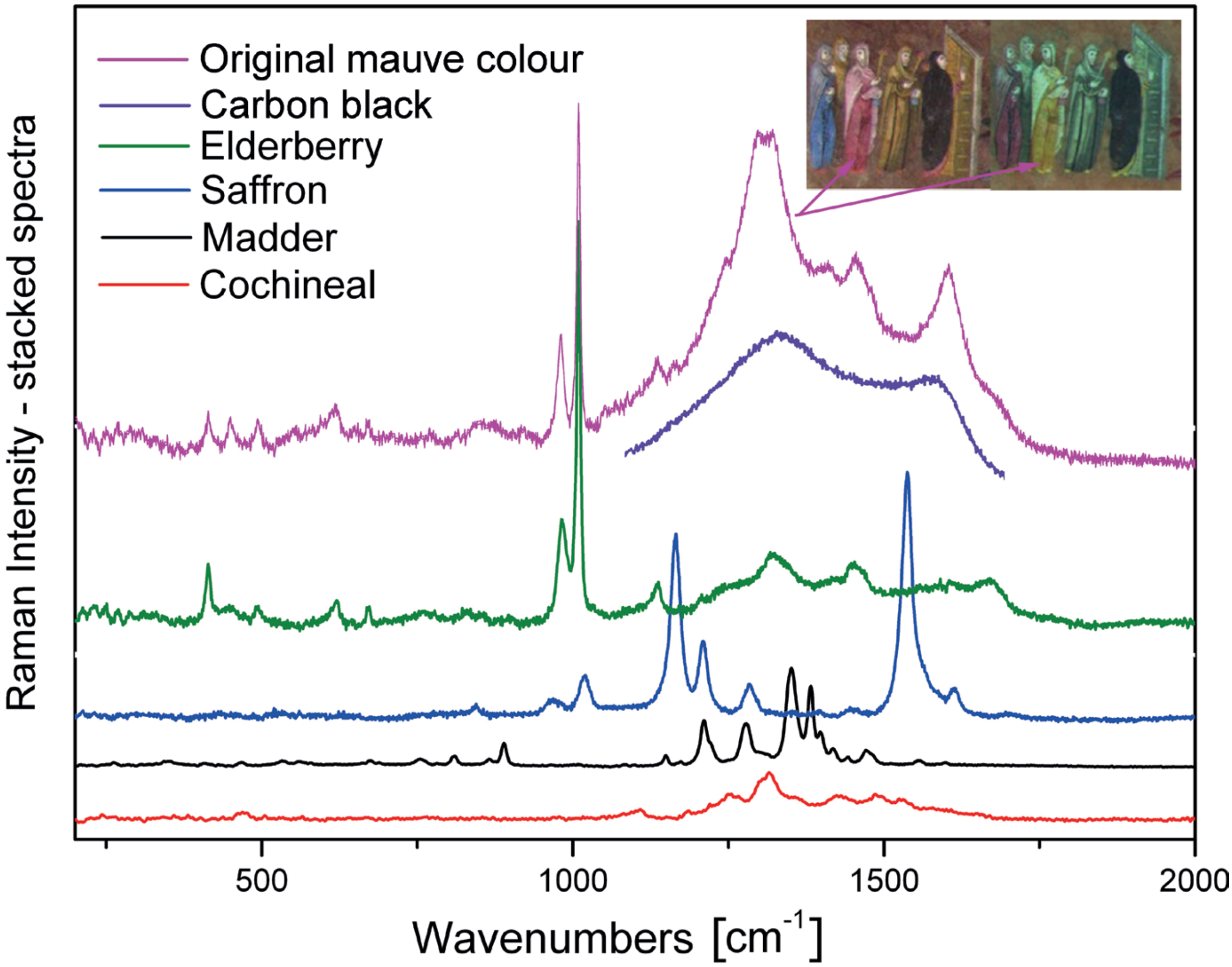

Fig. 8: Raman spectra of lakes (from bottom): cochineal (*Porphyrophora hamelii*), Madder (*Rubia Tinctorum*), Saffron (*Crocus Sativus*), (Carbon black), Elderberry (*Sambucus Nigra*), original mauve colour. Carbon black spectrum is reported to support the discussion in the text. The inset shows, marked with an arrow, the measurement point on the original (left) and the elaboration in false colours (right), courtesy of TEA s.a.s.

crocetin (*Crocus Sativus*) and anthocyanines (*Sambucus Nigra*).

Fig. 8 reports the Raman spectra of four laboratory samples compared with a typical spectrum collected from the original mauve areas. As can be seen, the best correlation was obtained for elderberry lake.

The differences between Raman spectra of the laboratory elderberry lake and the original mauve colour are due to the presence of a small amount of carbon black in the original lake that causes an enlargement of the bands in the 1200–1600 cm^{-1} region, as can be seen in Fig. 8, where the spectrum of carbon black is plotted only in the region where it shows characteristic bands. The two intense peaks at 981 and 1009 cm^{-1} in the elderberry lake are related to the presence of aluminium sulphate, necessary for its manufacturing.

To confirm the Raman data, FORS spectra (Fiber Optics Reflectance Spectra with a Zeiss MCS 600 spectrometer) were recorded from the original mauve colour and the prepared elderberry lake, in collaboration with the Physics Laboratory of Icrcpal.

There was a perfect concordance between the spectra. In the visible part of the spectrum, both show characteristic signals at 496, 524 and 564 nm, confirming the attribution of the mauve colour to elderberry lake.

4.2.3 Inks

All the black inks presented the characteristic Raman spectra of carbon black. Only the posterior comments to the text were written with iron-gall ink, detected by Raman and infrared and confirmed by the intense iron peak in XRF.

Table 2: (semi)quantitative calculation for the concentration of elements found in the silver-ink.

Element	Non-corroded ink (%)	Corroded ink (%)
Ag	69.83	69.79
Ca	28.64	28.11
Fe	0.23	0.64
Cu	1.11	1.16
Zn	---	0.22
Au	0.06	0.03
Pb	0.14	0.06

Table 3: Position of the characterising bands (nm) of original purple-dyed page, laboratory parchment sample dyed with orchil + sodium carbonate, and laboratory parchment sample dyed with orchil.

Sample	Peak 1	Peak 2	Correlation
original parchment	547.6 ± 0.4	594.6 ± 0.2	$R^2 = 0.999$ $\chi^2 = 3 \cdot 10^{-6}$
orchil + sodium carbonate	545.1 ± 0.8	592 ± 2	$R^2 = 0.995$ $\chi^2 = 7 \cdot 10^{-5}$
orchil	555 ± 2	589.6 ± 0.5	$R^2 = 0.998$ $\chi^2 = 2 \cdot 10^{-5}$

The golden ink had the same composition as the gold used for the illuminations. The gold was quite pure, containing only a small amount of iron.

The silver used for the text presented a different conservation state in the manuscript. XRF spectra (Fig. 9) showed that the silver had a different composition, in relation to its state of degradation, as can be seen in Table 2. It always contained copper, which is suspected to be responsible for the corrosion of the parchment substrate,[22] particularly evident in the last 15 pages that Leoni had reinforced with crêpeline.

A quantitative analysis of the XRF data, within the limitation of such a technique applied to thin supports, shows that the concentration of copper is not higher in the more corroded areas; but in these areas there is a greater amount of iron (about 3 times that found in the non-corroded regions), and zinc is also present. A more complicated degradation mechanism, involving contemporary redox reactions catalysed by iron and copper in the presence of zinc, should be imagined and investigated to understand the different behaviours of the two inks.

The presence of traces of gold (Au) is attributable to a contamination of the ink, whereas lead (Pb) and calcium (Ca) arise from the manufacture of the writing support.

4.2.4 Tyrian purple: truth or legend?

Scholars and art historians supposed that the parchment of such a precious manuscript must have been dyed with Tyrian purple (6,6'-dibromoindigo extracted from *Murex*), which is extremely expensive.

XRF analyses did not reveal the presence of bromine, even after a prolonged acquisition time of 1 hour, suggesting the use of a dye other than Tyrian purple.

Raman spectra collected from many pages were of very low quality because they were affected by an intense fluorescent band that masked all Raman signals; and infrared spectra could not help characterise the dye, as they were dominated by the signals of the collagen substrate. Even FORS spectra collected from the Codex at the Icrcpal physics laboratory did not match those of Tyrian purple.[23]

A perfect match was found with the parchment samples dyed with orchil, prepared in the chemistry laboratory.

The deconvolution (Origin software, Gaussian multipeaks fit) of the region 500–700 nm allowed us to find the exact position of the bands for the analysed samples of parchment dyed with orchil, of those dyed with orchil and sodium carbonate and of the original parchment. The results are reported in Table 3.

The band positions reported in the literature for orchil are located at 549 and 595 nm and are in good agreement with the positions calculated for the original purple-dyed parchment and the parchment dyed with orchil with sodium carbonate added.[24] Pure orchil has a band position different from that found in the original parchment.

In a previous work carried out at the Icrcpal Chemistry Laboratory during the restoration of some pages of another

[22] van der Most et al. 2010.

[23] Aceto et al. 2014a.

[24] Aceto et al. 2014 a.

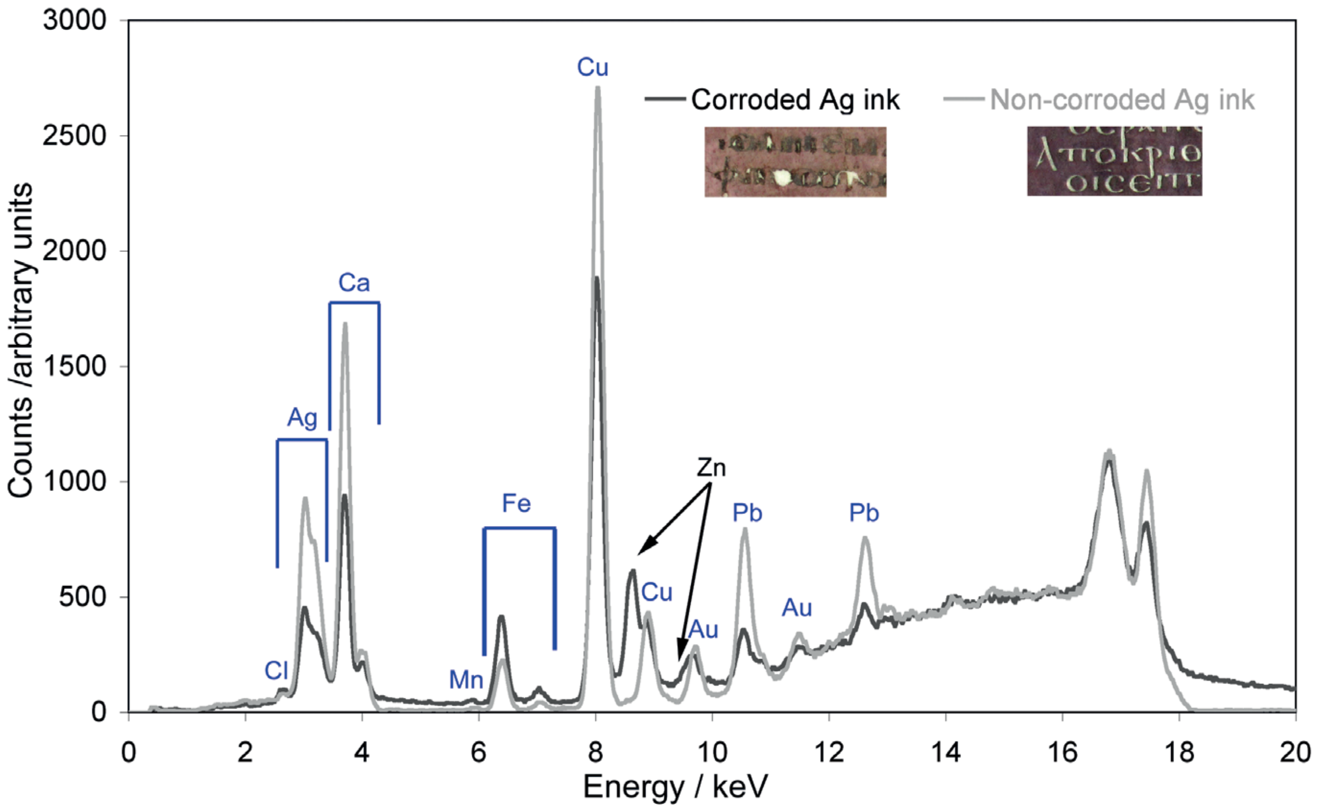

Fig. 9: XRF spectra of two different silver-inks. Black line: corroded. Gray line: non-corroded. In the figure the common elements are written in blue, whereas the element present only in the corroded areas is written in black.

purple codex, the *Sarezzano Codex* (fols 72ff., Tortona, Archivio Diocesano, fifth–sixth century), XRF showed a noticeable presence of bromine in the dyed parchment, but the infrared spectra did not show the typical features of 6,6'-dibromoindigo. In this case, Tyrian purple was not used to dye the parchment, as confirmed by the FORS analyses reported in.[25]

It seems indeed very important, from the historical point of view, to extend the analyses of purple codices, in order to elucidate whether a real Tyrian purple could have been used.

Until now, in fact, there is no evidence of its use for writing purposes.

In the case of the *Codex Rossanensis*, the positive synergy between all the different approaches allowed the complete characterisation of the manuscript, its dating (in particular on the basis of the biblical text) and the attribution of the discovered pictorial palette to a specific geographical area. Moreover, the chemistry laboratory was able to discover, replicate and characterize a peculiar lake, elderberry lake. To the author's knowledge, this was the first time that experimental evidence has been shown for the use of that lake in such an ancient document.

Furthermore, the characterisation of the illumination of Mark the Evangelist inspired by Sophia (p. 241) gave a scientific answer to the scholars who supposed that the illumination did not belong to the original manuscript, but could be dated to the twelfth century and realised with pigments different from those applied in the remaining manuscript. What differentiates such a miniature from the others present in the codex is that it maintains the freshness of the original colours, because it was not subjected to any previous invasive restoration.

All the experimental results show that the same palette was used throughout the entire codex. In particular, Raman and FORS results show the peculiar use of elderberry lake and of orpiment mixed with indigo to obtain, in the supposed posterior miniature, the precise shade of green, already found on page 3, that was considered original.

As a result of all the documented analyses, the findings of the historians and Bible scholars, the careful restoration and the valorisation, UNESCO has added the codex to the World Heritage List, and it is now conserved in the renewed Museo Diocesano di Rossano.

[25] Aceto et al. 2014 b.

5. Conclusions

The few examples presented in this paper allow us to draw some conclusions.

Methodologically, all problems related to cultural heritage artefacts must be addressed with a multidisciplinary approach that includes several and complementary techniques and competences.

It should also be emphasised that no single non-destructive technique can be claimed to be the 'resolving' one and that the cooperation between all the 'souls' involved in conservation, from scientists to humanists, can add important information to the knowledge of our history.

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Ed. by Michael Friedrich, Harunaga Isaacson, and Jörg B. Quenzer

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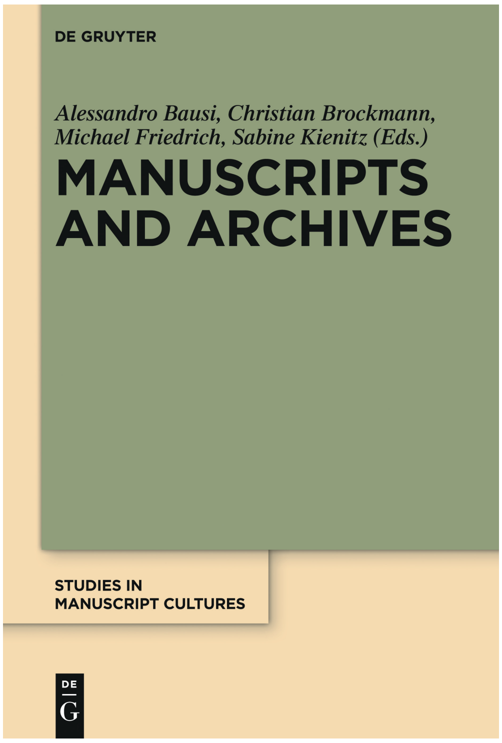

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Archives are considered to be collections of administrative, legal, commercial and other records or the actual place where they are located. They have become ubiquitous in the modern world, but emerged not much later than the invention of writing. Following Foucault, who first used the word archive in a metaphorical sense as 'the general system of the formation and transformation of statements' in his 'Archaeology of Knowledge' (1969), postmodern theorists have tried to exploit the potential of this concept and initiated the 'archival turn'. In recent years, however, archives have attracted the attention of anthropologists and historians of different denominations regarding them as historical objects and 'grounding' them again in real institutions. The papers in this volume explore the complex topic of the archive in a historical, systematic and comparative context and view it in the broader context of manuscript cultures by addressing questions like how, by whom and for which purpose were archival records produced, and if they differ from literary manuscripts regarding materials, formats, and producers (scribes).

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