Printing materials and technologies in the $15^{th} - 17^{th}$ century book production: an undervalued research field

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Abstract

We present a systematic non-invasive investigation of a large corpus of early printed books, exploiting multiple techniques. This work is part of a broader project - *Argeia* - aiming to study early printing technologies, their evolution and, potentially, the identification of physical/chemical fingerprints of different manufactures and/or printing dates. We analyzed sixty volumes, part of the important collection of the Ateneo Veneto in Venice (Italy), printed between the 15^{th} and the 17^{th} centuries in the main European manufacturing centers.
We present here the results of the imaging analysis of the entire corpus and the X-Ray Fluorescence (XRF) investigation performed, focusing on the XRF data and their statistical treatment using a combination of Principal Component Analysis (PCA) and Logistic Regression. Thanks to the broad XRF investigation - more than 200 data points - and to the multidisciplinary approach, we were able to discriminate the provenances of the paper - in particular for the German and Venetian volumes - and we potentially identified a chemical fingerprint of Venetian papers.

Keywords: Early printed books, Ancient Inks and papers, Non-invasive analysis, X-Ray Fluorescence (XRF), Principal Component Analysis (PCA), Logistic Regression.

1. Introduction

We performed an extensive physical/chemical investigation of sixty scientific printed books, from the preliminary imaging analysis to a series of point measurements. Due to the high historical value of the objects, we used only non-invasive and non-destructive techniques such as imaging analysis and X-Ray Fluorescence (XRF) investigations.
The sixty books, part of the Ateneo Veneto collection [1] were printed between the 15^{th} and the 17^{th} century in some of the main early European manufacturing centers: Basel (now Switzerland); Amsterdam, Leiden and Rotterdam (now the Netherlands); Paris, Lion and Strasburg (now France); Cologne, Herbert and Frankfurt (now Germany); Florence and Venice (now Italy).
The books cover a variety of topics, and they include important documents such as the astronomy text *"De reuolutionibus orbium coelestium"* of Nicolaus Copernicus, printed in Basel in 1566; medical manuals such as the *"Exercitationes anatomicae, de motu cordis & sanguinis circulatione"* by William Harvey, printed in Rotterdam in 1660; physics and mathematics textbooks like *"Meditationes de natura plantarum, et Tractatus physicomathematicus de aequilibrio praesertim fluidorumthe"* by Giovanni Maria Ciassi, printed in 1677 in Venice.
An important fact is that all the books in the corpus were stored together for more than two centuries in Venetian convents and afterwards in the Ateneo Veneto. This unique and uniform conservation history allowed the evaluation of results without the interference of different degradation processes.
Until the early 15^{th} century, all documents were written by hand using a variety of materials - supports, inks and binders. The invention of the "industrial" printing by Johannes Gutenberg in 1455 [2], [3] radically changed the world of texts in Europe.
The re-adaptation of the existing screw press and the use

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of movable metal types made the production of books extremely rapid, more abundant in numbers and increasingly less expensive compared to the traditional one [4]. In few decades, an almost total conversion from handwritten to printed books occurred [5].
Moreover, the traditional variety of writing supports were replaced by mass-produced papers, more homogeneous and standardized. Likewise, the inks radically changed: from the widespread use of the Iron-Gall inks for handwritten documents [6], [7], [8], [9], [10] to the use of carbon-based inks [11].
Our work follows previous investigations of the origins of printing with advanced analytical techniques.
We would like to mention, in particular, the important investigations of the Gutenberg Bible inks [12], [13], [14], [15] , the work of Manso et al. on elemental analysis of ancient papers [16], [17], [18] and the investigation of paper degradation by Stephens et al. [19] and Dupont [20].
Moreover, important background is the pioneering and broad study of ancient papers performed by the Barrow's Lab published in the 1974 [21] and significantly expanded by Barrett et al. in 2016 [22].
However, even these extensive efforts provide a limited picture of the very large collection of early printed specimens. More work is needed, and our present program is a contribution in this direction. Specifically, we consider here the historical evolution from handwriting to printing technologies, a very interesting and multifaceted issue.

2. Materials and Methods

The large size of the corpus and the need for significant comparisons of the results imposed the *a priori* definition of the methodology for the analysis. In particular:
⋆ We performed imaging analysis of all the bindings (when present), the first pages, the title pages and at least of three internal pages (chosen as explained below);
⋆ We performed the point investigations on three pages of each book: a page in the first half, one in the center and one in the last half. For each page, we investigated three different points: in the center, 3 cm from the internal binding and 3 cm from the lateral edge;
⋆ We analyzed by XRF the previously defined pages acquiring a spectra of the paper and at least one of the inks, focusing on characters with different fonts and/or dimensions, on different printing techniques - type (using metallic surface) and xylographies (using wooden surface) and on tables;
In addition, we applied the same methodology for pages with interesting features such as peculiar conservation problems, special characters or colored inks.

2.1. Visual inspections and Imaging analysis

All the volumes are generally well preserved, the paper integrity is essentially maintained and the readability of the texts is excellent. As expected, we observed some traces of humidity, generally localized along the external edges, and some paper foxing.
The entire corpus was printed using black carbon-based inks (in section 2.2 details on the ink composition). Only in few cases, we found colored pigments: for example, in the title page in Fig.1, printed in black and red, and in some illustrations like in Fig.2. More often, we found handmade annotations like the one in Fig.3 written with Iron-Gall inks (in section 2.2, one finds chemical details on the colored and on the handwriting inks).
These preliminary considerations were confirmed by an extensive imaging analysis of all the books, from Visible imaging to Infrared Reflectography and Ultraviolet Fluorescence. All the imaging analysis were performed with a commercial camera - modified removing the UV-IR cut filter - and using the appropriate external components for specific acquisitions – a high-pass filter at 850 nm for IR inspection and a combination of IR-UV cut-filter and yellow gelatine for UV fluorescence.
As for the visual inspection, the imaging analysis highlighted a quite homogeneous preservation condition of the corpus.
However, there are notable exceptions: on the one hand Venetian books and on the other hand German (and partially Swiss) books, as shown in Fig.4.
On the left-hand side of Fig.4 an example of a Venetian book: they are extremely well conserved, with perfect readability of the text and exceptionally white paper. Moreover, the UV imaging - Fig.4[c], left-hand side - reveals an intense and diffused fluorescence, probably related to the use of whitening agents in the paper treatment.
On the contrary, a few Swiss books and - even more - all the German volumes are affected by strong paper yellowing – as shown on the right-hand side of Fig.4. Furthermore, in some cases this seriously affects the readability. The UV fluorescence imaging emphasized this phenomenon and occasionally revealed features like those of Fig.4[c] (right-hand side), probably related to an unidentified paper treatment.
Literature reports a strict link between the use of gelatin size (animal glue) and Alum ($KAl(SO_4)_2$) in the paper

making process and the preservation conditions of the historical specimens. While the Alum seems to age more rapidly the paper, the gelatin instead appears to have a protective role and its high content is correlated to the brightness and good preservation of the paper [19], [20], [22], [23].
Considering our XRF results - in detail in section 2.3 - the use of more gelatin and less Alum for the Venetian books could be an explanation of the better preservation conditions of these books.
As discussed in previous literature [12], [13], [14], [15] and as proven by our XRF analysis, the books are printed with carbon-based inks. This was also confirmed by our Infrared Reflectography investigations. Figure 3 shows a comparison of the visible light imaging and the IR Reflectography of printed and handwritten texts. Whereas printed characters - carbon-based inks - remain perfectly readable, handwritten texts - iron-based inks - disappear. Indeed, the carbon-based inks are strong IR absorbers whilst the iron-based inks are transparent to the IR radiation [24].

2.2. XRF spectroscopy

We performed XRF analysis on a subset of the corpus - 32 books.
We used an ARTAX 400 (Mo anode) spectrometer by BRUKER. In order to meaningfully compare of the results, we used the same acquisition parameters for all measurements: 30 keV, 1300 μA, 0.65 mm collimator without filters and without an He flux. For the spectra analysis we used the software "SPECTRA" by BRUKER. The peak/element assignations and the spectra interpolations were performed automatically by the software and carefully checked step-by-step. Following the previously explained methodology, we acquired 206 spectra including pages with particular features like different printing techniques - type (using metallic surface) and xylographies (using wooden surface) - and/or special fonts. The elemental analysis highlighted a general homogeneity in the materials: the papers analysis shown the ubiquitous presence of K, Ca and Fe and frequently of Mn and the inks investigation revealed the omnipresence of K, Ca, Fe and Mn and frequently of Cu and Zn.
The presence of K, Ca and Fe in the papers could be directly linked to the paper production. Indeed, as previous mentioned, while the K is linked to the Alum used as a mordent, Ca was used in all the phases of the paper production: from the gelatin size to the whitening agents [16], [17], [18], [19], [20], [22], [23]. Moreover, traces of metals in water are likely responsible for Fe

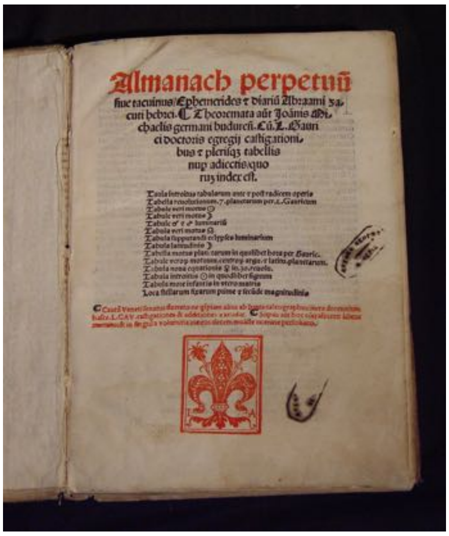

Figure 1: Colored title on the first page of *Almanach noua plurimis annis venturis inseruientia...* by Abraham ben Samuel Zacuto, printed in Venice in 1525.

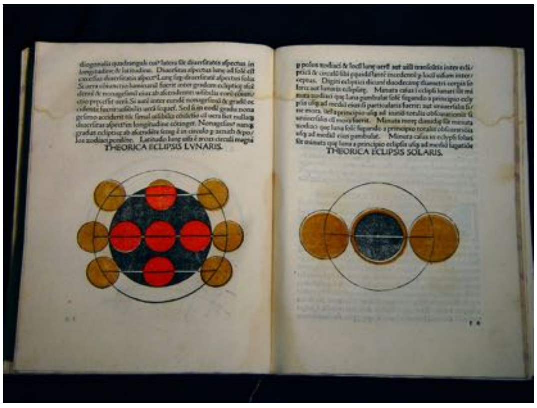

Figure 2: Colored illustration of page 54 of *Nouiciis adolfscentibus [!] ...* by Ioannes de Sacrobosco, printed in Venice in 1485.

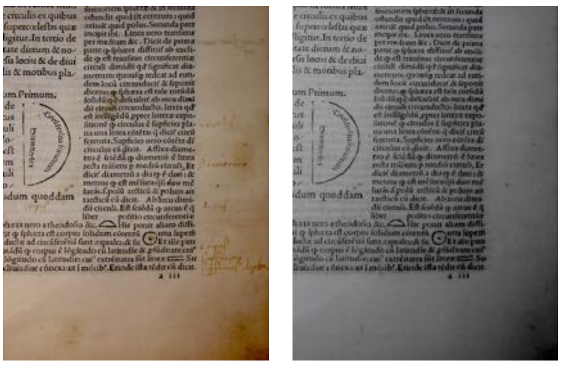

Figure 3: Comparison of Visible (Left) and IR reflectography (Right) images of a detail of page 3 of *Sphera mundi cu[m] tribus commentis nuper editis ...* by Ioannes de Sacrobosco, printed in Venice in 1499. Note that the handwritten annotations disappear in the IR picture.

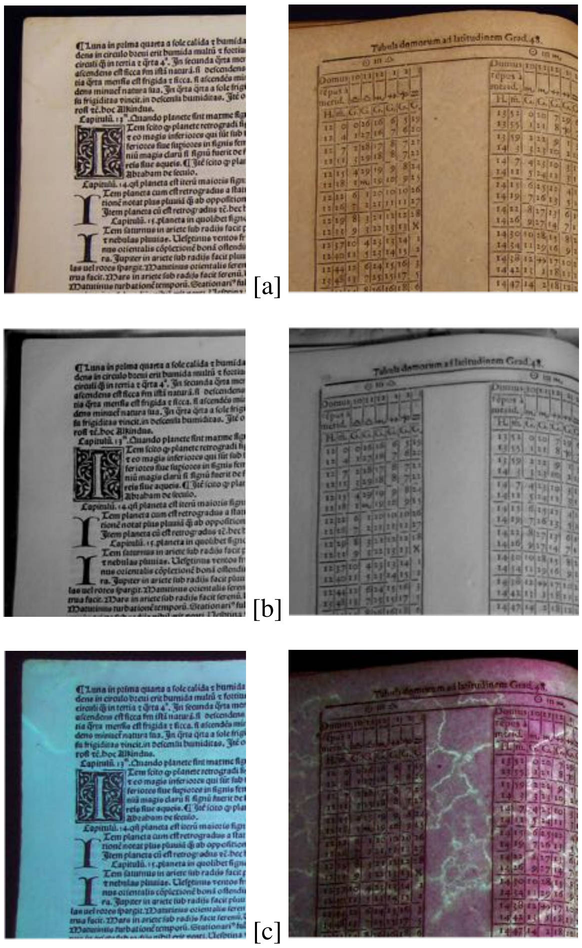

Figure 4: Comparison of Visible [a], Infrared [b] and UV Fluorescence [c] images of a detail of page 10 of *Opusculum repertorii pronosticon in mutationes aeris tam via astrologicaand..* by Firmin de Beauval (Venice, 1485). On the right: similar comparison for a detail of page 41 of *Ephemerides Ioannis Stadii Leonnouthensis mathematici...* by Jean Stade (Cologne, 1581).

and Mn detection and an additional source could be identified in the particle transfer from the metal types during the printing process [16].
The inks investigation revealed the use of carbon-based inks for all the black features of the books - from the characters to the illustrations.
We found the ubiquitous presence of K, Ca, Fe and Mn and the frequent presence of Cu and Zn.
While K and Ca could be linked to the use of fillers, for the other heavy elements contain we can hypothesize different ink recipes [12], [13], [14], [15] or the transfer of particles from the metal types [16].
In Basel, Cologne and some book from the (modern) Netherlands we also found Pb, not present elsewhere.
In addition to the black printed inks, we analyzed the handwritten annotations and the colored text and illustrations shown in Figs 1-3 of the previous section. In the red ink of the title page of Fig.1, we detected a large amount of Hg and a fraction of Pb - Fig.5, top - suggesting the use of a mixture of Vermilion and Red Lead. Except for some traces of Hg - most probably related to impurities due to use of mercury for the previous letters - the spectrum of the black ink of the same page confirms its carbon-based nature.
The ink spectrum of the red text of Fig.2 yielded a result very similar to the previous red ink. The analysis of the yellow pigment detected As, Pb and some traces of Sn suggesting a mixture of an Arsenic-Lead pigment with Orpiment or Realgar - Fig.5, middle.
The analysis of the annotation in Fig.3 revealed a quite consistent amount of Fe and Zn indicating the use of an iron-based ink - Fig.5, bottom.
Note that the Ca and Fe peaks in all the ink spectra are mainly related to the emission from the paper substrate. This complicates the data analysis, specifically for the low-intensity spectra of the black inks. In order to correct them for the paper contributions, we adopted the following procedure.
We subtracted from each ink spectrum the corresponding paper spectrum, multiplied by a calibration factor. This factor was used to take into account the attenuation of the paper signal due to the superimposed ink layer.
To estimate the calibration factor, we measured with a microscope the average ink thickness of several samples from similar printed books. For each sample we acquired a magnified image of the side edge of the sample and we measured the ink thickness obtaining an average value of $27 \pm 7 \mu m$. Then, considering the homogeneity of the chemical composition of the inks and their thickness, we calculated the factor approximating the ink layer as a carbon film with the (photon-energy dependent) absorption coefficient tabulated by Ref. [25].
The above procedure specifically brought to light small but visible differences between the black ink spectra and the paper spectra, so that the former cannot be entirely attributed to the paper. As shown in Fig.6 , whereas the heavy element signals like Hg are clearly related to the ink also in the raw spectrum, only the appropriate correction reveals the right contribution of light elements like K and Ca to the ink spectra.

2.3. Statistical analysis

To effectively evaluate all the many acquired XRF data - more than 200 spectra - and to investigate the small differences between production sites and years,

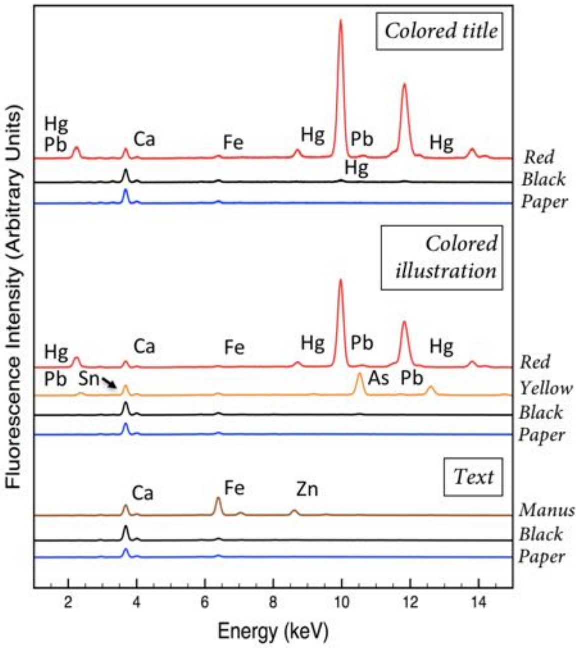

Figure 5: XRF analysis of the inks shown in Figs.1-3. *Top - Inks of the colored title of Fig 1*: The Hg and Pb found in the red inks suggest the use of a mixture of Vermilion and Red Lead; *Middle - Inks of the colored illustration of Fig 2*: this red ink is similar to the previous one; As, Pb and Sn in the yellow ink indicate the use of a combination of Lead-Tin Yellow and Orpiment or Realgar; *Bottom - Inks of the text of Fig 3*: the presence of Fe and Zn in the handwritings indicates the use of an Iron Gall Ink. The Ca and Fe peaks in all spectra are mainly related to the substrates.

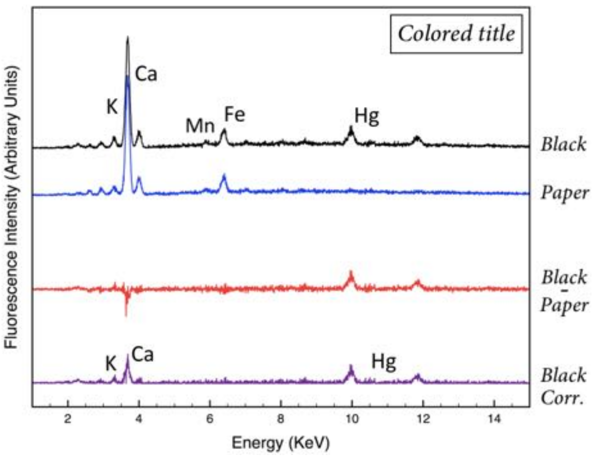

Figure 6: Example of spectra correction.*Top:* zoom of the black ink and the paper the spectra of the colored title of Fig 1. *Middle:* the subtraction of the paper spectrum from the ink spectrum leads to errors and to underestimates the content of light elements (here K and Ca). *Bottom:* Corrected black ink spectrum.

we performed a Principal Component Analysis (PCA) [[26], [27]].

PCA is a dimensionality reduction technique which projects datapoints to few, mutually orthogonal (i.e. linearly uncorrelated) dimensions, made from linear combinations of original features (also called predictor or independent variables). Each principal component attempts to combine features in order to explain the maximum possible variance in the observations.

Unfortunately, the intrinsic homogeneity of the data impedes a clear analysis using just PCA. For this reason, we combined it with another technique - Logistic Regression. This method can estimate the probability of a binary response - e.g. the confirmation or not of an *hypothesis* (e.g. if an observation is *paper or not paper*, printed in *Venice or not*, etc.) - based on one or more predictor variables (e.g., the chemical elements), and determine the effect of these variables on the probability of a given response. For a detailed discussion of the method, see e.g. [28].

After correcting of the original XRF spectra (as explained in detail in the previous section), we applied these two methods to the counts of each detected element. To perform Logistic Regression, we only considered as predictor variables the elements detected for most datapoints (K, Ca, Mn and Fe) and we discarded datapoints without any of these values. We further excluded outliers if an observation was more than 3 standard deviations from the respective mean, and removed datapoints from under-represented categories (such as colored inks). Finally, the dataset was standardized. For consistency, both PCA and Logistic Regression were performed on the same dataset.

We explored three hypotheses, by encoding them as nominal (dependent) variables:

⋆ **Hypothesis 1: Paper - not Paper**

To assess the differences in composition between papers and inks, we evaluated this hypothesis considering as *not Paper* all black inks, either inks for types or xylographies.

• *PCA*: The analysis and the related plot of datapoints over the first (PC1: x axis) and second (PC2: y axis) principal components, given in Fig.7, shows a clustering of the paper on one side and of the other materials on the other, determined by PC1. This component, which explains 53% of the total variance, is equally weighted on K (negative), Ca (-) and Mn (-), with an slightly higher weight of Fe (-). PC2 (22% of variance), weights quite heavily on Ca (-) and slightly less on Mg (+), and does not seem to affect the clustering. Unfortunately, due to the similarity of the inks, we are not able to further distinguish between type and xylography inks.

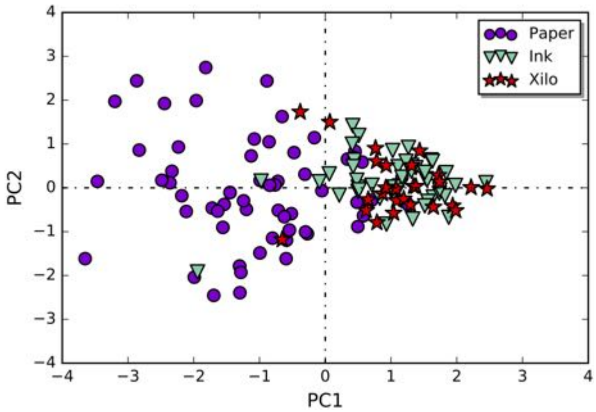

Figure 7: PCA analysis of the XRF results. PC1 (53% explained variance), slightly more weighted on Fe (-), explains the clustering of papers (left) and other materials (type inks and xylographies). PC2 (22%) is quite heavily weighted on Ca (-) and slightly less on Mn (-).

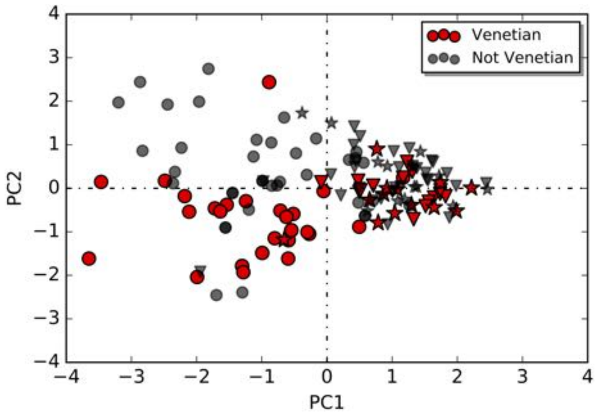

Figure 8: Same PCA results of Fig.7. Venetian materials are highlighted in red. Venetian papers are clustered in the third quadrant (bottom-left), meaning they contain more Ca.

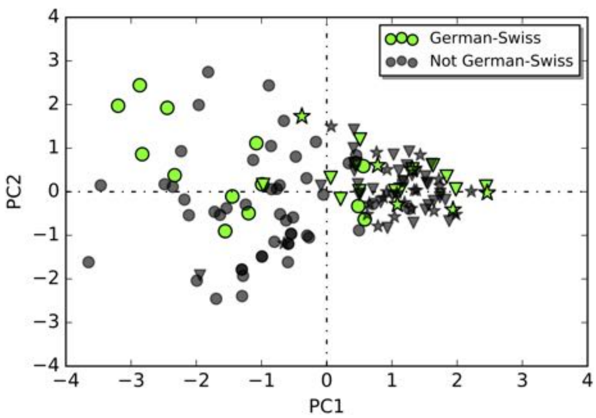

Figure 9: Same PCA results of previous figures, with German/Swiss items highlighted in green. Here, opposite to Fig.8, German/Swiss papers are clustered in the second quadrant (top-left), meaning they contain less Ca).

• *Logistic Regression*: PCA results are confirmed and strengthened: we found a significant strong and positive correlation of Fe with the paper and a weakly positive correlation of K (more details on the statistical results are in the Appendix - section 5). This means that the paper contain more Fe and slightly more K than the inks.

In addition, we probed the sub-classification of type inks and xylographies, but did not find any statistically relevant difference.

⋆ **Hypothesis 2: Venetian - not Venetian**

To further investigate differences between the extremely well preserved Venetians books and the rest of the corpus, we analyzed the categories *Venetian - not Venetian*.

• *PCA*: Using the same PCA results shown in Fig.7 and highlighting in red the Venetian data, the clustering of Venetian papers becomes visible over the second principal component, but this distinction does not extend to inks - Fig.8.

• *Logistic Regression*: Taking in account previous results - papers clustering and the homogeneity of type inks and xylographies - we investigated this hypothesis considering only paper datapoints.

The regression analysis identified a significant, strong and positive correlation of Ca with Venetian papers and a weak negative correlation for K. This means that Venetian papers generally contain more Ca and slightly less K than papers from outside Venice.

Considering these results, we can hypothesize that the particularly good preservation conditions of Venetian books is linked to different paper recipes, in particular to a recipe with more gelatine size (one of the main non-organic elements is Ca) and less Alum (see previous-mentioned references).

⋆ **Hypothesis 3: German/Swiss not German/Swiss**

Similar to the previous analysis, we investigated the differences between German or Swiss books and the rest, again only considering paper signals for Logistic Regression.

• *PCA*: The PCA plot in Fig.9 shows a partial clustering of German/Swiss papers (in green), opposed to Venetian papers over the second component.

• *Logistic Regression*: Even if the balancing of analyzed population is not optimal (50 non German/Swiss papers, of which 31 Venetians) a significant correlation of Ca (-) and Fe (+) and a weak correlation of Mn (-) with German/Swiss papers were identified.

These results, combined with PCA and results from the previous analysis *Venetian - not Venetian*, seems to confirm our hypothesis of a different use of the gelatine and Alum in the paper and identify a potential explanation of the observed paper differences.

We performed several other tests, in particular to investigate the evolution in time of papers recipes. Considering that we were unable to differentiate among inks, and the imbalance in our population - the most ancient analyzed books are all from Venice - we focused on Venetian papers, organising our dataset in two categories: *Pre 1515 - Post 1515*.
The year 1515 was selected to balance our sample population, and to correspond to the year of the death of Aldo Manuzio, a leading Venetian printer, valued and admired throughout Europe. Moreover, although the current scientific hypothesis sets the year 1500 as the date which divides early printed books from *incunabulas*, we can argue that at least the first decade of the 16^{th} century still witnesses the application of the same techniques from the previous century, allowing us to move forward this limit to 1515.
PCA did not reveal any evident clustering, but Logistic Regression identified a negative correlation of Mn with the Post-1515 papers.

3. Conclusions

The preliminary visual inspection and the imaging analysis revealed the general good condition of the corpus. Moreover, they highlighted two exceptions: the white paper and perfect readability of the Venetian volumes and the strong paper yellowing of the German and - partially - the Swiss examples.
Despite the general homogeneity of the materials, a PCA analysis allowed to clearly differentiate between the paper and other materials - type and xylography inks.
Moreover, the combination of Logistic Regression with PCA highlighted a potential chemical fingerprint of the differentiation between Venetian and German/Swiss books, especially for papers. Indeed, we can hypothesize a direct link between the exceptional conservation state of Venetian papers and their high Ca content - also related to the presence of gelatine - and low K amount - linked to Alum. The opposite trend is present in German/Swiss books, confirming this hypothesis.
In addition to the imaging analysis and the XRF investigations we performed further point analysis like Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance (FTIR-ATR), colorimetric analysis and pH contact investigations. In future work, we intend to integrate these results and to expand our investigations by enlarging our corpus and focusing on the ink binders. We will exploit further non-invasive and non-destructive laboratory techniques and, only on existing accidental detachments, carry out analysis on fragments using synchrotron radiation sources. Furthermore, different statistical techniques will be applied and compared to corroborate our hypotheses, in particular to better investigate the evolution of papers and ink recipes over time.

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5. Appendix

As mentioned in previous sections, the statistical analysis has been performed on the counts of each detected element of corrected XRF spectra. For consistency, PCA and Logistic Regression were performed on the same standardized dataset, excluding outlier datapoints and under-represented categories (such as colored inks).
The final dataset consists of 139 datapoints: 59 from Venetian items (paper, type inks and xylographies), 36 from German/Swiss books and 44 from other countries. Of these, 67 are papers, divided in: 31 Venetian, 17 German/Swiss and 19 from other countries.
⋆ *Hypothesis 1: Paper - not Paper*
Out of 139 items of the population, 67 are papers. Logistic Regression highlighted a strong positive correlation of Fe with paper (P value=0, confidence interval positive) and a weakly positive correlation of K with paper (P value=0.115). In table below the detailed results.

Hypothesis 1: Paper - not Paper

	dy/dx	std err	z	P>|z|	[95.0% Conf. Int.]	
K	0.0417	0.026	1.576	0.115	-0.010	0.094
Ca	0.0267	0.027	0.986	0.324	-0.026	0.080
Mn	0.0253	0.031	0.811	0.418	-0.036	0.087
Fe	0.2514	0.034	7.306	0.000	0.184	0.319

⋆ *Hypothesis 2: Venetians - not Venetians*
As mentioned we performed the analysis only on paper datapoints. Out of 67 papers of the population, 31 are Venetian. Logistic Regression highlighted a strong positive correlation of Ca with Venetian papers (P value=0, confidence interval positive) and a weakly negative correlation of K with Venetian papers (P value=0.077).

Hypothesis 2: Venetians - not Venetians

	dy/dx	std err	z	P>|z|	[95.0% Conf. Int.]	
K	-0.0810	0.046	-1.768	0.077	-0.171	0.009
Ca	0.2646	0.028	9.595	0.000	0.211	0.319
Mn	0.0547	0.049	1.123	0.261	-0.041	0.150
Fe	-0.0772	0.066	-1.164	0.245	-0.207	0.053

⋆ *Hypothesis 3: German-Swiss - not German-Swiss*
As the previous analysis, we investigate only paper datapoints. Out of 67 papers, 17 are German/Swiss. Note that the population balance is not optimal: of 50 non German/Swiss papers, 31 are Venetians. Logistic Regression highlighted: - a strong positive correlation of Fe with German/Swiss papers (P value=0, confidence interval positive); - a strong negative correlation of Ca with German/Swiss papers (P value=0.001, confidence interval negative); - a weakly negative correlation of Mn with German/Swiss papers (P value=0.113).

Hypothesis 3: German-Swiss - not German-Swiss

	dy/dx	std err	z	P>|z|	[95.0% Conf. Int.]	
K	0.0367	0.036	1.005	0.315	-0.035	0.108
Ca	-0.1877	0.056	-3.333	0.001	-0.298	-0.077
Mn	-0.0636	0.040	-1.585	0.113	-0.142	0.015
Fe	0.1883	0.052	3.598	0.000	0.086	0.291