A Systematic Scientific Study of Coptic Inks from the Late Roman Period to the Middle Ages

Doctoral Dissertation

Tea Ghigo

Fakultät für Geisteswissenschaften
Universität Hamburg

Facoltà di Lettere e Filosofia
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Subject - Archaeometry

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Day of the oral defence: 20 October 2020.

First reviewer: Prof. Dr. Ira Rabin (Universität Hamburg).

Second reviewer: Prof. Alberto Camplani (Sapienza Università di Roma).

Other members of the commission: Prof. Dr. Oliver Hahn, Prof. Gianfranco Agosti, Prof. Paola Buzi.

Eidesstattliche Erklärung

Hiermit erkläre ich an Eides statt, dass ich diese Arbeit selbstständig und ohne fremde Hilfe verfasst, keine anderen als die angegebenen Quellen und Hilfsmittel benutzt und die wörtlich und inhaltlich übernommenen Stellen als solche kenntlich gemacht habe.
Ich habe mich erstmals und nur an der Universität Hamburg zur Zulassung zu einer Doktorprüfung beworben. Kein Teil dieser Dissertation ist bislang veröffentlicht.

Hamburg, im Mai 2020

Tea Ghigo

Once upon a time two wise people told me we must know where we come from, to understand where we are going.
There is where my journey began.

Una volta, non molto tempo fa, due saggi mi dissero che dobbiamo conoscere da dove veniamo per capire dove vogliamo andare.
È allora che è iniziato il mio cammino.

To my parents.
First reins and then pillars in the path of over twenty years that culminates in this work.

Ai miei genitori.
Prima briglie e poi pilastri di un percorso lungo più di vent'anni che culmina in questo lavoro.

To my partner.
My anchor and my safe harbour.

Al mio compagno.
La mia ancora ed il mio porto sicuro.

Abstract

Purpose This doctoral dissertation addresses the material analysis of inks used in Egypt between the late Roman period and the Middle Ages, complementing the information provided by previous sporadic studies.

It is based on the examination of 162 manuscripts produced in different areas of Egypt during the time span considered. Half of these are Coptic literary texts. Their inks are compared with those found on Coptic documentary texts and on literary and documentary texts written in Greek and Latin. This research explores the variety of types of ink used and aims at unveiling possible distribution patterns needed to lay the foundation for a geo-chronological map of the history of inks.

Methods An interdisciplinary approach involving cooperation between the humanities and the natural sciences was adopted.

The PAThs project[1] fosters the material study of inks as an integral part of the examination and description of Coptic literary codices and provided a historical dimension for many of the manuscripts that were analysed.

The BAM[2] and the CSMC[3] granted the use of non-invasive techniques and portable equipment to facilitate access to museums and libraries located in England, Germany, Ireland, Italy and Spain. Manuscripts were examined using near-infrared reflectography, X-ray fluorescence and occasionally other spectroscopic techniques.

Findings The results show the contemporaneous use of different types of ink.

No correlation is observed between the writing medium and the support or the language. However, there is a strong association of iron-gall ink with literary texts whereas contemporaneous documentary texts were written predominantly with carbon ink.

In addition, the results obtained on some of the medieval literary codices suggest the existence of regional trends in the chemical composition of iron-gall inks produced within a relatively short period.

Mixed inks seem to have been used frequently in the period investigated. However, they could not be unequivocally identified using the current protocol. This dissertation suggests and discusses possible solutions to overcome the restrictions encountered.

Conclusions The present work shows that the different types of ink used in Egypt between Late Antiquity and the Middle Ages could be exploited as a foundation to develop a geo-chronological map describing the evolution of inks. To serve this purpose, the current analytical protocol should be broadened to include techniques that allow for a routine identification of the organic ingredients of inks. In addition, data should be complemented with the analysis of a substantial number of dated and located manuscripts.

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[1] PAThs ("Tracking Papyrus and Parchment Paths: An Archaeological Atlas of Coptic Literature") is an ERC advanced project based at Sapienza University of Rome

[2] Bundesanstalt für Materialforschung und -prüfung, Berlin

[3] Centre for the Study of Manuscript Cultures, University of Hamburg

Kurzfassungen

Ziel Diese Dissertation befasst sich mit der Materialanalyse von Tinten, die in Ägypten zwischen der spätrömischen Zeit und dem Mittelalter verwendet wurden, und ergänzt die Informationen aus früheren sporadischen Studien.

Sie basiert auf der Untersuchung von 162 Manuskripten, die im betrachteten Zeitraum in verschiedenen Gebieten Ägyptens hergestellt wurden. Die Hälfte davon sind koptische literarische Texte. Ihre Tinten werden mit denen verglichen, die in koptischen Dokumentartexten sowie in literarischen und dokumentarischen Texten in Griechisch und Latein zu finden sind. Diese Forschung untersucht die Vielfalt der verwendeten Tintentypen und zielt darauf ab, mögliche Verteilungsmuster aufzudecken, die erforderlich sind, um die Grundlage für eine geochronologische Karte der Geschichte der Tinten zu legen.

Methoden Ein interdisziplinärer Ansatz, der die Zusammenarbeit zwischen Geistes- und Naturwissenschaften umfasst, wurde angenommen.

Das PAThs-Projekt[4] fördert die Materialstudie von Tinten als integralen Bestandteil der Untersuchung und Beschreibung koptischer literarischer Kodizes und bietet eine historische Dimension für viele der analysierten Manuskripte.

Die BAM[5] und die CSMC[6] gewährten den Einsatz nicht-invasiver Techniken und tragbarer Geräte, um den Zugang zu Museen und Bibliotheken in England, Deutschland, Irland, Italien und Spanien zu erleichtern. Manuskripte wurden unter Verwendung von Nahinfrarotreflektographie, Röntgenfluoreszenz und gelegentlich anderen spektroskopischen Techniken untersucht.

Ergebnisse Die Ergebnisse zeigen die gleichzeitige Verwendung verschiedener Tintenarten.

Es kann keine Korrelation zwischen dem Schreibmedium und dem Träger oder der Sprache festgestellt werden. Es gibt jedoch eine starke Assoziation von Eisengallustinte mit literarischen Texten, während zeitgenössische dokumentarische Texte überwiegend mit Kohletinte geschrieben wurden.

Darüber hinaus deuten die Ergebnisse einiger mittelalterlicher literarischer Kodizes auf regionale Trends bei der chemischen Zusammensetzung von Eisengallustinten hin, die innerhalb eines relativ kurzen Zeitraums hergestellt wurden.

Gemischte Tinten scheinen im untersuchten Zeitraum häufig verwendet worden zu sein. Sie konnten jedoch mit dem aktuellen Protokoll nicht eindeutig identifiziert werden. Diese Dissertation schlägt mögliche Lösungen vor und diskutiert diese, um die aufgetretenen Einschränkungen zu überwinden.

Schluss Die vorliegende Arbeit zeigt, dass die verschiedenen Arten von Tinte, die in Ägypten zwischen der Spätantike und dem Mittelalter verwendet wurden, als Grundlage für die Entwicklung einer geo-chronologischen Karte verwendet werden könnten, die die Entwicklung der Tinten beschreibt. Zu diesem Zweck sollte das derzeitige Analyseprotokoll um Techniken erweitert werden, die eine routinemäßige Identifizierung der organischen Inhaltsstoffe von Tinten ermöglichen. Darüber hinaus sollten die Daten durch die Analyse einer erheblichen Anzahl datierter und lokalisierter Manuskripte ergänzt werden.

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[4] PAThs ("Tracking Papyrus and Parchment Paths: An Archaeological Atlas of Coptic Literature"), ERC advanced project, Sapienza Universität Rom

[5] Bundesanstalt für Materialforschung und -prüfung, Berlin

[6] Centre for the Study of Manuscript Cultures, Universität Hamburg

Estratto

Scopo Questa tesi di dottorato analizza la composizione materiale di inchiostri usati in Egitto tra il periodo tardo-Romano ed il Medioevo, espandendo e corredando dati ottenuti in precedenza durante studi sporadici.

Si basa sull'analisi di 162 manoscritti prodotti in diverse aree d'Egitto. Circa la metà sono testi letterari scritti in Copto, i cui inchiostri sono confrontati con quelli usati in testi documentari in Copto e in testi letterari e documentari in Greco e Latino. Questo lavoro di ricerca esplora la varietà degli inchiostri utilizzati e tenta di portare alla luce profili di distribuzione utili a porre le basi per una mappa geo-cronologica che ne descriva l'utilizzo e l'evoluzione.

Metodi La metodologia applicata è fortemente interdisciplinare e si basa su una cooperazione internazionale tra le Scienze Naturali quelle Umanistiche.

Il progetto PAThs[7] delinea una dimensione storica per molti dei manoscritti esaminati e promuove lo studio materiale degli inchiostri come parte integrante dell'analisi e descrizione di manoscritti Copti letterari.

Il BAM[8] e il CSMC[9] rendono possibile l'impiego di tecniche non invasive e strumentazione portatile per facilitare l'accesso a musei e biblioteche in Germania, Inghilterra, Irlanda, Italia e Spagna. I manoscritti sono esaminati per mezzo della riflettografia infrarossa e della fluorescenza di raggi X oltre all'applicazione occasionale di altre tecniche spettroscopiche.

Risultati I risultati ottenuti mostrano l'uso contemporaneo di diversi tipi di inchiostro.

Non è stata osservata alcuna correlazione tra inchiostro e supporto scrittorio o lingua. Invece, è stata rilevata una forte connessione tra inchiostro ferrogallico e testi letterari mentre i testi documentari coevi sono prevalentemente scritti con inchiostro a base di carbone.

Inoltre, i risultati ottenuti su alcuni codici letterari medievali potrebbero suggerire l'esistenza di differenze regionali nella composizione chimica di inchiostri ferrogallici prodotti in un periodo relativamente ristretto.

Gli inchiostri misti sembrano essere utilizzati con una certa frequenza durante il periodo esaminato. Tuttavia, il protocollo analitico impiegato non ne permette l'identificazione univoca. Questa tesi suggerisce e discute possibili soluzioni per superare tale limite.

Conclusioni La ricerca condotta suggerisce che la diversità nella composizione degli inchiostri impiegati in Egitto tra la tarda Antichità e il Medioevo può essere utilizzata per gettare le basi di una mappa geo-cronologica che descriva l'evoluzione dei materiali scrittori. A tal fine, l'attuale protocollo analitico deve essere ampliato includendo tecniche che permettano l'identificazione di composti organici. Inoltre, i dati raccolti andrebbero corredati attraverso l'analisi di un numero cospicuo di manoscritti certamente datati e localizzati.

[7] Tracking papyrus and parchment PAThs. An archaeological Atlas of Coptic Literature. Progetto ERC basato all'Università di Roma La Sapienza

[8] Bundesanstalt für Materialforschung und -prüfung, Berlino

[9] Centre for the Study of Manuscript Cultures, Università di Amburgo

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1 Introduction

1.1 Background, motivation and approach

1.1.1 State of the art[10]

In the last two decades, a significant amount of scientific research has been carried out in all areas of the cultural heritage field. The technical investigation of cultural artefacts has involved an examination of a variety of different materials, such as pigments[11], textile fibres[12] and plastics[13], to mention only a few. Despite this, the study of simple but essential media like black writing inks has largely remained a marginal subject, finding little space in the scientific literature, and being scarcely represented at international conferences.

A quick look at recent and ongoing research on writing media reveals that the greater part of it is striving to understand the mechanism of corrosion typical of iron-gall inks, since these are widely diffused and the process is potentially damaging[14]. On the other hand, only a minority of studies is dedicated to characterising the composition of the inks used in manuscripts, with most of those investigations covering the study of the writing media used in manuscripts and drawings produced in Europe from the late Middle Ages onwards[15]. Far fewer studies are dedicated to older materials, although some have investigated the inks produced in ancient times, primarily in areas around Egypt, since the climatic conditions have allowed for a better conservation of the writing supports. In particular, the studies from the 1990s undertaken by Delange et al., Macarthur, and Nir-El and Broshi represent seminal works in the investigation of inks on manuscripts produced in ancient times in Hellenistic Egypt, Coptic Egypt and Hellenistic Middle East, respectively[16]. In addition, there have been other

[10] This paragraph presents the state of the art before the present investigation begun in November 2017. Since then, other contributions to this field of study were published. Many of them resulted from the research carried out in parallel to this study by the BAM Bundesanstalt für Materialforschung und -prüfung, Berlin) and CSMC (Centre for the Study of Manuscript Cultures, University of Hamburg): Maltomini et al. forthcoming; Nehring et al. forthcoming; Rabin, Hahn, and Kaska 2019; Rabin, Wintermann, and Hahn 2019

[11] Robinet and Corbeil 2003; Di Stefano and Fuchs 2011; Edwards et al. 2014; Steger et al. 2019

[12] Müller et al. 2004; Müller et al. 2006; Pozzi et al. 2012; Kakoauei, Kakouei, and Kumaran 2014

[13] Shashoua 2003; Ploeger, McGlinchey, and de la Rie 2015; Alcantara-Garcia and Ploeger 2018

[14] Rouchon-Quillet et al. 2004; Kolar and Strlič 2006; Rouchon-Quillet and Bernard 2015

[15] Hahn et al. 2004; Rabin, Hahn, and Geissbühler 2014; Aceto et al. 2017; Díaz Hidalgo et al. 2018

[16] Delange et al. 1990; Macarthur 1995; Nir-El and Broshi 1996

sporadic studies mostly examining the period up to the first centuries of the Christian era[17], while a large span of history between the first centuries of the Common Era and the early Middle Ages, normally referred to as "Late Antiquity"[18], has been left almost completely unexplored. Indeed, especially in the case of Egypt, scholars have often neglected the importance of this crucial transitional period, and it is only in recent times that its systematic investigation has begun[19].

*

Although it is almost 40 years old, the study on the history of inks by Monique Zerdoun Bat-Yehuda[20] is still the only work systematically addressing the evolution of black writing inks from the Mediterranean area to Asia over the time span ranging from Late Antiquity to the Renaissance. In her work, Zerdoun collects recipes for the preparation of inks found in different literary sources and tries to identify the ingredients mentioned, despite the complications imposed by different languages and historical contexts.

Probably due to logistical difficulties, this type of systematic approach has never been attempted using archaeometry to reveal the composition of inks produced between Late Antiquity and the Middle Ages. Even though in recent years non-invasive analytical techniques have often met with the favour of curators responsible for the care of collections, a study of this scale requires obtaining access to a fair number of institutions, often with the additional struggle of understanding which pieces are worth studying. This, together with the challenges of dealing with a consequential number of well-preserved, dated and located manuscripts, has often discouraged scholars and scientists.

Even if arduous, such a systematic study on a large geographical area and time frame would represent a valuable contribution to manuscript studies. The origins of manuscripts from Antiquity and Late Antiquity are often unknown, and manuscripts frequently circulated on the antiquities market for some time before they ended up in the institutions where they are currently preserved[21]. For this reason, palaeography and codicology are often jointly required to reconstruct the historical context of the documents. These disciplines are based on comparing the distribution patterns that characterise the type of script, the handwriting, the

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[17] Brun et al. 2016; Christiansen, Cotte, et al. 2017

[18] The term "Late Antiquity" is used rather loosely here. A more detailed description of the periodisation can be found in note 1 of the article "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use", given in the appendix to this thesis: "It should be stressed that the definition of different historic periods is a nontrivial issue. Given the different schools of thought regarding the division into periods that exist for ancient history, it is difficult to generalise, and every generalisation leads inevitably to a simplification of the reality. Intending to use such simplification for mere classification purposes, the authors would like to clarify how they interpret the subdivision of historical periods. The time span from the death of Alexander the Great (323 BCE) to the battle of Actium (31 BCE) is referred to as Hellenistic period. It follows the Roman period which ran until the fourth century CE, when the Late Antiquity started. The Middle Ages began in the seventh century CE when the Arabs conquered Egypt"

[19] Pernigotti 2006

[20] Zerdoun Bat-Yehuda 1983

[21] Nongbri 2018, 9–15

book format or the graphic layout of a statistically relevant number of manuscripts whose historical context is well known with those displayed by an undated and unprovenanced object, on the assumption that similar patterns correspond to the same time frame or geographical area. However, a systematic analysis of inks could also assist by revealing distribution patterns in the type and composition of writing media, which could be collected in a geo-chronological map describing the technological evolution of inks. Once enough data are available, this tool would be able to complement the information provided by palaeography and codicology and help to place manuscripts in space and time.

Furthermore, archaeometric studies of parchment and paper codices performed in the past have demonstrated that a scientific approach can offer relevant insights in retracing the history of the manufacture of individual manuscripts. For instance, the identification and characterisation of different writing media has been successful in discriminating the writing phases involved in the production of codices and in distinguishing the work of different scribes[22].

1.1.2 Purpose

Researchers at the BAM (Bundesanstalt für Materialforschung und -prüfung, Berlin), and the CSMC (Centre for the Study of Manuscript Cultures, University of Hamburg) believe in the contribution that archaeometry can bring to the field of manuscript cultures and have often fomented an interdisciplinary approach to the study of written artefacts. Their joint effort often aimed at revealing the historical and technological evolution of black inks. With the intention of gaining new insight into the writing materials and supports used in Egypt between Late Antiquity and the Middle Ages, in November 2017 these institutions began collaborating with the ERC-funded project "PAThs – Tracking Papyrus and Parchment Paths: An Archaeological Atlas of Coptic Literature", based at Sapienza University of Rome. This dissertation is the direct outcome of the research carried out during this collaboration[23].

The PAThs project is dedicated to the study of Coptic literary production, that is, to the corpus of manuscripts, with almost exclusively religious content, produced in Egypt between the 3rd and the 12th centuries CE and written in Coptic, the last phase of the Egyptian language. The continuous production of Coptic manuscripts from Late Antiquity to the Middle Ages offers a unique opportunity for a systematic scientific study of inks produced between the 3rd and 12th centuries over a relatively large geographic area, including the whole of Egypt and northern Nubia. In addition, the climatic trends that have always characterised this region favour the conservation of organic materials (e.g., papyrus and parchment), thus making it easier to access many objects whose state of conservation is suitable for archaeometric analysis.

[22] Rabin, Hahn, and Geissbühler 2014; Aceto et al. 2017; Geissbühler et al. 2018

[23] The research contained in this work was funded by the European Research Council's Horizon 2020 Programme under an ERC Advanced Grant 2015 destined to support the project "Tracking Papyrus and Parchment Paths: An Archaeological Atlas of Coptic Literature. Literary Texts in their Geographical Context: Production, Copying, Usage, Dissemination and Storage" (http://paths.uniroma1.it/), Project no. 687567, principal investigator Paola Buzi

These favourable conditions may help this investigation to provide the first contribution for a geo-chronological map describing the history of writing media.

Previous scientific studies on Coptic texts have revealed that iron-gall ink was used as far back as the end of the 4th century CE; see, for example, the recent discussion of a manuscript of the book of Proverbs preserved at the Staatsbibliothek in Berlin[24]. Therefore, one of the aims of this project is to reveal some of the earliest evidence of this type of ink, with the hope of casting light on the transition between carbon-based inks and iron-gall inks. On a more general level, it also addresses the validity of suggestions made in the past that the use of one or another type of ink might have depended on the writing support[25]. While addressing these questions, the archaeometric analysis performed also offers some support to palaeography and codicology, revealing details about the history of production and the usage of the manuscripts that are examined.

Even though it was not part of the initial plan, this investigation also ended up studying manuscripts written in other languages than Coptic. Thanks to this, the present research can explore any correlations between the writing medium and the different languages used in Egypt during Late Antiquity[26].

1.1.3 The role of PAThs and the historical context of Coptic literature

Beginning on 1 November 2016, and still ongoing, the PAThs project is intended to provide an in-depth diachronic understanding and effective representation of the geography of Coptic literary production[27]. This project applies a cross-disciplinary approach, combining a broad range of disciplines for the first time in Coptic studies. Philology, codicology, archaeology and digital humanities join forces to provide a new perspective on the production, copying, usage, dissemination, and storage of Coptic literary works in relation to the geographical contexts of origin of both the texts themselves and their related writing supports.

The aim of PAThs is to produce a digital archaeological atlas of Egypt between Late Antiquity and the Middle Ages, where the currently scattered information about each of the manuscripts is collected, studied and reorganised. This versatile tool has been freely accessible online since February 2019. The information is available for the scholarly community to search at different chronological, regional and thematic levels and it is constantly updated thanks to the work of the PAThs researchers. This digital tool is intended to illustrate the strong interconnection between "settlements, as revealed by the archaeological investigations, and

[24] Ghigo et al. 2018. This is reproduced as "An attempt at a systematic study of inks from Coptic manuscripts" in the appendix. Note that the dating of this codex is controversial. However, the latest palaeographical and codicological research indicates that it cannot be earlier than the end of the 4th century CE; see https://atlas.paths-erc.eu/manuscripts/24

[25] Macarthur 1995

[26] Buzi 2018a; Camplani 2015a; Bagnall 1993, 230–60; Choat 2009

[27] Buzi, Bogdani, and Berno 2018

intellectual production, as revealed by manuscripts"[28], and to provide a new comprehensive perspective on the spread and development of Coptic literature and manuscript culture[29].

From the very beginning, it was decided that the work of PAThs should be based on the sharing of ideas and results, contributing to create a true collaborative network involving other projects with similar or complementary purposes and encouraging the contribution of other scholars and researchers. For this reason, all the data collected in the PAThs database and the atlas are freely and easily accessible, reusable and exportable[30]. The original platform resulting from this multidisciplinary and collaborative approach provides an ideal space in which to introduce, for the first time in a systematic fashion, information on the composition of the writing media as an integral part of the description of manuscripts. At the same time, the potential of archaeometric analysis in revealing connections between different milieu where Coptic literature was produced can be explored.

In parallel, the archaeometric analysis of Coptic inks expands the studies on the history of writing media that have long been undertaken in the BAM and the CSMC and collects relevant information for sketching a geo-chronological map of the historical evolution of inks. To achieve this, information on the date and the place of production of the manuscripts under investigation is essential. Even though it is possible that the ingredients used to produce a particular ink were traded along commercial routes (and future research must aim at understanding in detail such pathways), as a first approximation it is reasonable to assume that an ink was composed from the materials available locally.

In fact, however, when it comes to Coptic Egypt, it is extremely difficult to gather a sufficient number of literary manuscripts with the information on their date and place of production explicitly given in, for instance, the colophon. Therefore, the present investigation must often rely on a reconstruction of the history of each manuscript using traditional approaches such as palaeography and codicology. For this purpose, the PAThs project has played an important role, not only providing information derived from previous studies but also complementing this with insights made on the basis of the latest codicological and palaeographical research carried out by its interdisciplinary team.

In some cases, only a partial reconstruction of the historical context of particular manuscripts was possible. The PAThs project is relatively recent and still ongoing, and therefore not all collections have been thoroughly studied yet. Furthermore, it is very much the case that Coptic literature often comes from unattested discoveries and has reached modern collections through the antiquities market[31]. Therefore, the scarcity of information about a manuscript often precludes the possibility of completely reconstructing its historical context, even cross-linking the information coming from a variety of disciplines. Moreover, even when the archaeological context of a manuscript is attested, the fact that manuscripts

[28] Buzi, Bogdani, and Berno 2018, 40

[29] Buzi 2017

[30] https://atlas.paths-erc.eu/ (last accessed 4 December 2019)

[31] This is the case, for instance, with the Bodmer Papyri and the Nag Hammadi codices

were often circulated after their production means that the place a manuscript was found does not always correspond to the place in which it was produced, generating ambiguity.

To complement the data obtained from the analysis of Coptic literary inks, it was decided to include in this investigation manuscripts that had not been studied in the framework of the PAThs project. In particular, documentary manuscripts written in Greek, Latin and Coptic and literary manuscripts in Greek and Latin were added to the corpus.

Broadening the horizon of the investigation in this way had a double purpose. On one hand, it provided an opportunity to collect data on the composition of inks on manuscripts that in some cases displayed an explicit indication of the date and place of issue, giving some anchoring points for the geo-chronological map. On the other, it contributed to the achievement of a more comprehensive insight into the complex socio-cultural reality that characterised Egypt during Late Antiquity. Despite the different languages and genres, Greek, Latin and Coptic documentary and literary texts were of course produced in the same areas and even in the same environments. Therefore, they represent valuable terms of comparison and permit the results obtained on the Coptic literary texts included in the PAThs atlas to be seen in a much broader context.

It must be stressed that not all the accessible manuscripts from outside the PAThs atlas have an inherent indication of dating in their texts. Each document belongs to one of three cases:

1. Manuscripts displaying either a date or a specific reference to a particular historic period. The reliability of the information collected is in this case very high.
2. Manuscripts studied in recent times whose date has been proposed by scholars on the basis of palaeographical patterns which have been observed on several precisely dated manuscripts. In this case the reliability of the information collected is medium-high.
3. Manuscripts studied prior to the digital era, when it was still rather difficult to gain access to quality facsimiles of the texts studied. As this may have hampered the process of palaeographical dating, the reliability in this case is medium-low.

Further information on the dating and place of provenance of the analysed manuscripts will be given in Chapter 4 along with the analytical results.

1.2 Corpus

1.2.1 The “agile” approach[32] adopted to define the corpus

When this research began, the full corpus of manuscripts to be analysed was not yet completely determined, only outlined. This was the result of an intentional choice: to model

[32] The “agile” approach was initially defined in the field of software development and later applied to project management. It offers extreme flexibility and the possibility of responding to issues as they arise within the project, making the necessary changes to optimise time, costs and results. See

the corpus on the basis of the results obtained rather than to define a priori which specific groups of manuscripts to study. As was expected, every episode of analysis was relevant to gain insight into the materials and technologies of ink manufacturing. As a result, the "analytical schedule" was often rearranged. For instance, it was decided to perform a set of analyses focused on documents from Bawit (further details in § 1.2.2.3) after finding evidence of an unusual type of ink on a papyrus fragment coming from there.

This research was fortunate in that it could count on the good relationships that the members of PAThs and the BAM have with many organisations to gain access to manuscripts preserved in different institutions: the Museo Egizio in Turin, the Ägyptisches Museum und Papyrussammlung in Berlin, the Staatsbibliothek zu Berlin, the Cambridge University Library, the Chester Beatty Library in Dublin and the Biblioteca Apostolica Vaticana in Rome. In addition, the first rounds of analysis were quite successful and awarded the project a certain visibility. As a result, access was granted to a high number of fragments preserved in the Palau Ribes collection in Barcelona and the Roca Puig collection in Monserrat due to the interest and enthusiasm the curators there showed towards the aims of this project. Although the historical context of many of the manuscripts preserved in these collections had not been studied in depth, their investigation was pivotal in revealing an unexpected correlation between the type of text and the type of ink (see § 4.2.9 and the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use")[33].

In the end, over the course of about two years, *in situ* analyses were carried out in eight different institutions. The corpus of manuscripts examined included texts in different Coptic dialects (most of them in Sahidic, with a minority in Bohairic and Akhmimic) as well as Greek and Latin manuscripts. No texts originally written in Arabic were investigated, although several marginal notes in Arabic were encountered, and a complete translation into Arabic was found in the margins of a Coptic Bohairic codex from the Monastery of Saint Macarius.

In addition to the analyses, the growing interest in archaeometry, and in the natural sciences applied to the study of art and archaeology in general, gave birth to a fruitful collaboration with the Museo Egizio in Turin that went beyond the simple analysis of its collections. The scientific studies performed on some of the papyri in its collection were displayed in the temporary exhibition "Archeologia Invisibile" open to the public from the 13 March 2019 and available also in a virtual tour[34]. The aim of the display was to address the principles of the application of the natural sciences to the study of archaeological objects and give examples of the instrumentation used and the results that can be found.

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https://www.cio.com/article/3156998/agile-project-management-a-beginners-guide.html (last accessed 5 February 2020)

[33] Ghigo, Rabin, and Buzi 2020

[34] https://museoegizio.it/esplora/mostre/archeologia-invisibile/ (last accessed 28 November 2020)

1.2.2 The institutions involved and the manuscripts studied[35]

1.2.2.1 Museo Egizio in Turin

At the Museo Egizio in Turin, the investigation focused on a group of papyrus leaves that the king of Sardinia purchased in the 1820s from Bernardino Drovetti, an Italian explorer and art collector who entered in Egypt as an officer in the Napoleonic army at the end of the 18th century. Later, the king appointed the philologist Amedeo Peyron to arrange the leaves as part of the first nucleus of the collection at the Museo Egizio[36]. The provenance of these codices is not mentioned in any modern document. However, some scribal subscriptions found on their leaves seem to indicate that they once belonged to the library of the cathedral of Thi(ni)s, nowadays Ğirğā, located not far from Abydos[37].

The library of Thi(ni)s is a unique example of an entire well-preserved institutional library from the end of Late Antiquity, probably dated to between the end of the 7th and the beginning of the 8th century CE. It constitutes the last example known so far of an entire Egyptian library transmitted by papyrus codices, and is therefore a valuable object of study. Furthermore, it represents a significant witness of the literary tastes and dogmatic orientations prior to the "9th-century Coptic book revolution" which saw not only the gradual emergence of multiple-text manuscripts (MTMs), but also the creation of new codicological and palaeographical features[38]. This is sufficient in itself to explain the importance of acquiring scientific information about the technical aspects of these codices. In addition, however, the palaeographical studies undertaken in the framework of the PAThs project have revealed that the codices from Thi(ni)s were most likely manufactured in a very limited time frame and were written by few copyists. They therefore offer the possibility of examining what should be a very homogeneous library from a material point of view. For all these reasons, the codices from Thi(ni)s were chosen as the starting point for this investigation of the composition of inks.

1.2.2.2 Staatsbibliothek zu Berlin

Most of the leaves examined at the Staatsbibliothek were originally part of the library of the White Monastery in Sohag (Upper Egypt). This became one of the most important locations of Coptic literary production under the strenuous guidance of Shenoute (ca. 350–465/466 CE)[39]. What remains of its library dates back, for the most part, to the 9th–11th centuries CE. The leaves examined at the Staatsbibliothek date to the 10th–11th centuries CE and were part of a set of manuscripts bought in 1887 on the antiquities market in Luxor. This purchase included 69 parchment leaves which are now bound in 11 modern volumes[40]. Parchment

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[35] This section introduces the historical context of the manuscripts investigated. These manuscripts form part of different ancient collections and are nowadays preserved in several institutions. Their corresponding shelfmarks are reported along Chapter 4 together with the analytical results.

[36] Buzi 2018b

[37] Orlandi 1974

[38] Buzi 2019a; Buzi et al. 2017; Buzi 2018b

[39] Orlandi 2002; Buzi 2016

[40] Buzi 2014, 61–64

codices from the library of the White Monastery were often broken up while circulating on the antiquities market, and so fragments corresponding to those preserved at the Staatsbibliothek are nowadays to be found in several European and non-European collections. The White Monastery manuscripts belong to a particular phase in Coptic library production, characterised by the appearance of codices that were manufactured with specific attention to their aesthetic appearance. Because they were objects of ritual and devotion, they are large in format and are decorated using many different colours and complex patterns. It is worth stressing that we learn from the colophons that some of the codices from this library were produced outside the White Monastery, in a professional scriptorium in Touton in the Fayyum[41].

1.2.2.3 Palau Ribes and Roca Puig collections in Barcelona and Montserrat

The manuscripts preserved in these two collections presented a great opportunity for study, because of the extraordinary access that was granted to a high number of papyri, including those preserved under glass, which require a greater logistical effort for their care. While working on these manuscripts it was decided to expand the domain of investigation to literary texts not necessarily written in Coptic, as well as to documentary texts in Greek, Latin and Coptic, in order to gain a more comprehensive picture of the complex reality of Egypt between Late Antiquity and the Middle Ages. Over a number of periods of analysis it was possible to study three groups of manuscripts each coming from a different context: a group of early Christian papyri (of these, some are part of the well-known "Bodmer Papyri" and are written in Greek and Latin, while another is a papyrus roll written in Coptic), a group of documentary texts from Bawit and a miscellaneous group of literary and documentary texts from different areas of Egypt that proved to be important for comparison.

Literary fragments from the Bodmer Papyri

According to the reconstruction made by Jean-Luc Fournet, some fragments in the Palau Ribes and Roca Puig collections are part of the so-called Bodmer Papyri, whose leaves are now preserved in different institutions around the world: the Bodmer Foundation in Cologny, the Chester Beatty Library in Dublin, the library of the University of Mississippi, and the university in Cologne[42]. In 1949 Martin Bodmer, a rich collector from Switzerland, moved from Zurich to Cologny to take part in the International Committee of the Red Cross. According to Paul Schubert, the fact that Bodmer was part of the governing body of this institution may explain why he was able to export an important array of papyri from Egypt during the 1950s, thanks to the cooperation of his supplier Phocion J. Tano[43].

The papyri were acquired in several tranches up until 1960, when Martin Bodmer ceased importing them from Egypt. During that period, Ramón Roca Puig and José

[41] Nakano 2006
[42] Fournet 2015
[43] Schubert 2015

O'Callaghan also acquired some fragments which probably came from the same finding[44]. The lot acquired by Bodmer was later partly dismembered, often on the initiative of Bodmer himself, such as with the leaves he donated to Pope Paul VI which are now preserved in the Biblioteca Apostolica Vaticana. The greatest loss for this collection happened when Bodmer sold a large number of papyri to Hans Kraus, a German dealer in rare books, to build the endowment for the maintenance of the Bodmer Foundation in Cologny. Unfortunately, no inventory of this purchase exists[45]. As a result of all these factors, precisely which manuscripts belong to the Bodmer Papyri corpus is still debated.

The place and circumstances of the finding of the Bodmer Papyri remain partly unknown. Shortly before his death in 1972, Phocion Tano revealed that they had been found a little east of Nag Hammadi, near the town of Dishnā[46]. These "Dishnā papers", as the Bodmer Papyri are sometimes known, were discovered at a similar time and in a similar area to the Nag Hammadi Coptic codices and they were circulated on the market by the same antiquities dealer[47]. Because of these coincidences, scholar have often wondered if there may be a link between the two groups of manuscripts.

The Bodmer Papyri have been palaeographically dated to between the 4th and 5th centuries CE. As for their provenance, the work of James Robinson has promoted the idea that these manuscripts were part of the library of the Pachomian Monastery of Pbou, located near where the papyri were probably found[48]. However, there is disagreement with the idea that the Bodmer Papyri were originally in a monastery, with many scholars arguing, among other things, that the numerous classical Greek texts forming part of the collection could hardly be part of a monastic library. An educational urban setting has often been proposed as an alternative: according to some scholars, this would better explain the presence of both classical and Christian texts that were copied at the same time, and the use of Latin in some cases[49]. Despite the many hypotheses that have been formulated, however, the origin of the Dishnā papers remains at present an open question.

The Roca Puig collection preserves 26 of originally at least 28 papyrus bifolia forming part of the so-called Codex Miscellaneus. Some of these were acquired by Ramón Roca Puig in the 1950s in Cairo, and others were acquired in 1973 through an exchange with the Bodmer Foundation. Roca Puig reports being told that the codex came from the area of the Thebaid in southern Egypt; however, this information cannot be taken as certain. The 26 bifolia preserved in Montserrat are divided into seven textual units containing religious and non-religious texts written in Latin or Greek, as well as a drawing displaying a mythological episode. The final section of the codex contains a list of words in Greek that was connected to the practice of stenography[50].

[44] Robinson 2011, 46
[45] Robinson 2011, 6
[46] Robinson 2011, 33–34
[47] Lundhaug and Jenott 2015, 1–21; Nongbri 2018, 108–15
[48] Robinson 2011, 17; Robinson 1990
[49] Fournet 2015; Camplani 2015b; Nongbri 2018, 208–15
[50] Torallas Tovar and Worp 2006

The roll of Athanasius

The roll of Athanasius is a papyrus that contains the translation into Sahidic Coptic of Athanasius' letter to Dracontius. It is the earliest Coptic exemplar of this epistle and given that it is exceptionally well preserved, it represents one of the highlights of the Roca Puig collection. The roll measures 92 cm wide and the text is divided into columns, five on the recto and one on the verso. According to Sofía Torallas Tovar, the text of the letter contains some elements from the Akhmimic dialect, which suggests that it was produced in the area around the ancient city of Panopolis. Furthermore, references to historical facts contained in the text indicate that the original letter was written after 353 CE. This copy in Coptic probably dates from the end of the 4th century CE[51].

Documentary papyri from Bawit

During the first set of analyses undertaken at the Palau Ribes collection an unusual type of ink probably containing tannins and copper was found on a documentary text from the Monastery of Apa Apollo in Bawit (further details in § 4.2.6). Therefore, it was decided to perform a specific study on documentary texts having the same provenance, in an attempt to find further evidence of this type of ink.

The Monastery of Apa Apollo was founded in around 386–388 CE. It experienced a great period of prosperity between the 7th and 8th centuries CE and then fell into a slow decline until it was occupied by the Arabs around 1167–1169 CE[52]. Extending over an area covering more than 900 × 400 m^2, it was one of the biggest complexes in Egypt. It consisted of common buildings such as churches and kitchens as well as private cells for monks and also included a variety of shops and commercial activities. It is possible, and indeed plausible, that there were also a scriptorium and a library, given that a literary codex was found in 2017 during the excavations at Bawit. On the base of palaeographical and codicological similarity with this codex, Anne Boud'hors recently suggested that some literary fragments nowadays preserved in different collections might also proceed from Bawit[53].

This large institution presented quite a complex and articulated administrative organisation that is recorded in numerous documentary papyri that have survived. To provide just a few examples, beyond the archimandrite who was the head of the administration, there were the brothers of the *andrismos*, responsible for collecting taxes, the father of the cell, head of a group of monks who lived together, and the numerous archivists and scribes employed in different sectors of the administration[54]. Interestingly, in his work Alain Delattre points out that the recycling of used papyrus leaves was very common in Bawit. Out of the 50 or so documents he edited in his work, almost 30 carry secondary texts dedicated to a monastery-internal use[55]. A similar trend is pointed out also by Sarah Clackson[56].

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[51] Torallas Tovar 2018
[52] Delattre 2007, 54–57
[53] Boud'hors in press
[54] Delattre 2007, 66–72
[55] Delattre 2007, 126
[56] Clackson 2008

According to María Jesús Albarrán, currently studying the documents from Bawit preserved in the Palau Ribes and Roca Puig collections, the documents examined in this project can be dated to the period of prosperity of the monastery[57], that is, to the 7th–8th centuries CE. Some of them have already been edited, while others are still unpublished.

Other literary and documentary papyri

As mentioned before, the number of manuscripts in the Palau Ribes and Roca Puig collections that were made available for analysis was extraordinary. Therefore, it was decided to perform a study on a substantial group of literary and documentary papyri from different areas and periods, including those written in Greek or Latin, as well as Coptic ones. This offered the possibility of comparing manuscripts produced in different environments. Although an effort was made to examine those manuscripts which displayed a secure date and place of production, this unfortunately turned out to be the case for only a minority of them. Nevertheless, the analysis of this group of manuscripts and the comparison of their results with those collected in other institutions, led to interesting considerations regarding the manufacture of Egyptian inks in Late Antiquity and their correlation with language, support and textual genre (see § 5.2). Further information around the dating and provenance of the individual manuscripts will be given in § 4.2.9.

1.2.2.4 Biblioteca Apostolica Vaticana in Rome

The library of the Monastery of Saint Macarius

The first set of analyses at the Biblioteca Apostolica Vaticana was dedicated to the study of a group of codices coming from the Monastery of Saint Macarius the Great (Dayr al-Anbā Maqār) in the Wadi Natrun.

The monastery was founded at the end of the 4th century CE, but its early library was lost during three barbarian raids in the first half of the 5th century CE. The formation of a new library after that was probably favoured by a couple of historical events. At the end of the 5th century CE the emperor Zeno endowed the monastery with an annual subsidy and supported the construction of new buildings in the monastery, thus enriching it materially. Furthermore, during the 6th century the patriarchal throne was transferred there, adding to the ecclesiastical importance of the site. Following these events, the library of the monastery grew to include a massive number of manuscripts. However, this group of books was once again dispersed when the monastery was sacked for the fourth time, at the end of the 6th century CE. It is not until after the Arab conquest that the monastery underwent a further period of restoration that came with a new wave of literary production. The monastery was sacked for the fifth and last time in 817 CE, and once again the library must have suffered great loss[58]. At present, no known leaf from the Monastery of Saint Macarius can be dated earlier than the 9th century CE.

Nowadays, most of the leaves from this library are preserved in the Biblioteca Apostolica Vaticana. Their presence in the Vatican collection is due to the activity of Giuseppe

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[57] Personal communication with María Jesús Albarrán, July 2019

[58] Evelyn-White 1926, 1:xxiii–xxiv

Antonio Assimani, who at the beginning of the 18th century travelled to Egypt at the behest of Pope Clement XI. Here he purchased the parchment leaves directly from the Monastery of Saint Macarius. Once they entered the Biblioteca Apostolica Vaticana, the parchment leaves were bound in 16 modern volumes (shelfmarks *Vat.copt.* 57 to 69)[59].

Most of the codices are dated to between the 9th and the 10th centuries[60]. They are written in Coptic Bohairic dialect using a Nitriot capital on only one column, as it is typical of the Coptic literary production of the Wadi Natrun area. Moreover, as is common in Coptic library production between the 9th and 11th centuries CE, these codices were manufactured with extreme attention to their aesthetic appearance. They are characterised by the choice of a large format and decorated with different colours and complex patterns.

The library of the White Monastery

After evaluating the analytical data collected on the codices from the library of the White Monastery preserved at the Staatsbibliothek in Berlin, it was decided to also analyse some leaves that had originally been produced in the Fayyum and later donated to the White Monastery and which were now in the Biblioteca Apostolica Vaticana. Some of these leaves are attributed specifically to the scriptorium in Touton, since they are decorated in the so-called Touton style[61], while others can be generically attributed to the area of the Fayyum either because of the presence of certain dialectal forms[62] or because of the system of superlinear strokes that are used, although in this latter case the attribution is dubious[63].

Literary texts from the Bodmer Papyri

During the second round of analysis at the Biblioteca Apostolica Vaticana, a papyrus codex dating to the 4th century CE and probably belonging to the Bodmer Papyri was examined[64]. The purpose of the analysis was to collect archaeometric data on the composition of inks from the early Christian period and to compare them with the results obtained on the Codex Miscellaneus and the roll of Athanasius preserved in Montserrat.

1.2.2.5 *Chester Beatty Library*

The analyses at the Chester Beatty Library focused on examining a number of different groups of manuscripts.

Literary texts from the Bodmer Papyri

In order to collect further data on literary manuscripts from early Christianity, a group of papyrus codices at the Chester Beatty Library which once again probably belong to the Bodmer Papyri were examined.

[59] Buzi 2019b
[60] Personal communication with Francesco Valerio, 9 November 2019. See also the manuscripts section of the PAThs atlas at https://atlas.paths-erc.eu/manuscripts
[61] Petersen 1954
[62] Louis forthcoming, 373–75
[63] Louis forthcoming, 146–47
[64] Fournet 2015

The Medinet Madi codex

In addition, an early Christian papyrus forming part of the Medinet Madi codices was included in the investigation. The Manichaean Coptic papyri from Medinet Madi were found by chance in the 1930s, although the circumstances of their discovery remain obscure: the archaeological report indicates that they were found in a wooden box in the ruins of a house[65]. Despite having been found in Lower Egypt, the dialect used to write these codices, known as Lykopolitan, indicates they were probably produced in a different area, between the regions of Thebes and Lykopolis. The codex is dated palaeographically to the 4th century CE[66].

The library of the Monastery of Apa Jeremiah

Archaeological excavations near Saqqāra brought to light buildings dating from the 6th century CE onwards, and showed that the Monastery of Apa Jeremiah disappeared around the middle of the 10th century CE. However, the *Chronicle* of the bishop John of Nikiou reports that Anastasius visited the monastery during his exile in Egypt, before becoming emperor of Byzantium (491–518). For this reason, the date of the foundation of the monastery has been conventionally set at 470 CE, older than the dating of the oldest building revealed in the excavations[67].

Between 1924 and 1925, Chester Beatty saw five small parchment manuscripts preserved in their original binding at a dealer in Cairo. They were believed to have been found together buried near the Giza pyramids. Beatty acquired the three codices which were in the finest condition, together with fragments of leather and bone belonging to the bindings. While the place of their discovery remains obscure, one of the volumes contains internal evidence that it once belonged to the Monastery of Apa Jeremiah at Saqqāra: an invocation contained in the colophon at the end of the Psalms in Dublin, Chester Beatty Library, *Cpt*. 815 presents a formula regularly in use at the Monastery of Apa Jeremiah which occurs repeatedly in inscriptions on the buildings and on tombstones there. According to Thompson, the script and the general format of the five volumes are proof that they must have originated in the same scriptorium, probably inside the monastery. Thompson adds that the three codices preserved in the Chester Beatty Library were written by three different scribes displaying very similar hands, with each codex penned by the same scribe from the beginning to the end. The date of the codices has been established as the 6th century CE on the basis of some coins that were found together with the manuscripts and which are dated between 527 and 602 CE[68].

1.2.2.6 *Ägyptisches Museum und Papyrussammlung, Berlin*

Analyses at the Ägyptisches Museum in Berlin focused on *Papyrus Berolinensis Gnosticus* 8502, an early Christian papyrus codex palaeographically dated to the 5th century. Carl Schmidt reported that the codex was acquired by an Arabic antiquities dealer in Akhmim.

[65] Schmidt, Ibscher, and Polotsky 1933
[66] Giversen 1986, xv–xvii
[67] Atiya 1991, 773
[68] Thompson 1932, ix–x

The dealer related that the codex was found wrapped in feathers in the cavity of a wall, and Schmidt concluded that the codex was produced in the town of Akhmim (ancient Panopolis) or nearby[69].

1.2.2.7 Cambridge University Library

The Michaelides collection

Analysis at the Cambridge University Library focused almost exclusively on Coptic leaves and fragments belonging to the Michaelides collection. George Michaelides was a collector of antiquities from Greece. After he died in 1973 the Cambridge University Library purchased part of his collection, which included texts in different languages; the British Library acquired another hoard from the same collection. Together, these two libraries acquired a total of around 240 Coptic fragments, both documentary and literary texts. Three-quarters of these are now preserved in the Cambridge University Library[70].

In an article from 1952, George Michaelides refers to a native Egyptian bringing him Coptic and Greek manuscripts from Fayyum[71]. Apart from this very sparse information, there is no other secure indication of the provenance of these fragments. The texts are unfortunately not related to one another; therefore, no connections can be made in that way. Based on their palaeographical features, the fragments can be divided in two groups, one probably dating to between the 6th and 9th centuries, and the other to between the 10th and 11th centuries[72].

Because there is little information on the historical context of the manuscripts in this collection, the data collected from them can be used solely as a term of comparison for other manuscripts. It is to be hoped that future research will reveal further information about the dating and provenance of these manuscripts, and the data collected through archaeometric analysis will acquire further meaning.

The library of the White Monastery

In addition to the Michaelides collection, two parchment leaves originally part of the library of the White Monastery library were examined at the Cambridge University Library. These leaves were produced in Touton, as indicated by the decorations made in the Touton style[73]. Together with the leaves from the White Monastery examined at the Biblioteca Apostolica Vaticana, they belong to a group of codices produced in the area of Fayyum and later donated to the monastery.

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[69] Schmidt 1903, 9:2
[70] Clackson 1993
[71] Michailides 1952
[72] Clackson 1993
[73] Petersen 1954

2 Writing tools, supports and inks

Generally speaking, the act of writing involves tracing characters on a support using a writing tool, with or without the application of a writing medium such as black or coloured ink.

In Egypt, during Late Antiquity, the writing tools of the scribe often included a reed pen (*calamus*) that could be trimmed on one or both ends, the latter being useful so that it could be employed with two colours of ink or for two different styles of lettering

[74]. In addition, there is evidence of pointed styluses probably used to write on wax tablets or to mark ruling lines. These tools were generally kept in a small box of wood, with several compartments. At the Morgan Library and Museum, a wooden box with a sliding cover and a shallow cavity for a removable metal inkwell is preserved[75], ceramic inkwells with or without wooden boxes have also been reported[76]. Aside from wooden cases, the use of pouch-like holders made of leather is documented[77].

Egypt is known for the use of a variety of writing supports. Besides finer materials employed in the making of books, there is evidence of ostraca, wooden tablets, bone, limestone flakes and cloth being used; in general, anything with a smooth surface[78]. A great number of ostraca have survived[79], as well as a number of Coptic magical texts on leather preserved in the British Library[80]. Papyrus was used from Antiquity and remained in use for a long time, first alongside parchment and later alongside paper, which was introduced into Egypt from Syria in the 9th century[81]. Papyrus was finally abandoned only during the 10th century, when Egyptians started manufacturing their own paper[82]. The Dead Sea Scrolls reveal that parchment was already in use during the 3rd century BCE, and in Egypt it was in use at the

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74 Buzi 2015

75 Depuydt and Loggie 1993, 2:601

76 Friedman 1989, 168–69

77 Bosson and Aufrère 1999, 276–77

78 Buzi 2011

79 John F. Oates, Roger S. Bagnall, Sarah J. Clackson, Alexandra A. O'Brien, Joshua D. Sosin, Terry G. Wilfong, and Klaas A. Worp, *Checklist of Greek, Latin, Demotic and Coptic Papyri, Ostraca and Tablets,* http://scriptorium.lib.duke.edu/papyrus/texts/clist.html, December 2019.

80 Crum 1934

81 Bloom 2001, 74

82 Bloom 2001, 74; Buzi 2015

beginning of the Coptic period, alongside papyrus. Later on, it seems that parchment codices were replaced by paper ones[83].

In what follows, papyrus and parchment, the two most frequent writing surfaces in the corpus of manuscripts, are described in detail, before black inks are discussed in depth.

2.1 Writing supports

2.1.1 Papyrus

In the *Alexander Romance* of Pseudo-Callisthenes, we find a statement asserting that papyrus grew nowhere but in Egypt:

> The dream that you saw is true, since your sealing the womb of your wife is a proof-laden oracle. For the seal is proof, indicating that your wife has become pregnant, for no one seals an empty vessel but rather a full and loaded one; and this, with papyrus. Since papyrus is found nowhere else but in Egypt, the man is Egyptian.[84]

However, the presence of this plant is attested also in other areas of Africa as well as in Syria, Judea and in Sicily. The reason behind this misconception must be that Egypt provided both the ancient Greek empire and the Roman empire with the writing support made from the papyrus plant[85]. Far from being used solely as a writing support, the plant was exploited in Egypt for a variety of uses. Its roots and stalk were commonly consumed as a foodstuff, either raw, boiled or baked. Moreover, its use to produce baskets, ropes, sandals and other common goods is widely documented. In addition, its stalks were used in the production of boats to navigate the Nile, and its crown was widely employed to manufacture different types of decoration[86].

The plant was not only harvested in the wild, but also cultivated, to maintain control over quantity and quality parameters. It is reasonable to assume that cultivated papyrus was used almost exclusively to produce papyrus paper, while other goods were obtained after harvesting wild-growing plants. Dated to 14/13 BCE, University of Warsaw, *P.Berlin* 13062 gives an idea of the dimension of a papyrus plantation[87]. This document states that each day, the lessees of a papyrus plantation send to their creditor an average of 200 sizeable bundles of stalks. Because of such a prolific industry, Egypt could supply the paper[88] needs of the entire ancient world.

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[83] Buzi 2015
[84] Wolohojian 1969, 29–30
[85] Lewis 1974, 3–4
[86] Lewis 1974, 21–32
[87] A. C. Johnson, Frank, and Broughton 1936
[88] In this instance, the word "paper" is being used to generically indicate any writing support

The process of manufacturing the writing support from the stalk of the plant is described by Pliny the Elder[89]. Although scholars have debated the meaning and translation of Pliny´s text, we can generally recognise three steps. First the stalk is cut into thin slices; then a first layer of contiguous slices is placed vertically (verso) and then covered with a layer of horizontal slices (recto); finally, the sheet thus obtained is pressed and left to dry[90].

Turner points out that the manufacture of papyrus decreased in quality from the Old Kingdom, when the leaves achieved a great fineness, to the Roman period, when the final product is thicker and coarser[91]. This assessment was confirmed during this investigation: the papyrus leaves from the library of Thi(ni)s (7th/8th century CE), for instance, are so thick that it was not possible to see through the sheets even after placing them on a light table. Though no reasons for the change of the thickness of papyrus leaves can be found in extant sources, it is generally believed that it was due to the decay of manufacturing skills. In fact, however, the idea that papyrus was intentionally manufactured to obtain thicker leaves because of the introduction of the reed pen, which could easily have pierced a thinner support, would seem to be compelling.

Sheets of papyrus were pasted together to form rolls known as *kollēmata*. The roll began with a *prōtocollon*, a leaf having fibres running vertically instead of horizontally. With the emergence of the codex around the 4th century CE, an innovation in the manufacturing process of papyrus occurred that led to the production of very long *kollēmata*, sometimes approaching two metres in length. It seems that rolls containing such long *kollēmata* were produced specifically to be cut into bifolia to be used in the making of codex quires[92].

From a material point of view, papyrus folia are rather heterogeneous writing supports whose thickness and structure can change widely even within a single small fragment. Despite having been flattened by the application of pressure during the manufacturing process, the leaves still present a morphology made of contiguous fibres that are visible to the naked eye. Furthermore, different deterioration processes affect the fibres in different ways, increasing the heterogeneity of the material and introducing different contaminants. As a result, archaeological papyrus turns out to have a very uneven distribution of chemical elements. While on one hand contaminants are a valuable source of information, because they register the state of the material during several phases of its existence, on the other they regrettably hamper the possibility of quantifying the elements contained in the ink using non-invasive analysis; this matter was thoroughly discussed in a recent work which provided some examples of the limitations of a non-invasive analytical protocol applied to the analysis of inks

[89] Pliny. *Naturalis Historia*, 13.22

[90] On this matter, the author would like to point out that during a practical experience of making papyrus the best results were obtained by hammering the fresh slices of the plant rather than compressing them with a rolling pin. The latter process caused the fresh slices to slide apart, resulting in sheets that presented lacunas

[91] Turner 2015, 2

[92] Buzi 2015

on papyrus manuscripts from Late Antiquity (see the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use")[93].

2.1.2 Parchment

The earliest reference to parchment production comes from the Roman writer Varro, and it is reported by Pliny the Elder[94]. According to him, the rivalry between the libraries of Alexandria and Pergamon led King Ptolemy to cut off the export of papyrus. Faced with a shortage of writing support, Pergamon reacted by "inventing" parchment. Richard Johnson tried to cast light on the veracity of this account[95]. After identifying the period of this narrative as the reign of Eumenes II (197–160 BCE), he pointed out that, a few years later, a war between the Egyptians and the Seleucids would have decreased papyrus production. According to him, it is likely that at the time of the rivalry between the two kingdoms, the threat of war in Egypt had reduced the trade of papyrus, and the library of Pergamon surely felt imperilled by the shortage of this material. However, it would be absurd to assert that parchment was invented at that time, given that we have previous records of documents written on parchment, for instance some of the Dead Sea Scrolls, dating back to the 3rd century BCE. Johnson concludes that the inhabitants of Pergamon did not invent parchment, but that they inaugurated its use in the Greek world.

The process of making parchment is reported in several medieval recipes. Skins first need to be washed and then soaked for several days in a bath of water and lime. Following this there is a mechanical de-hairing process, after which the skins are soaked again in a lime bath. After washing and soaking in fresh water, the skins are ready to be stretched on frames, where they are shaved with a knife and dried under tension. During the drying stage, the skins are frequently moistened with water and polished with pumice; chalk is sometimes employed for similar purposes[96].

The textual and analytical evidence (regrettably scarce) available on the process of parchment-making in Antiquity reveals some differences from medieval practices. The first physical and chemical examination performed on the Dead Sea Scrolls showed that no soaking in lime was involved, and de-hairing was assisted by enzymatic depilation, applying dung or flour to the skins or immersing them in a solution containing vegetal matter[97]. On the other hand, pumice and chalk were probably already used in the process in Antiquity, as suggested by the high amount of calcium found on the grain and flesh side of the *Great Isaiah Scroll* and the *Community Scroll*[98]. Furthermore, the finishing stage of parchment production in the case

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[93] Ghigo, Rabin, and Buzi 2020
[94] Pliny. *Naturalis Historia*, 13.21
[95] R. R. Johnson 1970
[96] On this process, see for instance London, British Library, *Harley* 3915, f. 148r for a recipe dating to the second half of the 12th century CE at http://www.bl.uk/manuscripts/FullDisplay.aspx?ref=Harley_MS_3915 (last accessed 7 February 2020)
[97] Reed and Poole 1964; Reed and Poole 1962
[98] Rabin 2017

of the Dead Sea Scrolls sometimes included the application of vegetable tannins, producing a hybrid between parchment and leather (the latter being tanned but not stretched)[99].

Based on the observation of a great number of fragments from the Dead Sea Scrolls, Rabin formulated a theory regarding the coexistence of two different traditions of parchment manufacturing during the Hellenistic period in Judaea. The eastern tradition produced tanned parchment, darker in colour; while the western tradition produced non-tanned or lightly tanned parchment, lighter in colour and similar to early Christian Greek parchment. In this reconstructed scenario, the fact that high amounts of sulphates were found in western tradition parchments may indicate that inorganic materials rather than enzymatic depilation were used during the de-hairing process[100].

In addition to the material evidence provided by the Dead Sea Scrolls, we have a textual description on the preparation of the parchment surface for writing. It comes from a Coptic papyrus dating probably to the 6th or 7th century and preserved at the Bodmer Foundation (*P.Bodm.* 58). It gives instructions on the use of pumice, white lead and alum in order to prevent the ink from running[101].

Parchment was generally made from the skins of various animals, although the prevalent use of sheep, goat or calf is documented. This material was already in use for writing purposes during the Coptic period, and remained in use alongside papyrus and later alongside paper, maybe because it was generally considered to be the best quality material[102], being at times twice as expensive as papyrus[103].

When it comes to archaeometric analysis, it is generally easier to examine inks on parchment manuscripts than on papyrus. Even though parchment can present an uneven thickness along the same folio of a manuscript, its structure is not as heterogeneous as that of papyrus. It generally presents a smooth surface which renders the analytical process slightly easier, although in some cases it needs to be locally flattened using small ceramics weights. However, when lime is applied for de-hairing rather than enzymatic depilation, great quantities of calcium are introduced into the support, making it sometimes difficult to understand how much calcium is contained in the ink and how much in the parchment.

2.2 Black inks

2.2.1 Between written recipes and analytical evidence

Information on the composition of the inks used in ancient times can either be detected using archaeometric analysis or collected by piecing together recipes, casual descriptions or any other hints available in literature. The combination of these two sources offers a

[99] Reed and Poole 1964
[100] Rabin 2017; Rabin 2016
[101] Crum 1905, 166–71
[102] Buzi 2015
[103] Bagnall 2009, 52–58

comprehensive framework and allows a comparison of what described in written sources and what was actually done while manufacturing inks.

Table 1 collects the information on the manufacturing of inks available prior to the start of this investigation, organised chronologically for each type of ink. The column "Ancient recipes" mainly displays information contained in Monique Zerdoun Bat-Yehuda's already mentioned work[104], while the column "Analytical evidence" reports the results from previous archaeometric studies of inks on original manuscripts. More recent analytical studies of historical inks, developed in parallel to this research, will be presented later along this dissertation.

It must be stressed that there is not necessarily an exact correspondence between the recipes and the analytical evidence reported in parallel for each type of ink. In fact, in addition to the pigments and additives reported in Table 1, ancient recipes often mention a series of organic compounds introduced in the mixture for different purposes, such as binders or scents. However, the analytical evidence collected never provides a full elucidation of the organic compounds. Even if it did, the exact attribution of an ink to a written recipe would be rather challenging, since in even the best cases archaeometric analysis would identify deteriorated materials rather than original ingredients.

Furthermore, it must be stressed that terminological difficulties have often hampered the unequivocal identification of some of the ingredients mentioned in recipes. Trying to approach this identification in a different way, scientists have sometimes applied chemical reasoning to the ingredients mentioned in ancient treatises[105], but some questions remain unsolved. For instance, this is the case of *chalcanthon* (a copper-based substance) and *misy*, recurring ingredients whose exact chemical composition in Antiquity is not yet known, although *chalcanthon* is identified as copper sulphate from the Middle Ages onwards. Similarly, the word *atramentum* (literally, "black") appears in recipes from Antiquity to the Middle Ages and has been translated as both "ink" and "vitriol" in medieval times[106].

[104] Zerdoun Bat-Yehuda 1983
[105] Bailey 1932
[106] For a detailed terminological discussion, see Zerdoun Bat-Yehuda 1983

Table 1 Previous information on the different types of ink from ancient recipes and analytical evidence, organised chronologically and reporting bibliographic sources.

Type of ink	**Pigment/ Colourant**	**Additives**	**Ancient recipes**	**Analytical evidence**
Carbon	Carbon black		1st century BCE, Vitruvius[a] 1st century CE, Pliny[b] 2nd–5th century CE, Papyri Grecae Magicae[c] 12th century CE, Eraclius[d]	For instance: Egypt, 15th century BCE (Turin, Museo Egizio, *S*.5065/2)[l]
Plant	Tannins		5th century CE, Martianus Capella[e]	Germany, 9th century CE (Stuttgart, Württembergische Landesbibliothek, *Bibl.fol*. 23)[m]
Plant + copper	Copper-gallate?	Copper-based compound*	3rd century BCE, Philo of Byzantium[f] (invisible ink for leather)	Egypt, 3rd–2nd century BCE (Paris, Musée du Louvre, *N* 2433 and others)[n]
Iron-gall	Iron-gallate among other complexes		1st century CE, Pliny, "*atramentum sutorium*"[g] (for the reaction between iron and tannins) 3rd century CE, Papyrus V of Leiden[h] 12th century CE, Theophilus[i]	Earliest evidence: Egypt, 4th century CE (Berlin, Staatsbibliothek, *Ms.or.oct*. 987)[o] Europe, 4th century CE (Vercelli, Museo del Tesoro del Duomo, *Codex Eusebii Evangeliorum*)[p] Europe, 6th century CE (Vienna, *Codex Vindobonensis Med.gr*. 1)[q]
Mixed carbon + copper	Carbon black	Copper-based compound	1st century CE, Dioscorides[j]	Middle East, 1st CE (Jerusalem, Shrine of the Book, 1*QGenAp*)[r,**] Egypt, 2nd century BCE–2nd century CE (Copenhagen, Carlsberg collection, *P*. 79, 649, 828, 839)[s,**]
Mixed carbon + lead	Carbon black	Lead-based compound		Herculaneum, ca. 1st century CE (Paris, Institut de France)[t,**]
Mixed carbon + tannin	Carbon black and tannins		9th–20th century CE, Arabic recipes[k]	
Mixed carbon + iron-gall	Carbon black and iron-gallate		9th–20th century CE, Arabic recipes[k]	Syriac manuscript from the 14th century CE[u]

* This complex has not been chemically characterised, yet. However, it has been experimentally observed that when copper sulphate is added to gallnut extract, the solution changes color to a darker brown.

** The metal compounds contained in these inks have not been identified yet. Therefore, it is not clear whether they should be considered as mixed inks.

[a] Vitruvius. *De Architectura*, 7.10

[b] Pliny. *Naturalis Historia*, 35.25

[c] Different recipes for carbon ink obtained by combustion of different ingredients are found in the corpus of the Papyri Grecae Magicae, for instance PGM I.232-237, PGM VII.993-1009, and PGM IV.3172-308. See H. D. Betz, ed. 1986. *The Greek Magical Papyri in Translation: Including the Demotic Spells*. University Press, Chicago

[d] Eraclius. *De Coloribus et Artibus Romanorum*, 3.53

[e] Martianus Capella. *De Nuptiis Philologiae et Mercurii*, 3.225

[f] Philo of Byzantium. *Mechanike Syntaxis*, 5.77

[g] Pliny. *Naturalis Historia*, 34.32. In this passage Pliny equates *chalcanthon* to *atramentum sutorium*, describing its use to blacken leather shoes (containing tannins). This is the earliest hint indicating that the reaction between iron and tannins, the basis of iron-gall ink, was in use, even if it was with a different purpose than the preparation of ink

[h] Preisendanz, Karl. 1931. *Papyri Graecae Magicae. Die Griechischen Zauberpapyri, Herausgegeben und Übersetzt von Karl Preisendanz. V. 2*. Berlin: Teubner, p. 83. Terminological issues prevent the unequivocal identification of this recipe with iron-gall ink

[i] Theophilus. *De Diversis Artibus*, 1.40. Terminological issues prevent the unequivocal identification of this recipe with iron-gall ink

[j] Dioscorides. *De Materia Medica*, 5.183

[k] Schopen, Armin. 2006. *Tinten und Tuschen des Arabisch-Islamischen Mittelalters: Dokumentation, Analyse, Rekonstruktion: Ein Beitrag zur Materiellen Kultur des Vorderen Orients*. Göttingen: Vandenhoeck & Ruprecht. See also Colini, Claudia. 2018. "From Recipes to Material Analysis the Arabic Tradition of Black Inks and Paper Coatings (9th–20th Century)." PhD Thesis, Hamburg: Universität Hamburg

[l] Festa, Giulia, Thomas Christiansen, Valentina Turina et al. 2019. "Egyptian Metallic Inks on Textiles from the 15th Century BCE Unravelled by Non-Invasive Techniques and Chemometric Analysis." *Scientific Reports* 9 (1):7310

[m] Hahn, Oliver. 2011. "Die Farben und Tinten im Stuttgarter Psalter-Naturwissenschaftliche Untersuchungen." In *Kupfergrün, Zinnober & Co. - Der Stuttgarter Psalter*, edited by Vera Trost, Andrea Pataki-Hundt, and Enke Huhsmann, 111–21. Stuttgart: Württembergische Landesbibliothek

[n] Delange, Elisabeth, Maurice Grange, Bruce Kusko, and Eve Menei. 1990. "Apparition de l'Encre Métallogallique en Égypte à Partir de la Collection de Papyrus du Louvre." *Revue d'Egyptologie* 41:213–17

[o] Ghigo, Tea, Olivier Bonnerot, Paola Buzi, Myriam Krutzsch, Oliver Hahn, and Ira Rabin. 2018. "An Attempt at a Systematic Study of Inks from Coptic Manuscripts." *Manuscript Cultures* 11:157–64

[p] Aceto, Maurizio, Angelo Agostino, Enrico Boccaleri, and Anna Cerutti Garlanda. 2008. "The Vercelli Gospels Laid Open: An Investigation into the Inks Used to Write the Oldest Gospels in Latin." *X-Ray Spectrometry* 37 (4):286–92

[q] Aceto, Maurizio, Angelo Agostino, Gaia Fenoglio, Pietro Baraldi, P. Zannini, C. Hofmann, and E. Gamillscheg. 2012. "First Analytical Evidences of Precious Colourants on Mediterranean Illuminated Manuscripts." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 95:235–45

[r] Nir-El, Yoram, and Magen Broshi. 1996. "The Black Ink of the Qumran Scrolls." *Dead Sea Discoveries* 3 (2):157–67

[s] Christiansen, Thomas, Marine Cotte, René Loredo-Portales, Poul Erik Lindelof, Kell Mortensen, Kim Ryholt, and Sine Larsen. 2017. "The Nature of Ancient Egyptian Copper-Containing Carbon Inks Is Revealed by Synchrotron Radiation Based X-Ray Microscopy." *Scientific Reports* 7:15346

[t] Brun, Emmanuel, Marine Cotte, Jon Wright, Marie Ruat, Pieter Tack, Laszlo Vincze, Claudio Ferrero, Daniel Delattre, and Vito Mocella. 2016. "Revealing Metallic Ink in Herculaneum Papyri." *Proceedings of the National Academy of Sciences* 113 (14):3751–3754

[u] Colini, Claudia, Oliver Hahn, Olivier Bonnerot, Simon Steger, Zina Cohen, Tea Ghigo, et al. 2018. "The Quest for the Mixed Inks." *Manuscript Cultures* 11:41–49

Carbon ink

Carbon ink is a very simple type of ink based on a dispersion of carbon particles in the form of charcoal or soot in a water-soluble binding agent. When used for writing it leaves a trace as black as coal. It is well known that this is the most ancient type of ink, having been used everywhere since Antiquity in drawing and writing. Extant recipes for carbon writing ink (*atramentum librarium*) are found in treatises by Vitruvius[107] and Pliny[108] dating to between the 1st century BCE and the 1st century CE. They both describe the preparation of carbon ink by mixing soot and gum arabic, and the same recipe is found in a medieval treatise written many centuries afterwards by Eraclius, dated to around the 12th century CE[109]. Furthermore, a group of recipes for carbon ink obtained through the combustion of different vegetal matter is found in the documents of the Papyri Grecae Magicae[110].

The existence of carbon ink since Antiquity has been frequently confirmed by analytical evidence. For example, at the beginning of the 20th century, Lucas detected carbon ink in an inkwell coming from an Egyptian tomb and dating to the 16th century BCE, as well as in several Egyptian manuscripts dating to the Roman period[111]. Recently, the analysis of some inscriptions on Egyptian linen have revealed the use of carbon ink on a funerary shroud as far back as the 15th century BCE[112].

Plant ink

Plant ink is based on tannins normally extracted from tree bark, gallnuts or any other vegetal matter containing a high amount of these substances. The colour of this ink can be of different hues of brown and can easily be distinguished from the solid black of pure carbon ink. A written recipe for plant ink can be found in a treatise written by Martianus Capella dating to the 5th century CE[113]. Here, he refers to a mixture of gallnuts and gum (*gallarum gummeosque commixtio*) used for writing. Curiously, this recipe is mentioned in the section on iron-gall inks by Zerdoun and it has been referred to as one of the first recipes for iron-gall ink in several scientific studies[114]. However, the formula reported by Capella does not mention the use of iron salt or any metallic salt in general, a fundamental ingredient in producing iron-gall ink. This mixture of gallnuts and gum arabic is rather the earliest evidence currently available of a written recipe for the preparation of plant ink. Analytical evidence of plant ink was reported in the Stuttgarter Psalter produced in Germany around the 9th century CE (Stuttgart, Württembergische Landesbibliothek, *Bibl.fol*. 23)[115].

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[107] Vitruvius. *De Architectura*, 7.10
[108] Pliny. *Naturalis Historia*, 35.25
[109] Eraclius. *De Coloribus et Artibus Romanorum*, 3.53
[110] Betz 1986; Christiansen 2017
[111] Lucas 1922
[112] Festa et al. 2019
[113] Martianus Capella. *De Nuptiis Philologiae et Mercurii*, 3.225
[114] For instance, Aceto et al. 2008
[115] Hahn 2011

Mixed plant and copper ink

In the 3rd century BCE, Philo of Byzantium describes the preparation of an invisible ink for writing on leather. The message is initially written by the sender using gallnut extract (which is invisible on leather because of its brownish colour) and is then revealed by the receiver, who sprays the leather with a mixture of water and *chalcanthon*[116]. Analytical evidence of an ink containing tannins and copper, similarly to Philo's recipe, was found in the Greek texts of some bilingual documents from Egypt preserved at the Louvre and dating to between the 3rd and 2nd centuries BCE (Paris, Musée du Louvre, *N* 2433, *N* 2416, *N* 2410, *N* 2422). On these manuscripts, elemental analysis detected a significant amount of copper but no iron, excluding the possibility that the text had been written using iron-gall ink. In addition, the presence of tannins was assumed from their brownish colour, although never scientifically confirmed[117].

Iron-gall ink

The pigment that is the basis of iron-gall ink results from a chemical reaction. It is commonly produced by mixing iron(II) sulphate (generally obtained from vitriol[118]) with the gallic acid contained in the gallnut extracts to form a black complex that becomes insoluble upon oxidation in air[119]. The first written recipe recorded so far describing the preparation of iron-gall ink is probably the one reported in the Greek text of Papyrus V of Leiden, dating back to the 3rd century CE. This was discovered in Thebes in the early 19th century by an adventurer calling himself Jean d'Anastasi[120]. The ink is prepared by mixing 1 drachma of myrrh, 4 drachmae of *misy*, 2 drachmae of *chalcanthon*, 2 drachmae of gallnuts, and 1 drachma of gum arabic. However, since the composition of *chalcanthon* and *misy* cannot yet be unequivocally identified, it cannot be demonstrated with certainty that this recipe does in fact describe the preparation of iron-gall ink.

Dated six centuries earlier, the recipe of Philo of Byzantium may suggest that the reaction between tannins and iron sulphate, the basis of iron-gall ink preparation, was already empirically in use, even if the author was not fully aware of the chemistry behind it: What if the *chalcanthon* that Philo used to make the gallnut extract in his invisible ink reappear, contained iron, as well as copper? In this case, the ink used on leather would have turned into a black complex, and the message would have been easily revealed. Similarly, a passage from Pliny suggests that the reaction between iron and tannins was empirically known at the beginning of the 1st century CE. He describes the use of *chalcanthon* to blacken leather shoes

[116] Philo of Byzantium. *Mechanike Syntaxis*, 5.77. It must be noted that Philo uses the expression *chalkou de anthous*, literally "flower of copper".

[117] Delange et al. 1990

[118] The extraction of vitriol in Antiquity is reported by Pliny, who describes the preparation of *chalcanthon* from natural and artificial waters containing sulphates (*Naturalis Historia*, 34.32). However, at present there is no evidence proving that *chalcanthon* and vitriol refer to the same compound before the Middle Ages.

[119] Rabin and Binetti 2014

[120] Preisendanz 1931

(the process of leather-making involved tanning to harden the surface)[121]. Nowadays we know that copper does not produce a black pigment when mixed with tannins. To work as a shoe blackener, the *chalcanthon* mentioned by Pliny must have also contained a quantity of divalent water-soluble iron. Rabin suggests that this misunderstanding regarding the nature and nomenclature of copper and iron sulphates must have had an impact on the production and diffusion of iron-gall inks as writing media[122].

Finally, it is worth discussing the case of a medieval recipe generally acknowledged as being the first European iron-gall ink recipe. It is found in a 12th century treatise written by the monk Theophilus[123]. He describes the preparation of an ink involving the mixture of hawthorn and wine, left to dry in the sun. Before writing, the dried ink is mixed with *atramentum*. Finally, Theophilus indicates that one should add a piece of incandescent iron to the mixture, if the ink is not black enough. In her monograph, Zerdoun discusses this recipe in detail, concluding that it describes either iron-gall ink or a mixed ink (iron-gall + carbon), depending on the translation of the word *atramentum*[124].

Although many scholars still believe that the appearance of iron-gall ink is linked to the European Middle Ages, when the main writing support was parchment, several material studies have demonstrated the existence of this type of ink on Egyptian papyri written centuries before the medieval era. As far back as 1922, Lucas published the results of an analysis of some parchment manuscripts from Egypt, dating to between the 7th and the 12th century CE. As he stated, "[i]f the date of the earliest specimen which is given at the 7th or 8th CE be accepted, then iron ink was known and used at that time, which is several centuries earlier than is generally supposed"[125]. To date, the earliest evidence we have of iron-gall ink was found in an Akhmimic book of Proverbs (Berlin, Staatsbibliothek, *Ms.or.oct.* 987) dating to the 4th century CE[126]. Outside of Egypt, this type of ink was found on the Vercelli Gospel (Codex Eusebii Evangeliorum) dating to probably the 4th century CE and preserved in the Museo del Tesoro del Duomo in Vercelli[127]; and also on the Vienna Dioscorides (Vienna, *Codex Vindobonensis Med.gr*. 1) dating to the 6th century CE[128].

Mixed inks

In recent years more and more attention has been paid to the category of mixed inks. These were already mentioned by Zerdoun, but have often been overlooked by scholars and scientists alike. The first extant recipe attesting the preparation of a mixed ink is reported in the 1st century CE by Dioscorides. He mentions the addition of *chalcanthon* to the preparation

[121] Pliny. *Naturalis Historia*, 34.32
[122] Rabin 2017
[123] Theophilus. *Schedula Diversarum Artium*, 1.40
[124] Zerdoun Bat-Yehuda 1983, 156–65
[125] Lucas 1922
[126] Ghigo et al. 2018
[127] Aceto et al. 2008
[128] Aceto et al. 2012

of a carbon ink obtained by mixing soot, gum arabic and animal glue and he explains that this substance possesses antiseptic properties[129].

A recent article focused entirely on this category of inks and on the difficulties encountered in their identification, with the aim of attracting attention to and stimulating reflection on the origin and use of mixed inks (see the appendix "The quest for the mixed inks")[130]. Analytical evidence of copper-containing carbon inks was found on the Genesis Apocryphon scroll from the Dead Sea Scrolls (Jerusalem, Shrine of the Book, 1*QGenAp*)[131], and on some letters from Pathyris (the modern city of Gebelein) and Tebtunis dating to between the 2nd century BCE and the 2nd century CE (Copenhagen, Carlsberg collection, *P*. 79, 649, 828, 839)[132]. Similarly, carbon inks on two small papyrus fragments from Herculaneum preserved at the Institut de France in Paris were found to contain a substantial amount of lead[133]. More recently, further examples of carbon inks containing transition metals were found on papyri from Hermopolis[134]. It must be noted that in these studies the metal compounds have not been identified, and therefore it is not clear whether these inks should be considered as mixed inks, although they have previously been referred to using this term[135]. For the time being, the only unequivocal evidence of a use of mixed ink was reported on a Syriac manuscript from the 14th century CE. Here, Raman analysis clearly registered the spectral feature characteristic of both carbon and iron-gall ink (see the appendix "The quest for the mixed inks")[136].

2.2.2 Short note on the complexity of historical iron-gall ink

The preparation of iron-gall ink is described in various treatises from the Middle Ages onwards. The majority of recipes describe its production as consisting of a mixture of three ingredients: vitriol, gallnut extract and gum arabic. The black pigment that forms the basis of this type of ink is obtained from the reaction between iron(II) and gallic acid, forming a black complex called iron-gallate[137].

The scientific community has investigated the chemical structure of the iron-gallate complex, however this is a controversial topic and no unequivocal answer has been reached so far. Until 2016, the cultural heritage community was using the structure proposed by Christoph Krekel[138]; but this was believed by Aldo Ponce to be inaccurate[139]. The latter proposed a new structure for historical iron-gall inks based on an amorphous octahedral

[129] Dioscorides. *De Materia Medica*, 5.182–183
[130] Colini et al. 2018
[131] Nir-El and Broshi 1996
[132] Christiansen, Cotte, et al. 2017
[133] Brun et al. 2016. The fragments were found in a box with the label "Objet 59", donated by the king of Naples to Napoleon Bonaparte in 1802
[134] Maltomini et al. forthcoming
[135] Christiansen, Buti, et al. 2017; Christiansen 2017
[136] Colini et al. 2018
[137] Krekel 1999
[138] Krekel 1999
[139] Ponce et al. 2016

framework, very different from the crystalline structure that can be obtained when the ink is prepared using pure iron sulphate. However, there are still unsolved questions even when it comes to this new proposed structure.

A recent work based on the investigation of inks reproduced following Iberian recipes (15^{th}–17^{th} centuries CE), showed that iron-polyphenol complexes other than iron-gallate can be found in iron-gall inks[140]. According to this study, the concentration of gallic acid extracted from gallnuts varies depending on the extraction method, and moreover, this polyphenol was often found to be a minor component in gallnut extract: together with gallic acid, variable amounts of other polyphenolic molecules were extracted as well. It was found that the chemical structure of the resulting inks investigated using Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) could not be represented solely by the iron-gallate complex.

In her doctoral dissertation, Claudia Colini[141] reports more than 130 Arabic recipes for iron-gall ink dating from the 9^{th} to the 20^{th} century. They describe the preparation of ink following a variety of methods and use, besides gallnuts, pomegranate, myrtle leaves and a long list of other sources of tannins. Lacking a substantial number of recipes describing the preparation of iron-gall inks in Egypt during Late Antiquity, one must consider that different methods and sources of tannins may have been in use then as well. These different vegetal materials all contain a variety of polyphenolic molecules besides gallic acid, and it is therefore possible that the resulting writing media contained a mixture of different iron-polyphenol complexes in addition to other complexes originating from the interaction between tannins and satellite elements contained in vitriol. For instance, laboratory experiments performed while conducting the present investigation showed that the complex of copper and gallic acid is characterised by a dark brownish colour and its behaviour at 940 nm is similar to that of iron-gallate.

The evidence discussed here suggests that the iron-gallate complex may not be sufficient by itself to represent the chemical structure and properties of iron-gall inks produced in Egypt during Late Antiquity. Further insights into the different families of tannins (namely, condensed and hydrolysable) contained in the vegetal matter used to produce inks may offer a further parameter for the classification of inks and help in understanding their chemical behaviour.

[140] Díaz Hidalgo et al. 2018
[141] Colini 2018

3 Methodology

3.1 Methods and equipment

3.1.1 Multi-analytical approach to the study of cultural heritage materials at the BAM and the CSMC

The analysis of cultural heritage materials performed in the framework of the Bundesanstalt für Materialforschung und -prüfung (BAM) in Berlin and the Centre for the Study of Manuscript Cultures (CSMC) at the University of Hamburg are based on a multi-analytical approach that combines different techniques to collect as much information as possible on the material composition of the cultural objects studied.

Before describing the working principles of different analytical methods in detail, it is important to define the terms "invasive analysis" and "destructive analysis". A method is defined as invasive when it requires a sample to be extracted from the object that is to be investigated. Depending on the amount of sample needed, it is possible to talk about micro-invasive techniques. If the sample that is extracted will be destroyed or irreparably damaged, then the analysis is defined as destructive. In the study of cultural heritage objects, non-invasive (therefore, non-destructive) techniques are widely employed. In some cases these techniques are available on portable devices, and the analysis can be performed *in situ*, while in other cases the object needs to be transported to a laboratory so that bench equipment can be used.

Most of the methods discussed in what follows are based on the interaction between electromagnetic radiation and matter, which may result in different phenomena: scattering, absorption and transmission. Each technique uses radiation from a different region of the electromagnetic spectrum and addresses one or more of these phenomena.

3.1.1.1 Microscopy

Optical microscopy

Optical microscopy is the most widespread tool for the study of any type of material nowadays. It includes a broad range of different techniques based on the use of visible light and transparent lenses to enhance the power of the naked eye, allowing for the morphological observation of micro-structures. For instance, stereomicroscopes capture the light reflected from the sample and are employed for the study of bulk structures. The light can also be polarised (a specific geometrical orientation of the oscillation of the electromagnetic wave is selected) and transmitted through the sample, with polarised light microscopy being applied in the mineralogical observation of thin cross-sections to reveal isotropic and anisotropic structures. The digital era brought great innovation in optical microscopy with the introduction of digital microscopy: this bears a number of advantages such as, for instance, the possibility of capturing and storing high quality images in 2D and 3D.

Electron microscopy

Electron microscopy uses a beam of electrons instead of visible light. The shorter wavelength of the electrons allows for a higher resolution than in optical microscopy, which is limited to approximately 0.2 μm. The electron bombardment of a sample leads to the emission of different signals: backscattered electrons that are reflected from the sample, secondary electrons that are ejected from the molecular cloud of the sample when it absorbs energy, and specific X-rays emitted during sample relaxation. High-resolution morphological information is obtained by observing the signal from backscattered and secondary electrons. In addition, electron microscopy provides information on the elemental composition of the sample, thanks to the analysis of the emission of characteristic X-rays.

3.1.1.2 Fibre optic reflectance spectroscopy (visible spectroscopy)

Visible reflectance spectroscopy uses radiation in the range of visible light (ca. 400–700 nm) and measures the intensity of the reflected light as a function of the wavelength. Fibre optic reflectance spectroscopy (FORS) owes its name to the optical fibres used to convey the irradiating and collected visible light.

Since different materials reflect light in a characteristic way, this method can be used for discrimination purposes. It is often used in the identification of pigments, although it generally does not produce conclusive spectra in the case of mixtures, overlapping pigments (in thin layers) or white and black colours.

3.1.1.3 Vibrational spectroscopy

Vibrational spectroscopy uses different types of radiation to excite vibrations of the chemical bonds in the sample. Specific vibrations (bond stretching or bending) of different functional groups are registered in different areas of the spectrum. These vibrations are influenced by the symmetry of the molecule and the chemical makeup. Therefore, they can be used for discrimination and identification purposes. Two different types of vibrational spectroscopy can be distinguished: infrared spectroscopy and Raman spectroscopy. These two techniques are often complementary to each other: permanent dipoles which are active infrared nuclei often have weak Raman signals, while non-polar moieties such as the covalent bonds between the nitrogen atoms in a nitrogen molecule N_2 are inactive infrared nuclei but have a strong Raman signal because they are polarisable (i.e. their electron cloud can be easily distorted by an external electric field).

Infrared spectroscopy

This technique uses a beam of infrared light to excite the chemical bonds of those functional groups in a particular compound that have strong dipole moments (e.g., C-H, N-H or C=O). Infrared spectroscopy measures the fraction of radiation that is absorbed or transmitted through the sample.

Initially, infrared instruments were of a "dispersive" type, meaning that they separated the infrared radiation into individual frequencies in order to collect a spectrum, plotting the different frequencies against the intensity of the vibration that was registered. This resulted in a very time-consuming procedure that was improved with the introduction of Fourier transform infrared spectroscopy (FTIR). This technique uses an interferometer to produce a signal (interferogram) encoding all the frequencies of the infrared radiation, and then applies a mathematical algorithm (the Fourier transform) to obtain the spectrum as a plot of the intensity of the vibration detected at each individual frequency.

Since infrared spectroscopy analyses the light absorbed or transmitted through the analyte, it requires a sample to be accurately prepared. Normally this involves pulverising the sample and blending it with potassium bromide (KBr) before pressing it into a pellet. However, recent technological developments have led to the introduction of alternative infrared spectroscopic techniques based on the analysis of reflected light, and these allow for the analysis of samples without previous preparation. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measures the fraction of infrared light reflected back from a surface. In this case, the signal obtained is often low for very absorbent materials. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) uses a crystal with a high refractive index to reflect the infrared light multiple times and create an evanescent wave that penetrates the sample between 0.5 and 2 μm below the surface.

Raman spectroscopy

Raman spectroscopy uses an intense monochromatic beam of light (e.g., a laser) to excite the sample, and addresses molecular vibrations based on the inelastic scattering of light. This phenomenon was first documented by Sir Chandrasekhara Venkata Raman in 1928. When a sample is irradiated, most of the light is scattered elastically. In this case the electrons are excited to a virtual state due to the interaction with the electric field of the laser, but during relaxation their vibrational energy decreases to the ground state and the light that is backscattered has the same energy as the incoming radiation (Rayleigh scattering). A small fraction of the light (approximately one photon in a million) is scattered inelastically, causing the incident light to change its energy. Two different types of inelastic scattering are possible: either the vibrational energy of ground electrons relaxes to an excited vibrational level (stokes), or the vibrational energy of excited electrons relaxes to the ground state (anti-stokes). The latter is less frequent than the former since in a relaxed molecule fewer electrons are found at excited levels. Raman spectroscopy measures the intensity of the light scattered inelastically (both stokes and anti-stokes) as function of the wavenumber.

The fluorescence of organic compounds, frequent in the case of archaeological materials, often disturbs Raman spectra. This phenomenon happens when the virtual energy of excited electrons overlaps an upper electron level. So, the higher the energy of the laser used, the more likely that fluorescence will occur and the more intense it becomes. On the other hand, the longer the wavelength of the laser, the lower the intensity of the Raman signal. To overcome these limitations, surface-enhanced Raman spectroscopy (SERS) has been introduced[142]. Surface enhancement refers to the massive enhancement (several orders of magnitude, up to 10^{11}) in the intensity of the Raman scattering that happens when molecules are adsorbed on atomically rough metallic surfaces or nanostructures. At the same time, fluorescence is quenched. To obtain this effect, colloids made of gold or silver nanoparticles are often employed since they can be easily prepared in the laboratory. In recent years, this technique has frequently been used in the field of cultural heritage, and it has successfully obtained well-resolved spectra of strongly fluorescent materials such as dyes and colourants[143].

Raman spectroscopy has the advantage of being non-invasive, unless inexpert hands are unaware of the power of the laser that they are using and accidentally cause the sample to burn. In contrast, SERS is micro-invasive at least, given that the application of the colloid to certain materials is often non-reversible, or the extraction of a sample is required. It must be stressed, however, that Raman spectroscopy is a surface technique (unless it is performed offset, as it is the case of SORS), therefore it provides only a limited insight for layered structures, such as paintings. The study of painting stratigraphies using Raman spectroscopy often requires the extraction of samples.

3.1.1.4 X-ray spectrometry

X-ray spectrometry includes a broad range of methods based on the use of high energy X-rays. They are frequently applied to examine a wide range of materials in cultural heritage[144]. Among these, X-ray absorption near edge structure, X-ray diffraction and X-ray fluorescence have often been employed to examine the chemical composition and crystal structure of inks and pigments[145].

X-ray absorption near edge structure (XANES) is an element-specific technique that consist in exciting the core electrons of a particular element and measuring the absorbed radiation. The analysis is performed by scanning the sample using X-rays having a range of energy that overlaps the binding energy of the core electrons of the element of interest (the absorption edge). The spectrum that is obtained plots the fraction of radiation absorbed as a function of the range of energy used to scan the sample. This technique can give information on the oxidation state of the element that is being investigated, since the higher the oxidation state, the higher the absorption energy will be. This happens because for higher oxidation

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[142] P. C. Lee and Meisel 1982; Schlücker 2014
[143] Pozzi and Leona 2015
[144] Schreiner et al. 2004
[145] Wilke et al. 2009; Duran et al. 2014; Hradil et al. 2016

states the nucleus is less shielded and thus exerts a higher effective energy on the core electrons.

X-ray diffraction (XRD) is used for the identification and characterisation of crystalline matter. The electrons in a crystal are organised in ordered cells that scatter radiation in a characteristic way. The direction of the diffraction depends on the size and shape of the unit cell of the particular crystal. The intensities of the diffracted waves result from constructive and destructive wave interference and depend on the type and arrangement of atoms in the crystal structure. To perform the analysis, a sample needs to be extracted, powdered and placed in an X-ray beam. The experimental angle is systematically changed in order to detect all possible diffraction peaks from the randomly oriented crystallites in the powder. Thus, the radiation that is diffracted gives information about the morphology and structure of the sample.

X-ray fluorescence (XRF) is a phenomenon that occurs when a core electron absorbs incoming energy from X-rays and is ejected from its shell (the energy of the X-rays must be equal to or greater than the binding energy of the electron). This creates a vacancy which is immediately filled by another electron from an outer shell (atom relaxation). The difference in energy between the outer and the inner shell is emitted in the form of radiation, which is characteristic of a specific element.

Recently, micro-XRF spectrometers have been developed to enhance the intensity of excitation (and therefore increase the signal) and reach a better spatial resolution. They are equipped with polycapillary optics that can focus the radiation onto a spot on the order of micrometres[146].

It must be stressed that the cross-section of the interaction between the element and the X-rays grows with the atomic number. As a result, the light elements of the second row of the periodic table cannot be detected using conventional XRF spectrometers. Furthermore, the signal intensity is affected by matrix effects that include the reabsorption of characteristic radiation by the sample under analysis. This phenomenon is inversely proportional to the atomic weight and directly proportional to the thickness of the sample, having a larger effect in the case of lighter elements and thicker matrices[147].

3.1.1.5 Reflectography

Reflectography is a common non-invasive method that produces images which reveal information on the chemical and physical nature of the sample under investigation. It consists in capturing the light that is reflected by an object in different spectral regions. The difference in reflectance or absorption of various materials can be used for the purposes of discrimination.

For instance, infrared reflectography (IRR) is often employed for the study of underdrawings of paintings. These were generally made with coal and this continues to absorb

[146] For a general introduction to micro-XRF, see Haschke 2014

[147] Pessanha, Guilherme, and Carvalho 2009

radiation above 1300 nm, where coloured pigments stop absorbing and become transparent. Therefore, infrared reflectography can provide images of the underdrawings hidden below several layers of paint. However, the equipment used to perform infrared reflectography is rather bulky. In contrast, near-infrared reflectography (NIRR) and ultraviolet reflectography are commercially available on small devices (approximately 10 cm in size) that can be easily transported.

Multispectral imaging (MSI) is a more complex technique that records the images produced at discrete wavelengths in the range between around 390 and 1100 nm. Consequently, it produces a large amount of information about the spectral properties of different materials. For cultural heritage objects the image data captured through multispectral imaging can be used to enhance and visualise ink and pigment residues and aid in the recovery of lost and damaged writing and painting.

3.1.1.6 Mass spectrometry

Mass spectrometry is a powerful technique that is used to identify unknown substances and study molecular structures. It measures the masses of the compounds within a sample and it is based on the ionisation of the chemical species in the analyte and their separation according to their mass-to-charge ratio (m/z).

A mass spectrometer consists of three main parts: an ionisation system, a mass analyser and a detector. It is equipped with a vacuum system to maintain a low pressure to increase the free path of particles, a fundamental requirement in performing this type of analysis. Nowadays, a broad range of ionisation systems and mass analysers are available, with the different combinations determining the specific features of each mass spectrometer.

Common ionisation techniques include:

- electron impact ionisation (EI)
- photoionisation (PI)
- chemical ionisation (CI)
- fast atom bombardment (FAB)
- secondary ions (SI)
- electrospray ionisation (ESI)
- inductively coupled plasma (ICP)
- matrix-assisted laser desorption (MALDI)

For gaseous phases, electron, photo or chemical ionisation are common. The sample is ionised using electrons, photons or chemical exchange. For condensed phases, fast atom bombardment (FAB) or secondary ion mass spectroscopy (SIMS) are often used. In these cases, the sample is ionised using high energy atoms (noble gases in the case of FAB and ions in the case of SIMS) that cause the sample to sputter and ionise in one single step. In recent years great improvements have been made in the field of atmospheric pressure ionisation (API), which is designed to ionise the sample at atmospheric pressure and then inject it into the vacuum chamber where the mass analyser and detector are located. Electrospray ionisation is the most common among API techniques; the electrospray is obtained by applying a large potential between metallic needles and it produces multiply charged ions, with the advantage that big molecules can be observed at lower m/z ratios. Inductively coupled plasma instead uses a high temperature plasma to ionise a liquid sample that has previously been nebulised into the system. Finally, matrix-assisted laser desorption uses a laser to desorb and ionise the sample from a condensed phase previously prepared by mixing the analyte and a matrix chosen to absorb the laser radiation.

Mass analysers can be either continuous or pulsed. Continuous mass analysers transmit a single m/z ratio to the detector. They are characterised by a lower signal-to-noise ratio, because when a particular m/z ratio is selected information about other ions is lost. Quadrupole mass spectrometers and sector mass spectrometers are examples of continuous mass analysers. The former consist of two couples of electrodes to which alternate voltage is applied. Under the effect of the electric field, ions are forced into the vertical and horizontal planes alternately, creating a three-dimensional wave whose amplitude depends on the m/z ratio of the ions; in this way, the quadrupole acts as a band pass filter for a specific m/z ratio. Sector mass spectrometers use magnetic and electric sectors positioned after the ion accelerator to deflect ions according to their m/z ratios. A time-of-flight mass spectrometer is a pulsed mass analyser that separates ions according to their different times of travel. The ions are accelerated using the same electric field along a tube, usually one or two metres long, which causes the ions to separate according to their m/z ratio. The mass spectrum obtained when the ions strike the detector is a function of time. A higher resolution is achieved by means of a reflectron, which is an electrostatic ion mirror that reverses the direction of the ions towards the detector placed near the starting point and compensates for minor velocity differences.

Mass spectrometry is usually employed in quantitative analysis. It uses calibration and a reference system to translate the individual intensities that are recorded into quantitative information about the composition of the analyte. Mass spectroscopy is thus a powerful technique for obtaining both qualitative and quantitative information. In spite of this, however, its application in the field of cultural heritage is often limited because it requires samples to be extracted, meticulously prepared and finally destroyed.

3.1.1.7 Principal component analysis

Principal component analysis (PCA) is a statistical methodology for data evaluation based on the individuation of one or more principal components in a determined data set. This allows the data matrix to be decomposed into a “structure” part and a “noise” part in order to project and visualise the “latent structure” in the matrix. A principal component is defined as the direction of maximum spread (or variation) of data in the set. Representing data using principal components helps in understanding which variables in a certain data set are correlated. Moreover, it is possible to determine which of the variables considered (if any) play a minor or irrelevant role and can therefore be excluded.

PCA has become commonly applied in the field of cultural heritage to evaluate large amounts of data collected using different spectroscopic techniques such as visible spectroscopy, FTIR or XRF. It helps in interpreting complex data sets deriving from composite materials that display different levels of deterioration, and PCA has supported the investigation of binders, patinas, mosaics and manuscripts, among other objects[148].

However, whether this method will produce meaningful results largely depends on the characteristics of the data set. PCA works best with big and multivariate data sets. In dealing specifically with inks, this methodology works well when the ink has a rather complex composition, such as in the case of iron-gall inks prepared with metallic salts containing substantial amounts of many different satellite elements. For instance, PCA has been applied to the characterisation of different hands in a medieval breviary whose inks were found to contain, among other elements, iron, copper, zinc, lead and mercury[149].

However, such a complex composition was never found in the iron-gall inks presented in this work, which at best were characterised by the substantial presence of iron and copper, lesser amounts of manganese and, occasionally, lesser amounts of zinc. Probably because of this, every attempt to apply PCA to this corpus failed to show interesting results. The principal components that were identified often coincided with the variable iron (for iron-gall inks) and potassium (attributed to the binder), and the main correlation that emerged was that between iron and copper, which is in any case expected for iron-gall inks. No other relevant information was revealed using this method.

3.1.2 The analytical protocol used for the analysis of manuscripts and inks

The standard protocol for the analysis of black inks consists of several imaging and spectroscopic techniques, namely NIRR, XRF, FTIR and Raman[150].

To begin, a primary screening is carried out by means of NIRR. Strictly speaking, optical differences between carbon, plant and iron-gall inks are best recognised by comparing their response to infrared light: carbon ink has a deep black colour, iron-gall ink becomes transparent above 1510 nm[151], and plant ink disappears at about 750 nm[152]. Working with visible and near-infrared light (940 nm), the ink typology can be determined by observing the changes in the opacity of the ink. Carbon-based inks show no change in their opacity when illuminated with near-infrared wavelengths, while the opacity of iron-gall inks changes considerably, and plant inks become transparent.

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[148] See, for instance, Alberghina et al. 2014; Luciano, Leardi, and Letardi 2009; Sarmiento et al. 2011; Aceto et al. 2017

[149] Aceto et al. 2017

[150] Rabin et al. 2012

[151] While the literature reports that iron-gall ink becomes transparent at 1200 nm (Mrusek, Fuchs, and Oltrogge 1995), recent experiments performed by the BAM and the CSMC have demonstrated that this threshold has to be raised to 1510 nm for freshly prepared iron-gall ink.

[152] Mrusek, Fuchs, and Oltrogge 1995

Next, an in-depth investigation is performed using XRF analysis to detect the presence of any inorganic components in the ink. In the case of vitriolic iron-gall inks, the detection of those elements that originally come from the metallic salt used in the preparation of the ink establish the fingerprint of this ink (i.e., the characteristic ratios of each of those elements to iron[153]; see § 3.2.3.2).

In specific cases that may require more insight and further investigation, FTIR and Raman spectroscopy can be performed. FTIR spectroscopy, commonly used for the investigation of organic materials, is applied to characterise the binding media. In contrast, Raman spectroscopy establishes the co-presence of carbon and iron-gall ink, since it can easily register a fingerprint spectrum from both substances. Finally, for the investigation of coloured inks and pigments, visible spectroscopy (FORS) is occasionally used on manuscripts displaying decorations and illuminations, with the purpose of complementing the XRF data in the identification of the pigments that were used.

The present investigation essentially made use of routine analysis – that is, NIRR and XRF – to examine writing inks and supports. In some cases, the fingerprint of iron-gall inks was established. Due to time restrictions, XRF was only performed on approximately 60% of the manuscripts that were analysed using NIRR. In a few cases, Raman and FTIR spectroscopy were applied in studying black inks, and FORS in analysing coloured pigments (for a complete overview of the methods used, see § 4.2.2). The equipment was in most cases portable, allowing the analysis to be performed directly *in situ*, thereby permitting access to a higher number of institutions and manuscripts.

3.1.2.1 Equipment

The following description of the equipment utilised in the analysis includes the camera for infrared reflectography and the mass spectrometer. These instruments are not currently part of the analytical protocol, and were not applied on original manuscripts during the present study. However, experiments on mock samples were performed to explore the possibility of implementing them in the near future (see § 4.1).

DinoLite USB microscope, AD413T-I2V

This small USB microscope measures only 10 cm and it is equipped with three different light sources: near-infrared (940 nm), ultraviolet (395 nm) and a white LED light (external). Comparing the visible light micrograph with the corresponding near-infrared one, the ink typology is determined by observing the changes in the opacity of the ink. As noted above, at 940 nm carbon-based inks show no change in their opacity compared with under visual light, while the opacity of iron-gall inks changes considerably, and plant inks become transparent.

Elio, Bruker Nano GmbH (formerly XG Lab)

This X-ray spectrometer features a 4 W low-power rhodium tube, adjustable excitation parameters and a 25 mm^2 SDD detector with energy resolution of <140 eV for Mn Kα. It was

[153] Hahn 2010; Hahn et al. 2004

used to collect measurement on single spots and has a beam size of around 1 mm. All measurements were performed at 40 kV and 80 μA, with an acquisition time of 2 min. Peak fitting and semi-quantitative data evaluation were conducted using Bruker's SPECTRA software.

ArtTAX 800, Bruker Nano GmbH

The ArtTAX is a micro-XRF spectrometer well known in the field of cultural heritage, which forms part of the standard equipment in the majority of large museums. It features a low-power, air-cooled molybdenum X-ray tube, polycapillary optics resulting in a beam spot of about 100 μm diameter, a CCD camera for sample positioning and an electrothermally cooled XFlash detector (SDD, area 10 mm^2) with an energy resolution of <150 eV for Mn Kα at 10 kcps. The movable probe is operated by XYZ motors that enable spot measurements to be performed as well as line and small area scans. The mobile XRF probe moves over the object at around 5 mm of distance and stops for the duration of a single measurement. All measurements were made in air along a line containing between 10 and 30 spots for analysis, operating at 50 kV and 600 μA, with an acquisition time of 30 seconds per point (live time). Peak fitting and semi-quantitative data evaluation were conducted using Bruker's SPECTRA software.

M6 JetStream, Bruker Nano GmbH

This XRF spectrometer uses a polycapillary lens to focus X-rays onto a small spot of variable size (75–850 μm diameter), two microscopes for sample positioning and for mapping larger areas, and an electrothermally cooled XFlash detector (SDD, 50 mm^2) with an energy resolution of <150 eV at 10 kcps. Its movable probe is mounted on a large frame allowing for the mapping of surfaces up to 60 × 80 cm. Unlike the ArtTAX and the Elio, measurement is performed "on-the-fly", that is, while the probe is moving, using a 30 W low-power rhodium tube, operating at 50 kV and 600 μA, and with an acquisition time of 10–50 ms (live time). This is a bench instrument that provides high-resolution elemental maps of the object investigated. It requires either the artefact or a sample to travel to the laboratory for analysis.

i-Raman Plus, B&W Tek

This portable Raman spectrometer is equipped with a fibre optic probe (BAC100) connected to a diode laser operating at 785 nm. The microscope head (BAC151B; Olympus 50× objective) is equipped with a camera used to position the object. A CCD detector registers the signal. Measurements are typically carried out with an output power of 1–2% of the maximum laser power (~160 mW), corresponding to 1–3 mW, in the spectral range 175–4000 cm^{-1} with a spectral resolution of 4 cm^{-1}.

inVia Raman, Renishaw

This custom-tailored Raman spectrometer is equipped with two fibre optic probes connected to lasers operating at 532 and 785 nm. The laser power is of 200 and 300 mW respectively. The probes are connected to a digital camera (used to position the object) and a

CCD detector for signal registration. Measurements are typically carried out with a 50× lens and on 1–2% of maximum laser power in the spectral range 100–3600 cm^{-1} with a spectral resolution of 4 cm^{-1}. Similar to the JetStream, this is a bench instrument and requires either the object or a sample to travel to the laboratory for analysis.

JAZ-EL350, Ocean Optics

This modular fibre optic reflectance spectrometer features a tungsten-halogen light source and a 2048-pixel (Sony ILX511B) linear CCD array detector. The fibre optic reflection probe is customised with a sample holder that positions the probe at an angle of 45° and a fixed distance from the sample, and an LED endoscope of 5.5 mm diameter and 1.5 cm focal length produces a digital image of the area to be examined. The measurements are collected in a spectral range between 350–1000 nm, with a spectral resolution of 1.3 nm. The data are acquired using the SpectraSuite software.

Agilent 4100 ExoScan

The Agilent 4100 ExoScan is a portable FTIR spectrometer. It is equipped with two different probes: ATR (germanium crystal, with a measuring spot of 2 mm diameter and 2–5 μm depth of penetration) and DRIFTS (with a measuring spot of 10 mm). In both cases the spectral range goes from 600–4000 cm^{-1}, with a spectral resolution of 4 cm^{-1}.

Apollo camera, OPUS Instruments

This camera is used for infrared reflectography. It features a cooled indium gallium arsenide sensor with a spatial resolution of 128 × 128 pixels. The spectral range of the sensor is 900–1800 nm. The sensor is mounted inside the camera body on a XY-stage and can scan an area creating a TIFF image of spatial resolution of roughly 5000 × 5000 pixels (mosaic). Single 128 × 128 pixels images were acquired using 50 ms exposure time.

Atmospheric solids analysis probe Xevo G2-XS QTof, Waters

This mass spectrometer uses a heated nitrogen de-solvation gas to vaporise the sample and a corona discharge needle to induce ionisation. It is equipped with a high-performance quadrupole analyser whose parameters can be programmed with respect to certain mass values. It features a collision cell to induce fragmentation of selected ions and an orthogonal acceleration time-of-flight analyser with a maximum mass range of m/z 100000 and a resolving power of 40000 FWHM.

3.2 Analytical procedure

3.2.1 Preliminary operations

3.2.1.1 Handling of samples

The first step of the analytical procedure involved the handling of codices, leaves and fragments to safely position them on the workstation. Given the unicity and fragility of these objects, this non-trivial task was conducted using different strategies, tailoring the procedure to the physical conditions of each manuscript. These operations often represented the most time-consuming part of the whole procedure, especially in the case of big codices with a fragile binding. When working *in situ*, the personnel from the collection offered assistance, helping to establish and perform whatever procedure had the least impact on the physical condition of the manuscript. In general, three different cases can be distinguished:

1. Loose parchment leaves not bound in a volume, representing the easiest and least time-consuming objects to handle. This was the situation with some of the manuscripts from the White Monastery preserved in the Staatsbibliothek in Berlin and in the Biblioteca Apostolica Vaticana in Rome. The leaves were carefully extracted from the paper folder in which they were normally kept, limiting contact with the hands to the margins of the page, and then they were positioned on the workstation. While performing NIRR analysis using the DinoLite, the external visible lamp around the microscope was padded with Japanese paper before placing the device on the parchment leaf. This procedure limited the contact between the manuscript and the microscope, being particularly indicated in cases where the inks and pigments showed a fragile and brittle surface. For XRF analysis the leaves were placed on a cardboard passepartout, where a hole had been cut in cardboard so that X-rays would not penetrate it, and then lifted using some metal boys. If needed, the parchment was locally flattened around the area of analysis using further pieces of cardboard or cork padded with Japanese paper and kept in place by light ceramic weights designed for this purpose.
2. Parchment leaves bound in a volume. These required special care because of the physical conditions of the bookbinding, often very fragile even when “modern”. In this case, foam cushions of different shapes and dimensions were used to maintain the codex in position. The codices were opened at an angle slightly wider than 90°, allowing the analysis to be performed while ensuring minimum stress for the object. On the side of the codex that was maintained vertically with respect to the surface of the workstation, the leaves were held firm using padded lead snakes commonly used for conservation purposes. Then NIRR was performed following the procedure described previously. For XRF analysis, the leaf under examination was carefully lifted from the rest of the codex by at least a centimetre, using pieces of cardboard or cork padded with Japanese paper. This prevented the X-rays from penetrating through several folia.
3. Papyrus leaves, requiring the greatest attention because of the intrinsic fragility of the material itself. NIRR was performed without opening the glass frame in which the leaves were normally preserved: it was possible to place the microscope directly on the upper sheet of glass without causing any physical stress to the object, and the focus of the microscope could be adjusted through the glass directly onto the surface of the manuscript. Unfortunately, it was not possible to follow the same procedure for XRF analysis since the glass had to be removed to focus the X-ray beam on the writing

surface. After trying different procedures, it was established that the best solution was to partially remove the glass frame, making sure that the remaining glass was not interacting with X-rays in the area of the spectrum that was of interest. Removing only the upper glass was enough to properly perform XRF analysis and ensured a much safer handling procedure, as the papyrus leaves did not need to be directly manipulated at all since they could easily be moved by handling the lower glass. At the Palau Ribes collection the papyrus fragments were not preserved in glass frames but in blotting paper folders. However even in this case, it was decided to use clean glass in performing the analysis since this guaranteed the safest handling of the fragments. For XRF analysis, the glass was lifted from the surface of the table using metal boys. Pieces of cardboard and cork padded with Japanese paper which were kept in place by ceramic weights were used to temporary flatten the surface under examination.

3.2.1.2 Ensuring a good representation of the sample

Generally, for near-infrared reflectography and XRF analysis a minimum of five spots on inked areas on each manuscript were analysed. The ideal spot for analysis should display a good state of conservation, be far from the borders of the page where the risk of contamination is higher and correspond to a blank surface on the other side of the folio, given that X-rays pass easily through a leaf. For this reason, a limited number of spots were sometimes collected when there was text on both sides and it was densely disposed on the page. The number of spots also varied depending on the dimensions of the object, being of course higher in the case of bigger manuscripts, and very limited in the case of fragments that showed the presence of only a few lines of text. In addition, it was highly influenced by the complexity of the text. For example, on leaves containing a title, the main text, marginal notes and illuminations, a higher number of spots had to be analysed to obtain representative results for each part of the text. Besides the spots on inked areas, a variable number of measurements were collected on the support, with a higher number generally on the more heterogeneous papyrus surfaces; when time permitted, the same number of measurements were made on the papyrus surface as on the inked areas. Different analytical techniques were always applied to the same spots, after establishing that they were representative of a certain sample. This allowed for a direct comparison of the results.

3.2.2 Performing XRF analysis *in situ*

To conduct XRF analysis *in situ*, two different X-rays spectrometers were used: the Elio (Bruker Nano GmbH, formerly XG Lab) and the ArtTAX 800 (Bruker Nano GmbH). During the *in situ* analyses it was fundamental to adapt to the workspaces and the timing that was agreed with the personnel at each collection. The possibility of working with either of two different instruments, each featuring different characteristics in term of size, weight and safety requirements, offered greater flexibility when dealing with the regulations of different institutions.

The two instruments have different limits of applicability and different analytical advantages. The ArtTAX features the possibility of collecting XRF data along a line-scan of a certain number of points, each one about 100 µm in size. During data processing, it is possible to have the software calculate the accumulation spectrum, summing all the points in the line-scan. In contrast, the Elio collects XRF data on a single spot with a diameter of around 1 mm[154].

Clearly, among the main limiting factors in the choice of the spectrometer to be used are the width of the ink trace and the size of the letters. If the ink has been penned using a thin writing tool (e.g., a metallic point), XRF data should be collected using the ArtTAX, to ensure that the measurement is performed within the borders of the ink trace.

The data collected with the ArtTAX in the line-scan mode produce a profile of intensities for each element that is detected, showing the variation along the line. Usually, all the elements involved in the makeup of a substance under XRF analysis show the same intensity profile; in the case of iron-gall inks, the elements inherently associated with the ink follow the intensity profile of the iron, the main element of such inks.

In order to be easily interpreted, the intensity profile must show a certain homogeneity. This means that both the support and the ink need to be characterised by an even elemental distribution. Moreover, the intensity of the elements contained in the support should be significantly lower than the intensities in the ink, so that a line-scan measured at the interface between the inked and non-inked areas will produce an intensity profile showing a sharp increase in the elemental content while moving from the support to the ink, as seen in Figure 1. The similarity of the profiles here shows that iron, copper and manganese are associated with the ink, while calcium is not.

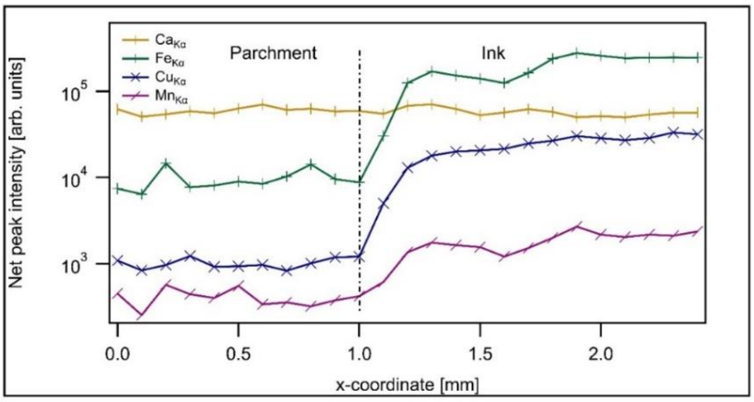

Figure 1 Net peak intensity profiles of different elements at the interface between non-inked and inked areas on Berlin, Staatsbibliothek, Ms.or.fol. *1348, f. 1.*

In the case of homogeneous supports and inks, even a shorter line-scan collected within the borders of a trace of ink would provide suitable qualitative data for the writing medium to be properly characterised, as shown in Figure 2. The similarity of profiles in this case shows that copper, iron, potassium and zinc are all associated with the ink. This procedure shortens

[154] Note that in this dissertation spot is not equivalent to point. A spot is an inked or non-inked area chosen for measurement and, in the case of the Elio, this coincides with the single point of analysis. For ArtTAX measurements, on the other hand, a point is one of the several XRF measurements collected along a line-scan, which in this case represents the spot

the time taken in the analysis (a shorter line-scan entails a shorter measurement time, provided that the measurement time per point remains the same), allowing for the examination of a higher number of manuscripts.

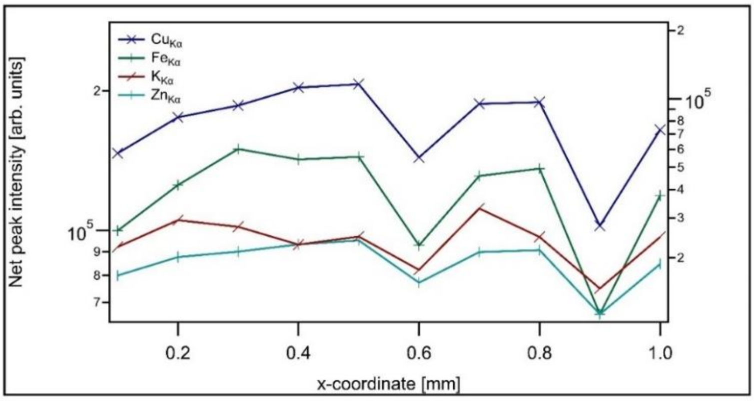

Figure 2 Net peak intensity profiles of different elements collected within the borders of an inked area on Berlin, Staatsbibliothek, Ms.or.fol. *1613, f. 1. The intensity of the elements Fe and Cu is represented on the scale on the left, while K and Zn follow the scale on the right.*

During this investigation, these ideal conditions were sometimes observed for parchment manuscripts but never for papyri. In fact, most papyrus leaves show a very heterogeneous elemental distribution, due to the inhomogeneous structure of the papyrus itself, consisting in a series of fibres of different dimensions. The heterogeneity of papyrus as a writing support impacts the ink as well, which is generally characterised by an uneven cross-sectional thickness along the manuscript, affecting the intensity profile. Figure 3 shows the case of a line-scan collected on papyrus. The line-scan reveals the extreme heterogeneity in the distribution of the elements both in the support and in the inked area. The intensity of iron increases sharply when moving from the papyrus to the ink, creating the impression that this element is associated with the writing medium. However, the right extremity of the graph reveals that the intensity of iron is even higher on a different area of the support. This means that it is not possible to deduce unequivocal results.

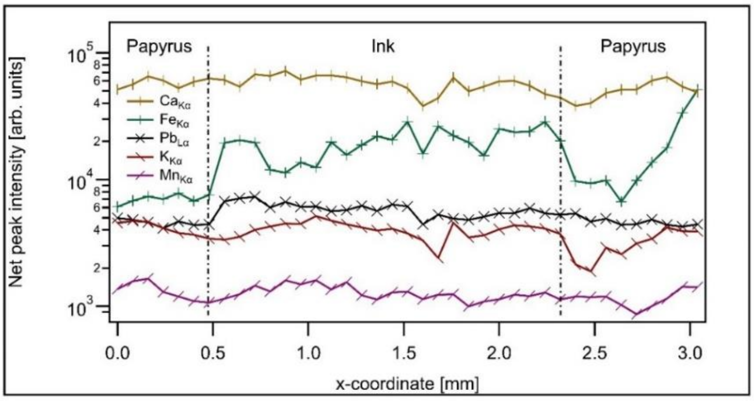

Figure 3 Net peak intensity profiles of different elements at the interface between non-inked and inked areas on Florence, Biblioteca Laurenziana, P. Laur II *21*[155].

[155] The data presented in this figure are courtesy of Oliver Hahn and Ira Rabin and were acquired during a systematic study of the papyri preserved at the Biblioteca Laurenziana and at the Istituto Vitelli in Florence.

When XRF analysis is performed on extremely heterogeneous materials, in order to obtain satisfactory semi-quantitative results a very high number of spots must be collected on the same folio, both on inked and non-inked areas. The use of the ArtTAX spectrometer in this case would be extremely time-consuming (assuming that the minimal line-scan should contain at least ten points at a distance of about 10 μm from each other, resulting in a time of five minutes for each line-scan if the measurement settings described in § 3.1.2.1 are maintained). Considering that time management is essential during *in situ* analysis, performing XRF using the Elio is in these cases proved more satisfactory. A two-minute measurement performed with the Elio delivers results on a larger spot than the one measured with ArtTAX (1 mm vs 100 μm), averaging the heterogeneity of the support.

However, the best compromise between measurement time and result quality is obtained by using both spectrometers, when possible. First, a long ArtTAX line-scan (of at least twenty points) is collected at the interface between inked and non-inked areas. This time-consuming first step allows for an accurate qualitative identification of the elements in the ink and a discrimination of possible contaminants. In a second step, the Elio is used to perform measurements on a high number of spots, ideally analysing the same number of spots of non-inked areas as on inked areas in order to have a proper representation of both the support and the ink. In this way, the qualitative information provided by the long line-scan at the interface between the inked and non-inked areas is adequately complemented by the statistical semi-quantitative information collected on several spots of the sample.

3.2.3 Data treatment

3.2.3.1 A first glance at the XRF results: evaluating and discarding contaminants

The intensity profiles measured using the ArtTAX spectrometer along a line-scan not only allow for the identification of the elements contained in the ink: elements that are not inherently part of the writing medium are also easily revealed, since they display a different intensity profile. This is particularly useful for manuscripts that have been affected by a combination of contamination and deterioration factors during their history.

In these cases, in order to convert the intensity profiles characteristic of a line-scan into a result that is representative of an inked or non-inked area, the mathematical calculation of the median of the measured net peak intensities represents the best choice, because it helps in discarding elements not contained in the writing medium. This process must be performed using a common spreadsheet software such as Microsoft Excel, given that the SPECTRA software only features the option of calculating the accumulated line, derived from the sum of net peak intensities of each element registered along all the points in a line-scan. In the case of archaeological material, it can be misleading to consider the accumulated line as being representative of the spot analysed. If the object examined presents contamination of a small area along the measured line-scan, the intensity values of one or more elements will be much higher for one or more points, and the accumulation process will simply result in their sum, producing a result which is not illustrative of the composition of the ink. In cases like this, the calculation of the median allows for the automatic elimination of the outliers and this should be performed before proceeding with the calculation of the fingerprint in the case of iron-gall inks.

In the case of measurements collected using the Elio it is not possible to apply these procedures, given that the device does not record line-scans. Therefore, the identification of the elements that make up the ink is obtained by a comparison between the elements contained in non-inked and inked areas. The risk of mistakenly considering contaminants as part of the composition of the ink can in this case be avoided by measuring a relevant number of spots on the same leaf, ideally acquiring data from as many spots on the ink as spots on the support, and analysing areas where the manuscript shows no signs of conservation interventions or any other possible contamination. Generally speaking, elements that are not consistently contained in the majority of the spots that are analysed on an individual manuscript are considered to be contaminants.

The elements that one would expect to detect using XRF are different depending on the type of ink. Carbon black is not characterised by the predominant presence of any element that is detectable using XRF. However, carbon inks may contain potassium, associated with the binder. Plant inks may contain potassium as well, associated either with the binder or with vegetal matter. In addition, there is evidence of carbon inks that contain metal and of plant inks that contain copper (see § 2.2.1). As for iron-gall inks, XRF analysis would be expected to detect significant amounts of iron along with, perhaps, manganese, copper and zinc if these were present in the vitriol used to prepare the ink[156]. Calcium and potassium can also be present in carbon, plant and iron-gall inks but the origin of these is difficult to determine since these elements are widely diffused in the animal and plant kingdoms. Potassium is generally attributed to the binder and in case of iron-gall ink it can be part of the metallic salt that was used in its preparation, being probably contained in the vitriol in the form of alum ($KAl(SO_4)_2$) or contained in the gallnuts.

Generally, it is easy to recognise the presence of transition metals in the ink, while it is sometimes challenging to determine whether calcium and potassium are part of the writing medium. Both calcium and potassium are light elements and their characteristic radiation emitted after X-rays excitation is more prone to be reabsorbed in the sample before reaching the detector (see § 3.1.1.4, matrix effects). This phenomenon depends on the thickness of the cross-section of ink under analysis, being more intense for thicker cross-sections. Because of this, for inks with uneven cross-sections throughout the page, the profile of intensity of calcium and potassium may vary a lot from one spot to another, thus making it difficult to unequivocally associate these elements to the ink under investigation. Moreover, calcium is often found in high amounts on parchment, because lime was used in the manufacture of this material; and sometimes on papyrus leaves, which were often preserved together with mummy cartonnages rich in calcium sulphate. In these cases, it may be difficult to establish how much calcium is contained in the ink and how much in the support.

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[156] Hickel 1963

3.2.3.2 *The fingerprint of iron-gall inks*

XRF analysis allows for the quantification of elements that are detected using only reference or fundamental parameter methods that require knowledge of the characteristics of the equipment and the matrix. However, neither of these methods deliver good results with thin-layer systems such as ink on paper, papyrus or parchment.

For this reason, the fingerprint model was initially developed as a tool to compare the composition of iron-gall inks on paper. A detailed study of an ink–paper system leads to the experimental definition of different coefficients accounting for the transmittance of the entire layered system, the penetration depth of the ink into the paper and the absorption of the paper. This makes it possible to obtain an exact quantification of the metallic elements that are characteristic of the vitriol used to produce the ink.[157]

However, an exact quantification is not always necessary in order to compare the chemical composition of different inks on a manuscript. Therefore, a simplification of this model was later introduced which does not require a detailed study of ink–support systems and yet produces satisfactory semi-quantitative results[158]. Because it can discriminate and characterise the different writing phases involved in the production of a codex, this simplified version of the fingerprint started to be used to complement traditional codicology, founding a new interdisciplinary field of research known today as "advanced codicology"[159].

The calculation of the semi-quantitative fingerprint is a two-step procedure using the data resulting from XRF analysis. Since X-rays penetrate both the layer of the ink and the underlying support, the first step consists in subtracting the net peak intensity of each element that was measured in the support from the corresponding element measured in the inked area. In a second step, the intensities of each element resulting from this subtraction are normalised to iron, on the assumption that a coherent writing phase is represented by the same ratio of the satellite elements to iron, this being the main component of the vitriol described in medieval recipes to make iron-gall ink.

As discussed in § 3.1.1.4, the phenomenon of X-ray fluorescence depends on the atomic mass of elements, with the fluorescence being more intense for heavier ones. Consequently, only elements having similar responses can be directly compared. For iron-gall inks, the elements of interest are iron, manganese, copper and zinc. Calcium and potassium are often contained in the ink as well, but since they are considerably lighter their response is not directly comparable with the other elements. Normalisation to iron can be performed to compare the amounts of calcium and potassium in different inked areas, but it must be kept in mind that these elements are more prone to be affected by matrix effects because they are light, and, as previously mentioned, this may lead to ambiguous results if the thickness of the support or of the cross-section of ink is rather heterogeneous along the surface of a leaf. Because writing inks and supports are inherently characterised by a certain level of

[157] Hahn 2010; Hahn et al. 2004

[158] Rabin et al. 2012

[159] See for instance the studies on Hamburg, Staats- und Universitätsbibliothek, *Cod.germ.* 6 in Rabin, Hahn, and Geissbühler 2014; Geissbühler et al. 2018

heterogeneity, the comparison of the intensities of calcium and potassium detected in different inked areas should be used cautiously for discrimination purposes.

The semi-quantitative fingerprint works well in the case of supports having a rather homogeneous spatial elemental distribution, such as parchment or European paper. In fact, since the contribution from the support needs to be subtracted in the first step, the accuracy of the semi-quantification depends on the number of measurements collected and on the distribution of the elements in the writing surface: the higher the heterogeneity, the higher the error. For this reason, the calculation of the fingerprint becomes problematic for inks on papyrus. Figure 4 shows the elemental map of iron for a piece of modern papyrus (mock sample), performed using the Tornado M4 (Bruker), a 2D micro-XRF spectrometer, whose probe contains an air-cooled low-power X-ray tube, polycapillary X-ray optics and an electrothermally cooled XFlash detector. The red ink on the papyrus is a mixture of minium and cinnabar, and therefore the distribution of iron is characteristic only of the papyrus itself. This is extremely heterogeneous and displays areas where a considerable amount of iron is accumulated in grains.

Figure 4 XRF map for iron collected using Tornado M4 spectrometer. Beam size: 50 μm, voltage: 50 kV, current: 600 μA[160].

This spatially inhomogeneous distribution is usually greater in the case of archaeological papyri that have been resting in sandy environments, rich in iron, or exposed to different deterioration agents. Such an intrinsic heterogeneity, fomented by centuries of degradation, impedes accuracy in the calculation of the semi-quantitative fingerprint for iron-gall inks on archaeological papyri. Consequently, in these cases the fingerprint should be used cautiously to discriminate different writing phases (see the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use")[161].

In applying the fingerprint model to the study of European manuscripts written on paper, the error was estimated to be around 10%[162]. In contrast, the error of the model when applied to manuscripts on papyrus is expected to be higher. Because papyrus leaves vary greatly in thickness, a standard error cannot be determined. Therefore, the value of the error needs to be calculated for each individual case.

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[160] The data presented are courtesy of Grzegorz Nehring and were acquired during a study investigating Herculaneum papyri

[161] Ghigo, Rabin, and Buzi 2020

[162] Hahn et al. 2004

4 Results and discussion

Before reporting on the results of the analysis, it is important to discuss in detail the limits of the analytical protocol applied and suggest possible solutions to overcome the difficulties encountered.

4.1 A step beyond the limits of the current analytical protocol

Figure 5 and Figure 6 show the results from an inked area on Montserrat, Roca Puig, Inv. 14 and an inked area on Montserrat, Roca Puig, Inv. 163, respectively. The XRF intensity profiles show that iron and copper are contained in these writing media, in addition to sulphur in the second case, indicating the presence of metallic salts associated with iron-gall ink. However, while in the first case near-infrared reflectography shows that the ink changes its opacity considerably and homogeneously as is typical for iron-gall ink, in the second case the change in opacity is quite heterogeneous. For instance, on the first letter on the left, some areas remain rather opaque. In this case, the possibility that some carbon was added to the mixture should be considered.

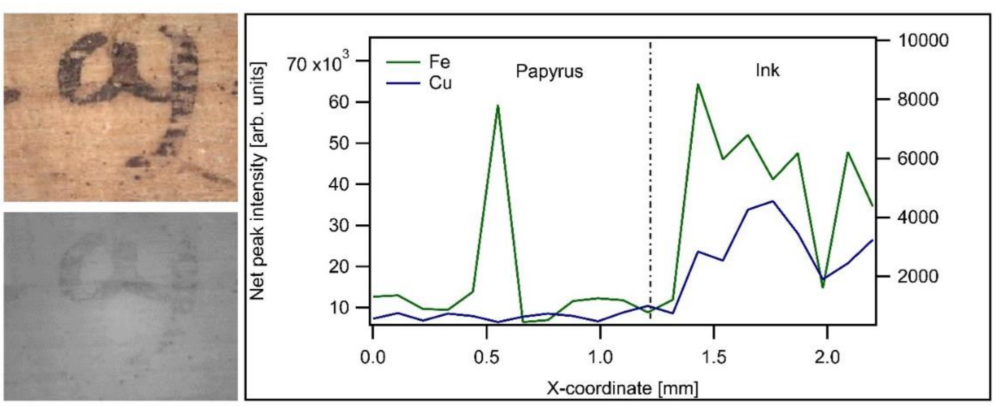

Figure 5 Visible and near-infrared micrographs (DinoLite, 50×) and XRF intensity profiles on an inked area of Montserrat, Roca Puig, Inv. 14. The scale of Fe is displayed on the left, while the scale of Cu is on the right.

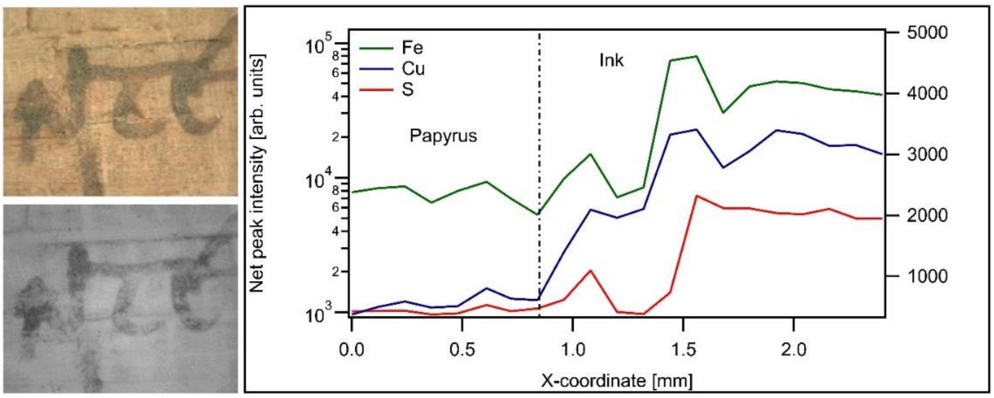

Figure 6 Visible and near-infrared micrographs (DinoLite, 50×) and XRF intensity profiles on an inked area of Montserrat, Roca Puig, Inv. 163. The scale of Fe and Cu is displayed on the left, while the scale of S on the right.

The ideal conditions under which the routine analysis performed (i.e., NIRR and XRF) can unequivocally discriminate different types of writing media occur when iron-gall inks are prepared according to a correct stoichiometry (proportion of gallic acid and bivalent iron). In this case, they will change their opacity in the near-infrared region, appearing very different from carbon inks, which remain opaque, and from plant inks, which become transparent. The current analytical protocol was initially designed for the study of late medieval iron-gall inks which typically appear different from plant and carbon inks when observed at 940 nm. In contrast, recent archaeometric studies on older inks, including those reported in this dissertation, suggest that the transition between carbon ink, very popular in Antiquity, and iron-gall ink happened using different mixtures whose identification sometimes evades the current protocol.

Mixed inks are rather challenging writing media to identify[163]. A dedicated publication has addressed the complications in characterising this category of inks (see the appendix "The quest for the mixed inks")[164]. When a mixed ink is produced, carbon pigments are blended with metallic salts, tannins or iron-gall ink. Therefore, the response of the resulting ink to near-infrared reflectography will result from the sum of the behaviours of the different ingredients. Generally, only the main component is detected. Therefore, depending on the amount of soot or charcoal used in the preparation, the ink may not appear completely opaque at 940 nm, thus preventing the reflectographic analysis from detecting carbon. In contrast, a mixture containing a large amount of carbon and tannin would be identified as pure carbon ink, unless a halo originating from tannin diffusion in the support is present around the letters and can be detected either visually or using ultraviolet reflectography.

Raman spectroscopy has in the past been applied to the characterisation of mixed inks containing carbon and iron-gall, since it can successfully register spectral features of both compounds. However, for the study of inks the use of bench equipment is often necessary for this type of spectroscopy, thus limiting the number of manuscripts that can be investigated. In contrast, the application of Raman spectroscopy to the analysis of pure tannin inks has proven

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[163] Rabin 2015
[164] Colini et al. 2018

to be extremely difficult. In the study of the Dead Sea Scrolls, it was possible to obtain satisfactory results when investigating tannins using a FT-Raman spectrometer featuring a 1064 nm laser[165]. However, this type of laser is not currently available on portable devices. Furthermore, strong Raman fluorescence of organic compounds often disturbs the spectra that are acquired. To overcome this difficulty, the application of SERS has been suggested (see the appendix "The quest for the mixed inks")[166]. However, the analysis of mock samples of tannin-based inks in this way have led to no immediate success. Furthermore, SERS involves the use of colloidal dispersions of nanoparticles and in some cases the application of water-based gels treated with chelating agents in order to extract a sample for analysis. Therefore, it is difficult to apply for *in situ* routine analysis.

*

The simplest method to unequivocally detect any amount of carbon in a mixed ink is the use of infrared reflectography performed using radiation at about 1800 nm, similar to what is done to detect underdrawings on painted objects.

To explore the inherent wavelength of disappearance of freshly formed iron-gallate complex, a routine experiment was set up. Laboratory tests were performed on a set of mock samples[167]. A band pass filter 1250–1510 nm and a long wave filter above 1510 nm were used to observe the behaviour of the inks in different spectral regions.

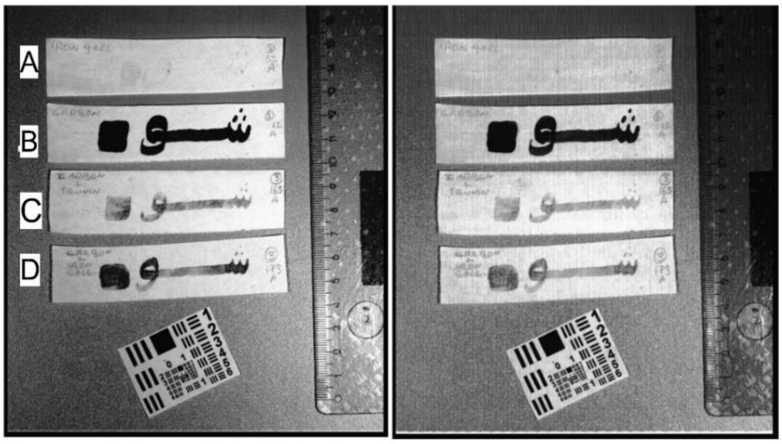

Figure 7 Infrared pictures obtained with a band pass filter in the range 1250–1510 nm (left) and a long wave filter above 1510 nm (right).

Figure 7 shows the results of the test on four different samples: (a) fresh stoichiometric iron-gall ink, (b) carbon ink, (c) mixed ink obtained by blending 50% tannin and 50% carbon, and (d) mixed ink obtained by blending 25% iron-gall and 75% carbon. It can be observed that fresh iron-gall ink is still partly visible in the range between 1250 and 1510 nm, but it becomes completely transparent above 1510 nm where only carbon ink remains visible. Samples (c) and (d), corresponding to the mixed inks, are still visible in the range above 1510 nm, revealing

165 Bicchieri et al. 2018

166 Colini et al. 2018

167 Warm thanks are due to Ivan Shevchuk for sharing the details and results of this preliminary test and to Claudia Colini for the preparation of the mock samples

that they contain carbon particles. This experiment shows that infrared reflectography above 1510 nm can be used to unequivocally detect carbon particles in mixed inks.

*

For the analysis of the organic compounds of inks, such as the different types of tannin, recent developments in forensic studies using quasi non-destructive methods based on mass spectrometry have opened up new possibilities. The atmospheric solids analysis probe (ASAP-MS), a new ionisation source, adopts a versatile micro-sampling technique that does not involve the use of any chemical reagents and can easily be applied anywhere. The micro-sample is collected by gently rubbing a glass rod (sample holder) on solid analytes or by immersing it in liquid analytes. In a second step, the sample holder is inserted in the instrument for examination. This dry micro-sampling technique is particularly versatile and suitable for precious and fragile materials, such as cultural heritage objects.

Preliminary tests were performed on mock samples. The results obtained are rather promising: characteristic components of the family of hydrolysable tannins were easily detected in different types of ink, including mixed ink. Figure 8 shows the case of a mixed ink containing carbon and iron-gall. The ions of pyrogallol (125.02 m/z) and gallic acid (169.01 m/z), which are characteristic of the hydrolysable tannins contained in gallnuts, are easily detected. For further information see the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use"[168].

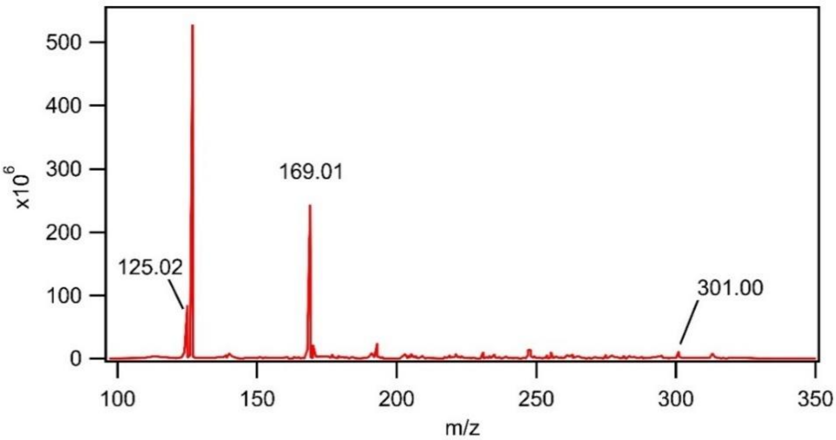

Figure 8 Mass spectrum of a mixed ink containing carbon and iron-gall. The ions of pyrogallol, gallic and ellagic acids are found respectively at 125.02, 169.01 and 301.00 m/z. The signal at 126.90 is due to the calibration of the equipment using iodide ions.

The use of ASAP-MS for routine analysis would improve the analytical protocol, and not only in detecting tannins in mixed inks. Potentially, it could allow for the distinction of different families of tannins (namely condensed and hydrolysable) and offer insight on other organic compounds contained in the writing media. This would help to obtain a finer classification and a better understanding of the chemical structure of different types of ink.

[168] Ghigo, Rabin, and Buzi 2020

4.2 Results on the manuscripts

4.2.1 Between semi-quantitative and qualitative data: what to expect from the results presented

As discussed in § 3.2.3.2, the semi-quantification of the elements in iron-gall inks (i.e., the fingerprint) should be performed rather cautiously in the case of manuscripts on papyrus. During this investigation, the fingerprint was used for the examination of iron-gall inks on papyrus only in the case of the Codex Miscellaneus of Montserrat (see the appendix "Between literary and documentary practices: The Montserrat Codex Miscellaneus and the material investigation of its inks")[169]. On this codex, seven different non-contiguous leaves corresponding to seven different textual units were investigated. Because of the heterogeneity of the support, the results obtained are not accurate enough to characterise precisely the different writing phases involved in the production of the codex: the comparison of the fingerprints provides only an indication. However, the great variation in the ratio I_{Cu}/I_{Fe} shows that the small single-quire codex was written in multiple phases. Furthermore, the comparison of the fingerprints suggests that in some cases the writing phases may have coincided with the different textual sections. This seems to corroborate the hypothesis brought forward by different palaeographic and codicological studies, which suggest that this manuscript was used as a notebook into which different texts were copied, rather than being a codex whose textual content was planned in this form from the very beginning[170]. Therefore, although an accurate semi-quantification was not possible, the examination provided meaningful results that supported manuscript studies. In the case of the other papyrus leaves written with iron-gall ink that were examined, the calculation of the fingerprint did not produce accurate or meaningful results. The calculation was omitted when time restrictions or restrictions imposed by the conservation state of the manuscript precluded the possibility of conducting a sufficient number of representative measurements, and in these cases, the discussion will be limited to the qualitative aspects of the inks.

In the case of parchment manuscripts, the fingerprint of iron-gall inks was used only occasionally, for various different reasons. For instance, the purpose of examining documents from the library of the White Monastery was to collect qualitative data on black inks and coloured pigments over a reasonable number of codices, in order to compare the types of ink used in manuscripts belonging to the same library, and as a result no detailed study was performed of the different writing phases in the production of each individual codex[171]. A similar situation characterised the analysis of the fragments from the Michaelides collection, where the calculation of reliable semi-quantitative data was in addition hampered by the poor

[169] Ghigo and Torallas Tovar 2020

[170] Torallas Tovar and Worp 2006; Fernández and Torallas Tovar 2010; Ammirati 2015a, 59; Ammirati 2015b, 16–18

[171] Only in the case of *Ms.or.fol* 1609, ff. 3 and 4, were the black inks systematically investigated, and the fingerprint model was used here to gain insights into the composition of the ink and establish whether these folios could have been written in a single phase. See Ghigo and Rabin 2020

state of conservation of many of the fragments. In contrast, at the Biblioteca Apostolica Vaticana, where only four codices from the Monastery of Saint Macarius were examined, time restrictions prevented a thorough investigation of the numerous writing phases that must have been at the origin of a rather complex codicological structure: the codices include both black and coloured decorations and a variety of marginalia and corrections in addition to the original text, which consists of the main text, titles and colophons. Even if it was not always possible to obtain semi-quantitative data on the black inks, the results obtained suggest that, when investigating a large geographic area and time span, qualitative data are sufficient to observe distribution patterns of the typology of ink.

Table 2 gives an overview of the techniques used in previous studies to identify different types of black ink in manuscripts from Antiquity to the Middle Ages[172]. For a detailed description of the different materials used in the production of these inks and for information on specific analytical studies and recipes, see § 2.2.1.

Table 2 Description of the different types of ink that have been detected in manuscripts dating from Antiquity to the Middle Ages, and the detection methods used in previous studies.

Type of ink	Colour	Detection
Carbon	black	NIRR, Raman
Plant + copper	brown	PIXE*
Iron-gall	black (brown when deteriorated)	NIRR, Raman, XRF, PIXE
Plant	brown	NIRR, FTIR
Mixed: carbon + copper	black	NIRR + XRF
Mixed: carbon + lead	black	NIRR + XRF
Mixed: carbon + tannin**	black	Extraction, ASAP-MS***
Mixed: carbon + iron-gall	black	NIRR + XRF

* Particle induced X-ray emission
** This type of ink is known from extant sources but has not been detected in a historical manuscript
*** Preliminary tests performed during this investigation suggested that ASAP-MS could successfully detect tannins in mixed inks of this type

The present investigation primarily made use of NIRR and XRF to characterise black inks. However, it was not always possible to apply both techniques to all of the manuscripts in the corpus, and therefore not all the inks examined during this investigation could be directly associated to one of the types presented in Table 2. Consequently, for the detailed discussion of the results presented here, the list has been reconfigured as follows:

1. carbon-based ink (C-based)
2. carbon ink (C)
3. carbon ink containing iron ($C_{(+Fe)}$)
4. plant ink (P)
5. iron-gall ink (IG)

172 Rabin 2017

6. iron-gall ink containing only iron (IG: Fe)
7. iron-gall ink containing iron and copper (IG: Fe, Cu)
8. iron-gall ink containing iron, copper and zinc (IG: Fe, Cu, Zn)
9. mixed ink (M)

The category "carbon-based ink" refers to inks that could be analysed only with near-infrared reflectography: their elemental composition remains at present unknown. On the other hand, the label "carbon ink" refers to those inks that could be analysed with both near-infrared reflectography and XRF analysis and that were found not to contain any additional metals besides, occasionally, calcium and potassium. To these two labels for carbon inks a third is added: "carbon ink containing iron". The analytical protocol used in this study did not always offer an unequivocal answer when trying to distinguish between carbon inks that contain iron as the result of an intentional addition (mixed inks) and those that contain it as the result of contamination from metallic tools and vessels. In some cases, the amount of iron associated with carbon may give an indication that an ink is of one or the other type. However, in the case of papyrus manuscripts the considerable heterogeneity of iron in the support often precludes even a semi-quantitative estimation of the amount of it that is in the ink; without this information, and without the possibility of determining the oxidation state of iron (and therefore gaining insight into which iron compound is present), no attempt at understanding the nature of these inks can be made. In order to represent these cases, the label "carbon ink containing iron" has been introduced.

Iron-gall inks are divided into categories according to their elemental composition, which is reflected in the label. In addition to the more specifically labelled inks, iron-gall ink whose elemental composition is unknown because no XRF analysis was performed is labelled simply "iron-gall ink".

The last category is that of the "mixed inks". The types of ink listed in Table 2 include carbon inks with added metals (copper and lead) that were found during the investigation of the Dead Sea Scrolls and papyri from Herculaneum and from Egypt[173]. However, the analytical techniques used to perform those studies do not allow for an identification of the metal compounds, therefore it is not clear whether the use of the term "mixed ink" is appropriate in those cases. The present investigation found no evidence of carbon inks that contained solely copper or lead, and consequently the category of mixed inks in this study refers either to inks containing carbon and substantial amounts of iron in addition to satellite elements associated with vitriol (found only in marginal notes on parchment codices, see § 4.2.7) or to inks containing carbon and displaying a brownish halo around the letters, indicating the diffusion of tannins in the support. The latter were found on documentary papyri and were associated with variable amounts of iron, copper and sometimes lead (see § 4.2.6).

Far from being precise and exhaustive, this list aims at offering a simplified framework for the representation of the results, within the range of possibilities and limitations of the

[173] Nir-El and Broshi 1996; Brun et al. 2016; Christiansen, Buti, et al. 2017

analytical protocol applied in this investigation. These categories will be used in the following sections to outline the results obtained on Egyptian writing media between Late Antiquity and the Middle Ages.

4.2.2 Overview of the corpus

The results presented in this chapter are based on the material analysis conducted on 162 manuscripts. A total of 216 leaves and fragments on different supports (2 ostraca, 125 papyri, 83 parchment and 6 paper leaves) were examined. Of these, 158 manuscripts (212 leaves and fragments) were investigated with NIRR to establish the type of black ink used, while XRF was conducted on 100 manuscripts (140 leaves and fragments). In addition, FORS was used in a limited number of cases to determine the nature of coloured pigments, while in a few cases an attempt was made to employ DRIFTS and Raman spectroscopies to gain insight into the molecular composition of the sample, but the analysis was unfortunately fruitless. Figure 9 summarises the distribution of the methods and supports within the corpus.

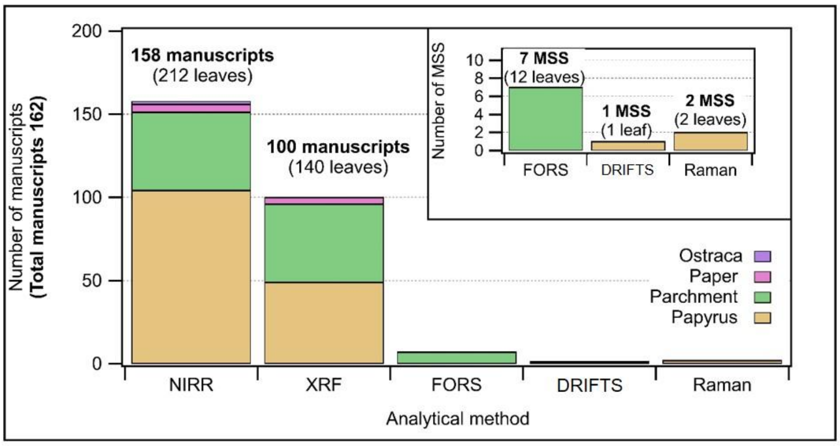

Figure 9. Distribution of the analytical methods used in studying the corpus of manuscripts. The graph presents the number of manuscripts studied and the corresponding number of leaves. The inset shows the detail for FORS, DRIFTS and Raman.

While deciding upon the corpus of the manuscripts for this study, an effort was made to achieve a homogeneous geo-chronological representation. However, this proved to be an extremely challenging task for several reasons.

Although curators were often enthusiastic about the possibility of contributing to this research, hosting an analytical session definitely involved considerable logistical efforts. Not only did the institution have to accommodate the mobile lab on their premises, but they also needed to organise the work of the conservation personnel to prepare the manuscripts and provide the necessary help to the scientific team. For this reason, the number of manuscripts that could be examined at any institution was highly influenced by the resources of that institution and, for those manuscripts that are not in the PAThs database, by the availability of scholars currently studying the manuscripts who could provide the necessary support.

Almost every set of analyses was focused on a particular group of manuscripts centred around a specific historical context, such as the papyrus codices produced in Thi(ni)s during the 7th or 8th century, the documentary papyri written in the 7th or 8th century in the Monastery of Apa Apollo in Bawit, or the literary codices written in the Monastery of Saint Macarius between the 9th and the 11th centuries. As a consequence, substantial data were collected on manuscripts from specific areas and periods, while no analysis was performed on manuscripts from other historical settings. Furthermore, getting access to older manuscripts represented a challenge. In particular, papyrus leaves from the first centuries of the Common Era are in general carefully guarded because of their fragile state of conservation, and access for analysis is not normally permitted.

Above all, the greatest obstacle was the lack of inherent information on date and provenance of many of the manuscripts investigated. In some cases, the combined study of their textual, palaeographical and codicological information allowed only for a partial reconstruction of their historical context (see § 1.1.3).

As a result of all these factors, the overall geo-chronological distribution of the corpus of manuscripts turned out to be uneven, as shown in the figures below. The chronological and geographical data for the manuscripts that are used in these figures were extracted from the *Archaeological Atlas of Coptic Literature* of the PAThs project, unless indicated otherwise in the specific tables describing individual manuscripts in the sections that follow.

Figure 10 shows that the chronological distribution of the manuscripts spanned from the 3rd century BCE to the 12th century CE, with the bulk of the corpus dating between the 2nd and the 11th centuries CE. Different writing supports are represented in this figure using different colours: yellow for papyrus, green for parchment, violet for ostraca and pink for paper. Papyrus and parchment are by a wide margin the most represented writing supports in the corpus. The graph appears to suggest that papyrus was almost exclusively the only writing support used until the 9th century CE, when it was suddenly replaced by parchment. In fact, however, this does not correspond to the true distribution of writing supports in the timespan and geographical frame considered, but rather reflects the specific choices that were made while establishing the corpus.

In almost 15% of cases chronological data are completely unknown since the manuscripts lack both an inherent indication of time and palaeographic dating. In addition, no geographical information is available for these leaves, which are those manuscripts that form part of the Michaelides collection preserved at the Cambridge University Library. As permission had been obtained to analyse this collection, it was decided to proceed with the analytical study despite the lack of dating and localisation, and to use the data that was collected for comparative purposes. It is to be hoped that future codicological and palaeographic research will provide these manuscripts with an appropriate historical context, giving new meaning to the material analysis presented in this work.

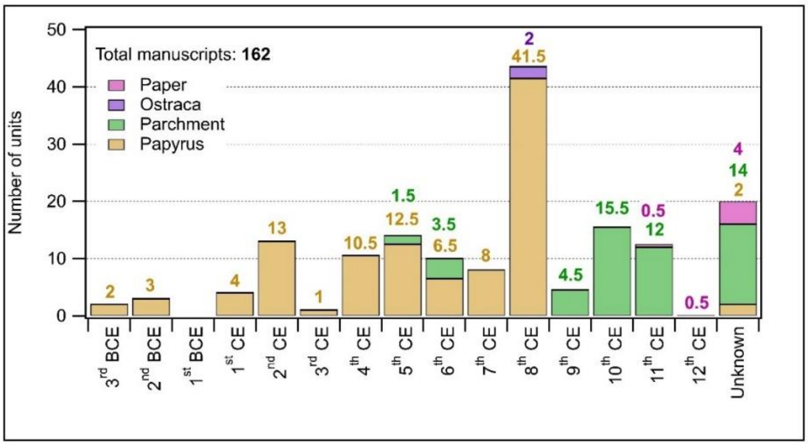

Figure 10. Chronological distribution of the corpus of manuscripts. Where a manuscript is known to date to one of two centuries, the count is given as 0.5 in each of the two adjacent centuries.

Figure 11 shows the distribution of languages in the documents plotted against the time span under consideration. Manuscripts in Greek are shown in green, Latin in purple and Coptic in yellow. There were two 4th-century bilingual manuscripts written in Greek and Latin in the corpus, and these appear twice in the figure. Once again, this distribution does not reflect the linguistic environment of Egypt at the relevant time but results from specific choices.

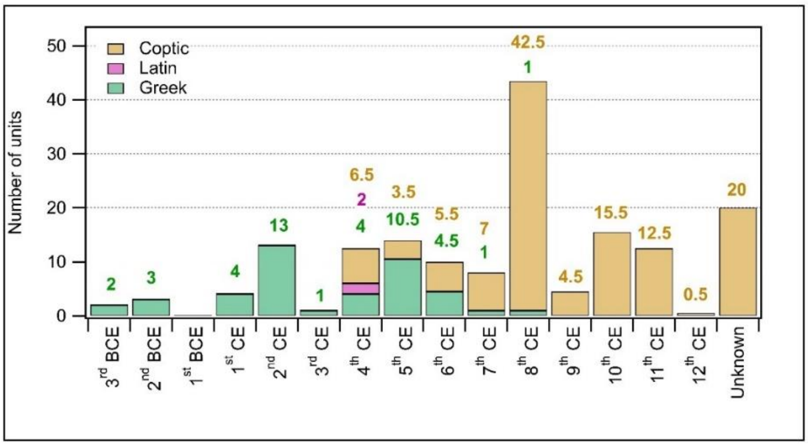

Figure 11 Distribution of the languages in the manuscripts, presented by the date of the manuscripts. Where a manuscript is known to date to one of two centuries, the count is given as 0.5 in each of the two adjacent centuries, while the two bilingual manuscripts are counted twice.

Figure 12 shows the geographical distribution of those manuscripts whose place of production is known (or believed to be known). It must be stressed that this representation does not include a chronological variable and therefore deprives these manuscripts of their historic dimension. The place of production is known for only 89 of the 162 manuscripts, a little more than 50% of the total. For the remaining manuscripts, information is available on where each manuscript was discovered or stored, but not on the specific place where it was produced. While carrying out the present investigation, it soon became clear that if it was limited exclusively to manuscripts whose place of production was uncontroversially known, the number of leaves that could have been examined would have been insufficient for an overview. Furthermore, some of the most important libraries of literary manuscripts produced during the relevant timespan would have been neglected. For instance, manuscripts from the library of the White Monastery would have been excluded; but the analyses of some of the codices from this library reveal interesting results despite their place of production in most cases being unknown (see the appendix "Gaining perspective into the materiality of manuscripts: The contribution of archaeometry in the study of the inks from the White Monastery codices")[174].

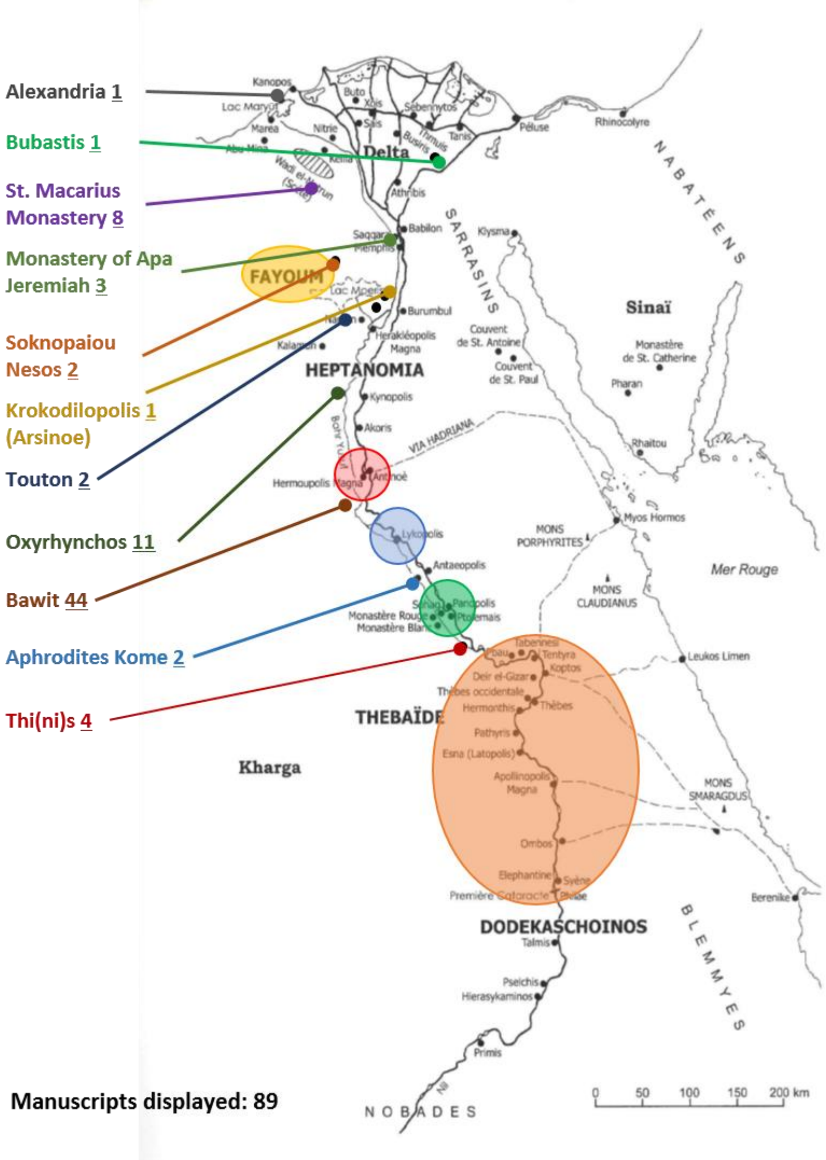

Figure 12 Geographical distribution of those manuscripts in the corpus whose place of production is known (89/162 manuscripts). The map of Egypt used to create this distribution has been extracted from: E. Wipszycka, Moines et communautés monastiques en Égypte, *Warsaw 2009 [*Journal of Juristic Papyrology, *Supplemetn XI], fig. 1.*

Comparing Figure 10 and Figure 12, it is possible to observe that the majority of information that was collected relates to manuscripts produced in the area of Bawit and to manuscripts from the 8th century CE – and indeed, a substantial number of documents having both these geo-chronological coordinates were analysed during the second set of analyses undertaken in the Palau Ribes and Roca Puig collections (see § 4.2.6).

[174] Ghigo and Rabin 2020

Throughout the following sections, leaves and manuscripts originally belonging to the same ancient library are grouped where this is possible, and reported in chronological order. This does not apply to the literary manuscripts from the early Christian period, which are gathered together in § 4.2.3 based on their palaeographic dating. Furthermore, the manuscripts from the Palau Ribes and Roca Puig collections (with the exception of those produced in Bawit) and those from the Michaelides collection are reported separately, since palaeographic and codicological studies have not yet assigned them to an ancient library. For each manuscript, details are given of the shelfmark, the CLM number (Coptic Literary Manuscript identification number, as reported in the PAThs atlas) where the document has one, and the analytical techniques applied, along with the results from the typological and elemental analysis of the inks.

4.2.3 Papyrus leaves from the early Christian period, some of them belonging to the Bodmer Papyri

Corpus

This group of literary papyri from the early Christian era includes two bifolia preserved at the Biblioteca Apostolica Vaticana in Rome, seven small leaves from the Codex Miscellaneus and the roll of Athanasius (Inv. 14) preserved in the Roca Puig collection in Montserrat, one bifolium preserved at the Staatsbibliothek in Berlin, another bifolium preserved at the Ägyptisches Museum in Berlin and four leaves (or fragmentary leaves) from four different codices, one of them Manichaean, preserved at the Chester Beatty Library in Dublin. All analysed leaves show a very simple layout composed only of the main text, with no decoration, and were written using only black inks. Table 3 provides a description of the relevant manuscripts; the information on date and provenance has been extracted from the PAThs database or from the bibliography given at the end of the table.

Table 3. Description of the relevant early Christian papyrus leaves in the corpus and the analytical techniques applied to them.

Shelfmark	Collection	Language	Date	Provenance	Methods	No. spots ink+supp.
Pap.copt. 9 (CLM 6295)	Rome, Biblioteca Apostolica Vaticana	Coptic	351–400	?	NIRR, XRF*	
Glass 39 (ff. 70 and 92)						8 + 9
Glass 45 (ff. 80 and 83)						7 + 2
Codex Miscellaneus[a]	Montserrat, Roca Puig	Greek and Latin	End of the 4th century CE	Area of Panopolis	NIRR, XRF**	
Inv. 145						4 + 2
Inv. 150						4 + 2
Inv. 154						2 + 1
Inv. 157						4 + 2
Inv. 161						2 + 1
Inv. 163						2 + 2

Shelfmark	**Collection**	**Language**	**Date**	**Provenance**	**Methods**	**No. spots** ink+supp.
Inv. 172						2 + 2
Inv. 14[b] (CLM 1206)	Montserrat, Roca Puig	Coptic	End of the 4th century	Area of Panopolis	NIRR, XRF***, Raman Renishaw	6 + 2
Ms.or.fol. 3065 (CLM 24)	Berlin, Staatsbibliothek	Coptic	301–400	Panopolis	NIRR	6
Cpt. 2018.2[c] (CLM 1022)	Dublin, Chester Beatty Library	Coptic	375–425	?	NIRR	10
Cpt. 2020[c] (CLM 38)	Dublin, Chester Beatty Library	Coptic	301–500	?	NIRR, XRF*	3 + 2
Cpt. 2026[c] (CLM 42)	Dublin, Chester Beatty Library	Coptic	341–400	?	NIRR	14
Pma B[c] (CLM 174)	Dublin, Chester Beatty Library	Coptic	301–425	Area of Lykopolis	NIRR, XRF*	6 + 6
P. 8502 (CLM 731) Glass 139–140[d]	Berlin, Ägyptisches Museum	Coptic	401–500	Area of Panopolis?	NIRR	4

[a] Fernández, Juan Gil, and Sofía Torallas Tovar. 2010. *Hadrianus P. Monts Roca III*. Orientalia Montserratiensia. Barcelona: Consejo Superior de Investigaciones Científicas
[b] Torallas Tovar, Sofía. 2018. "Athanasius' letter to Dracontius: A Fourth-Century Coptic Translation in a Papyrus Roll (P. Monts. Roca Inv. 14)." *Adamantius* 24:22–38
[c] Warm thanks are due to Olivier Bonnerot for performing the analysis on these codicological units
[d] Warm thanks are due to Grzegorz Nehring for performing the analysis on this codicological unit
* The XRF equipment used for this analysis was the Elio (Bruker Nano GmbH, formerly XG Lab)
** The XRF equipment used for this analysis was the ArtTAX (Bruker Nano GmbH)
*** The XRF equipment used for this analysis was the Elio (Bruker Nano GmbH, formerly XG Lab) and the M6 JetStream (Bruker Nano GmbH)

Among these codices, *Pap.copt*. 9 (Biblioteca Apostolica Vaticana), the Codex Miscellaneus (Roca Puig) and *Cpt*. 2018, 2020 and 2026 (Chester Beatty Library) are considered to be part of the well-known Bodmer Papyri[175]. However, regardless of which collection the manuscripts may have belonged to at a certain point in history, all presented here were produced within a similar timespan and it is therefore meaningful to compare the materials used in their manufacture.

The results obtained on the Codex Miscellaneus have been extensively discussed in a dedicated article. The literary sections (six of the seven sections, A to F) were written in several phases using an iron-gall ink containing both iron and copper (see the appendix "Between literary text and documentary practice: The Montserrat Codex Miscellaneus and the material investigation of its inks")[176]. On the other hand, the analysis of *Pap.copt*. 9 was only briefly presented in another publication, where the roll of Athanasius was also mentioned (see the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and

[175] See the subsection in § 1.2.2.3 on literary fragments from the Bodmer Papyri.
[176] Ghigo and Torallas Tovar 2020

use")[177]. The following paragraphs therefore aim at providing further details on these last two manuscripts as well as the results obtained on the other papyri.

Results

Rome, Biblioteca Apostolica Vaticana, Pap.copt. *9*

Figure 13 shows the results of the reflectographic and elemental analysis on this papyrus. The comparison of visible and near-infrared micrographs reveals that the ink changes its opacity, as is typical for iron-gall ink. XRF confirmed this result, detecting both iron and copper in the ink as can be seen from the peaks positioned at 6.4 and 8.0 keV respectively.

However, the near-infrared image shows that the loss in opacity is rather heterogeneous, being more prominent in some areas than in others. For this reason, the possibility that the ink contains some carbon in addition cannot be excluded. In fact, this manuscript is one of those which are not well characterised by the routine analysis that was performed. In this case, infrared reflectography at longer wavelengths could unequivocally establish whether any carbon was added to the mixture.

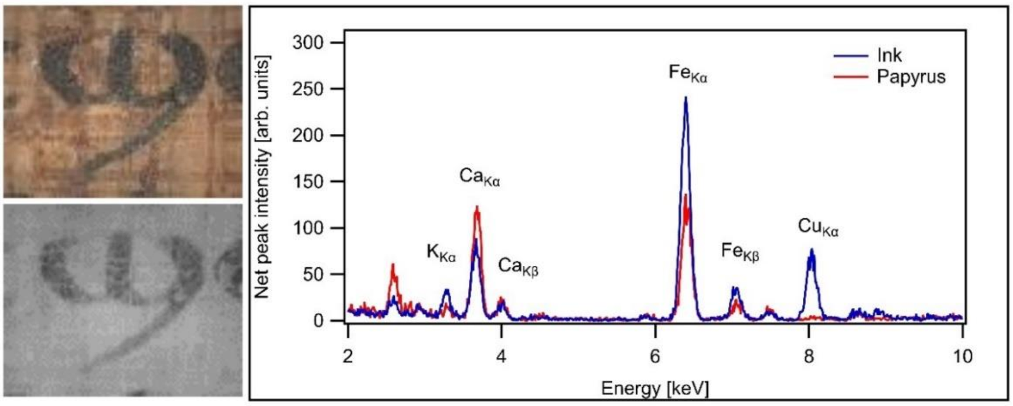

Figure 13 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (Elio spectrometer) for Rome, Biblioteca Apostolica Vaticana, Pap.copt. *9.*

Montserrat, Roca Puig, Inv. 14 (Roll of Athanasius)

Figure 14 reports the results of near-infrared reflectography on the roll of Athanasius, showing an extreme change in the opacity of the inked areas, which reveals that the roll was written in iron-gall ink. Furthermore, the elemental maps on a small sample reported in Figure 15 show that the ink contains iron, copper and lesser amounts of potassium[178]. A closer look at the map of iron reveals a rather heterogeneous distribution in the support, as is typical for papyrus. Because of the considerable change in opacity observed in the near-infrared region, an attempt was made at registering a Raman spectrum of this iron-gall ink to compare it to

[177] Ghigo, Rabin, and Buzi 2020

[178] The Athanasius' roll represented the only case in which a sample was available to be studied with bench equipment. Therefore, special thanks are due to Sofía Torallas Tovar and the monks from the Abbey of Montserrat for granting permission

spectra of mock-up inks prepared using different types of tannin. Unfortunately, this analysis did not lead to meaningful conclusions due to the high fluorescence of the ink.

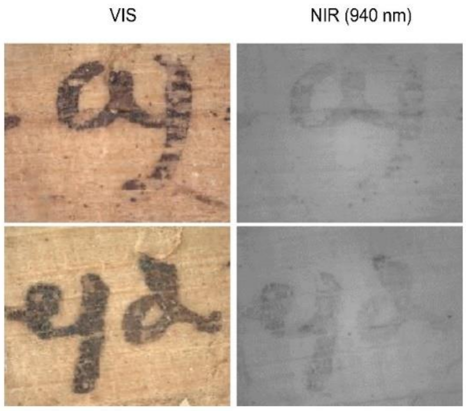

Figure 14 Visible and near-infrared micrographs (DinoLite, 50×) of two inked areas on Montserrat, Roca Puig, Inv. 14.

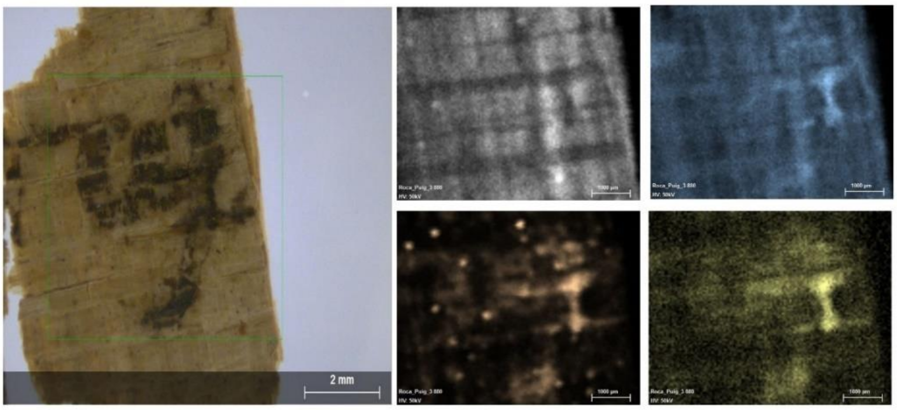

Figure 15 XRF maps of different elements for Montserrat, Roca Puig, Inv. 14. On the left is a micrograph of the sample, on the right the maps of Ca in white, K in blue, Fe in peach and Cu in yellow.

Berlin, Staatsbibliothek, Ms.or.fol. *3065*

The near-infrared analysis on a bifolium from this codex showed a considerable change in opacity in the near-infrared region, typical for iron-gall ink. Figure 16 illustrates the results of this analysis. Unfortunately, it was not possible to apply XRF to the study of this manuscript, and the elemental composition of the ink therefore remains unknown at present.

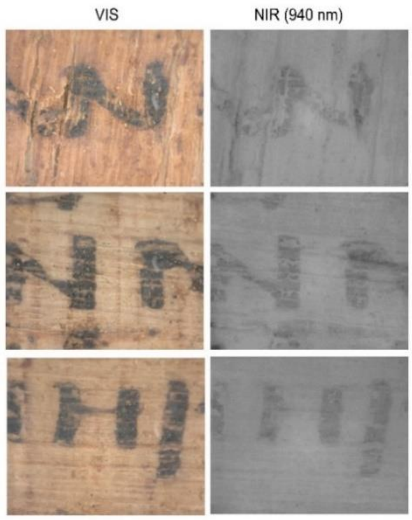

Figure 16 Visible and near-infrared micrographs (DinoLite, 50×) of three inked areas on Berlin, Staatsbibliothek, Ms.or.fol. *3065.*

Dublin, Chester Beatty Library, Cpt. *2018.2, 2020 and 2026*

Near-infrared reflectography on these three codices preserved at the Chester Beatty Library revealed that they were penned with different types of ink. Figure 17 shows the results obtained from the codices *Cpt*. 2018.2 and 2026. No change in opacity is observed between the visible and near-infrared micrographs, showing that these manuscripts were penned with a carbon-based ink. Unfortunately, XRF could not be applied to the study of these manuscripts, and it was therefore not possible to verify the presence of any element that might indicate whether the carbon was mixed with any metallic ingredients.

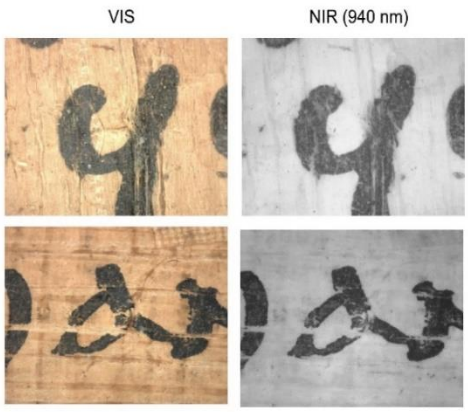

Figure 17 Visible and near-infrared micrographs (DinoLite, 50×) of Dublin, Chester Beatty Library, Cpt. *2018 (top) and 2026 (bottom).*

The manuscript Dublin, Chester Beatty Library, *Cpt.* 2020 is preserved in a cardboard box, and attached to the original binding. For this reason, it was not possible to handle the leaf at all. Both NIRR and XRF analyses were carried out on this document. While, as usual, the XRF analysis was conducted on inked and non-inked areas, it was regrettably not possible to verify if any trace of ink was present on the corresponding areas of the other side of the leaf. Consequently, the qualitative elemental results obtained on this codicological unit need to be considered very cautiously. The significant change in opacity under near-infrared light reveals that the manuscript was penned using an iron-gall ink (Figure 18). This result seems to find confirmation in the comparison of the XRF spectra which shows that the intensity of the Kα line of iron at 6.4 keV is higher in the ink than in the support. Furthermore, the peak at 8.0 keV seems to additionally indicate that the ink contains copper.

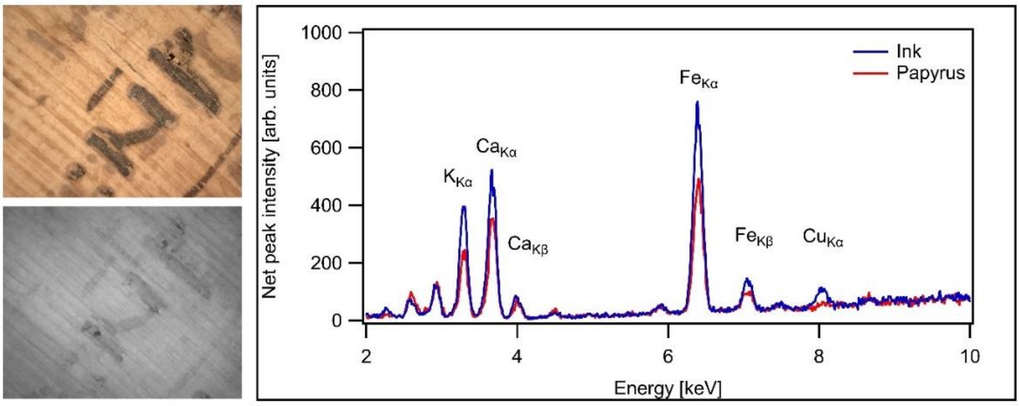

Figure 18 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (Elio spectrometer) on Dublin, Chester Beatty Library, Cpt. *2020.*

Dublin, Chester Beatty Library, Pma *B*

The manuscript Dublin, Chester Beatty Library, *Pma* B unfortunately displays a terrible state of conservation. The fibres of the papyrus are partly detached and extremely fragile over the entire surface of the leaf, and what is left of the text is barely visible, as can be seen in Figure 19. Because of this, it was not possible to apply near-infrared reflectography and the overall quality of the results that archaeometric analysis could achieve was rather poor.

Figure 19 Dublin, Chester Beatty Library, Pma *B. © The Trustees of the Chester Beatty Library, Dublin.*

Figure 20 shows the raw net peak intensity values for different elements on this leaf. Data from a total of twelve spots were collected: six on areas where the ink was not visible, and six in areas where the ink was visible. Due to the poor conservation state of the manuscript, it was not possible to establish with certainty whether areas where the ink was not visible did indeed give data that correspond solely to the support. However, Figure 20 shows that the content of iron is systematically higher in the areas where the ink is visible, which would be typical for iron-gall ink. Unfortunately, the quality of the data is not good enough to unequivocally assess whether copper, zinc or both these elements are also contained in the ink.

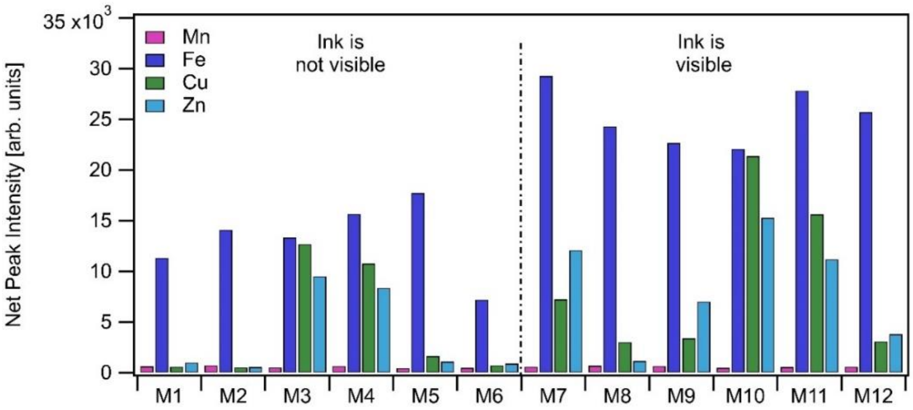

Figure 20 XRF raw net peak intensity values of different elements collected on six inked and six non-inked areas using the Elio spectrometer on Dublin, Chester Beatty Library, Pma *B*[179].

Berlin, Ägyptisches Museum, P. *8502*

The near-infrared reflectography performed on Glass 139–140 (corresponding to a single bifolium) of the *Papyrus Berolinensis Gnosticus* 8502 shows no change in opacity in the near-infrared region, revealing that the manuscript was penned using carbon-based ink (Figure 21). Unfortunately, due to conservation issues it was not possible to perform XRF on this codicological unit. The visual examination of these leaves revealed an interesting distribution pattern in the abrasion of the ink. One of the leaves in the bifolium shows a severe loss of pigment both on the recto and on the verso, as if one half of the quire had been handled more than the other or exposed to aggressive deterioration agents.

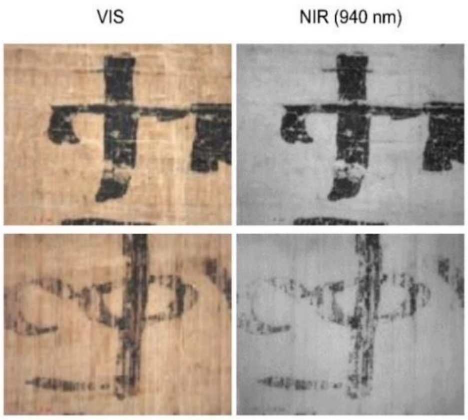

Figure 21 Visible and near-infrared micrographs (DinoLite, 50×) of two inked areas on Berlin, Ägyptisches Museum, P. *8502.*

179 The graph does not show the error bars relative to the experimental error. This is generally set at 10%, but the heterogeneity of the papyrus surface introduces an additional error that is hard to determine due to the different thickness and morphology of the leaves.

Discussion

The majority of manuscripts presented in this section were written using iron-gall ink[180] (six of the nine manuscripts: Rome, Biblioteca Apostolica Vaticana, *Pap.copt*. 9; Montserrat, Roca Puig, Codex Miscellaneus and Inv. 14 (roll of Athanasius); Berlin, Staatsbibliothek, *Ms.or.fol*. 3065; Dublin, Chester Beatty Library, *Cpt*. 2020 and *Pma* B). In fact, this was the case for most of the literary manuscripts examined in the framework of this research project (see the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use")[181].

Excluding Dublin, Chester Beatty Library, *Pma* B, whose state of conservation was too poor to achieve unequivocal elemental results, XRF analysis on all the manuscripts for which it was done revealed that the metallic salts used to manufacture the inks contained iron and copper, while zinc (which is often attested in European iron-gall inks[182]) was never detected.

Although the heterogeneity of the supports precluded the calculation of precise semi-quantitative data, the XRF results suggest that the ratio of copper to iron found in these inks was fairly high. This analytical result may reflect the information reported in extant sources: as Rabin has pointed out in one of her works, the understanding of the chemical properties of iron and copper sulphates was in Antiquity rather confused[183]. Pliny, for example, seems to be unaware of the fact that iron, and only iron, forms a black complex when mixed with gallnut extract[184] (for further discussion see § 2.2.1).

However, it should not be forgotten that when analysing ancient codices whose state of preservation has been affected by the passing of time, archaeometric observations can be affected by deterioration processes. In the specific case of the inks presented in this section, a closer look at the visible and near-infrared micrographs of Figure 13 and Figure 14, for instance, reveals a lacuna on the extreme right of the image in the first case, and a rather disintegrated ink surface in the second. This is the result of flaking and abrasion processes that have affected the ink slightly differently in one or another area. The heterogeneity of the papyrus surface, which is characterised by fibres of different shapes and dimensions, probably fostered this deterioration pattern. The partial loss of a superficial layer of iron-gallate pigment might result in enhanced amount of copper being measured. In fact, a previous study proved that zinc ions (often found as satellite ions in iron-gall inks, together with copper) are more mobile than iron ions and tend to migrate towards the borders of the trace of ink[185]. Similarly, copper might migrate deeper towards the support, while iron remains on the surface of the trace of ink and it is more prone to be affected by abrasion. To avoid falsification of semi-quantitative results due to deterioration, one should conduct a considerable number of measurements while monitoring the ratio of copper to iron: a varying ratio would point

[180] Although in the case of Rome, Biblioteca Apostolica Vaticana, *Pap.copt.* 9 and Montserrat, Roca Puig, Codex Miscellaneus it cannot be excluded that the ink contained some carbon as well.
[181] Ghigo, Rabin, and Buzi 2020
[182] Hahn et al. 2004; Aceto et al. 2017; Geissbühler et al. 2018
[183] Rabin 2017
[184] Pliny. *Naturalis Historia*, 34.32
[185] Kanngießer et al. 2004

towards the influence of deterioration processes. Because time restrictions allowed to perform a limited number of measurements, it was not possible to gain insight on this matter.

In contrast to the six manuscripts written with iron-gall ink, in three cases (Dublin, Chester Beatty Library, *Cpt*. 2018 and 2026; Berlin, Ägyptisches Museum, *P*. 8502) the ink used to pen the text of these literary manuscripts is carbon-based. As they seem to represent a minority, these cases are worthy of further discussion[186]. Since information regarding the place of production of many of the early Christian papyri in this study is missing or uncertain, one could imagine that iron-gall ink was predominantly used to write literary texts in some areas, while the situation was different in others. On the other hand, if these codices came from an area where the use of iron-gall ink in literary texts was already attested at the end of the 4th century (and Table 3 indicates that this is the case, for instance, for the area around Panopolis), they could represent evidence of a period of transition in which iron-gall ink was starting to be substituted for carbon ink. The fact that at present no analytical evidence of iron-gall ink has been found in Egypt prior to the 4th century would seem to provide additional support for this hypothesis. In this reconstructed scenario, the existence of literary texts written with a mixed ink containing both carbon and iron-gall ink seems plausible, and the Montserrat, Roca Puig, Codex Miscellaneus and Rome, Biblioteca Apostolica Vaticana, *Pap.copt.* 9 might represent this situation.

4.2.4 The library of the Monastery of Apa Jeremiah[187]

Corpus

At the Chester Beatty Library, four different folios from three literary parchment codices written in Sahidic Coptic and produced in the Monastery of Apa Jeremiah were examined. All the leaves show a simple layout where the main text is distributed in one single column. In addition, the margins are decorated with figures of animals, crosses and other geometrical patterns. No coloured pigments were used for the decoration, which was drawn using what was probably black ink, although it now appears rather brownish. Figure 22 shows, as an example, leaf 99r from codex *Cpt*. 814.

[186] On the use of iron-gall inks in literary texts from this period, see Ghigo, Rabin, and Buzi 2020, reproduced here in the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use"

[187] Warm thanks are due to Olivier Bonnerot for performing the analysis on these parchment codices

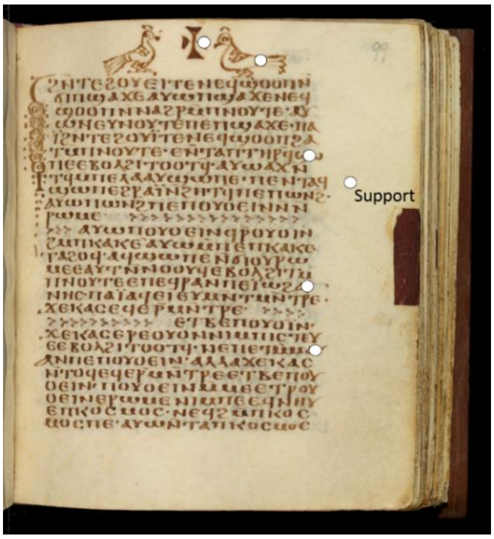

Figure 22 Dublin, Chester Beatty Library, Cpt. *814, f. 99r. The white dots indicate the areas of the decoration, main text and support chosen for analysis. © The Trustees of the Chester Beatty Library, Dublin.*

As well as the decoration in the margins of the single leaves, codex *Cpt*. 814 presents a so-called "edge of the book decoration", visible when the codex is closed. In addition, the long edge opposite the spine and the two short edges were dyed with a yellowish pigment. This practice is documented in European manuscripts from as far back as the 4th century[188], and its purpose may vary from purely aesthetic to providing protection against pests and micro-organisms.

Table 4 describes the leaves examined in this study, and the analytical techniques applied.

Table 4. Description of the leaves from the library of the Monastery of Apa Jeremiah in the corpus, and the analytical techniques applied.

Shelfmark	**CLM**	**Folio**	**Ink spots**	**Support spots**	**Methods***
Cpt. 813	64	3r		1	NIRR, XRF
		Main text	3		
		Decoration	2		
Cpt. 814	65	99r		2	NIRR, XRF
		Main text	3		
		Decoration	2		
		Edge of the book	1		
Cpt. 815	66	58r		1	NIRR, XRF
		Main text	4		
		Page number	1		

* The XRF equipment used for this analysis was the Elio (Bruker Nano GmbH, formerly XG Lab)

188 Hulan and Townes 2008

Results and discussion

Near-infrared reflectography showed that the main text and the decorations on the margins of all examined leaves were traced using iron-gall ink: Figure 23 shows the comparison between visible and near-infrared micrographs, revealing a considerable change in opacity, which is characteristic of this type of ink. In addition, the visible image reveals that the surface of the three codices is of a rather different colour: whitish for *Cpt*. 813 and yellowish for *Cpt*. 814 and 815. The surface of these parchment leaves was cleaned so well that is difficult to visually establish which side corresponds to the flesh and which to the hair. The flesh side is generally whiter and smoother, which causes the ink to lose adhesion in time. This could be the case for *Cpt*. 813, f. 3r: the visible image does show that the ink has flaked away in some areas.

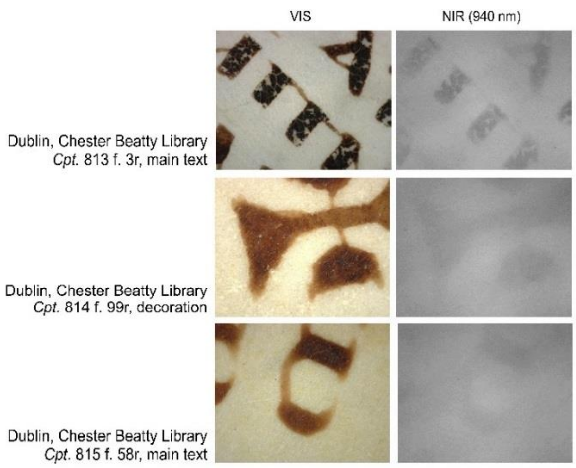

Figure 23 Visible and near-infrared micrographs (DinoLite, 50×) of the codices Dublin, Chester Beatty Library, Cpt. *813, 814 and 815.*

XRF measurements performed on inked and non-inked areas on *Cpt*. 813, f. 3r all revealed that it contains a considerable amount of lead, which is absent from *Cpt*. 814, f. 99r and *Cpt*. 815, f. 58r. Figure 24 shows the XRF intensities of calcium, lead, iron and copper measured on the support (**S**), two spots of decoration (d_1 and d_2) and three spots of text (t_1, t_2 and t_3) on *Cpt*. 813, f. 3r. The intensity of iron and copper is systematically higher in the inked areas than in the support, indicating that these elements are associated with the ink. However, this is not the case for calcium and lead, which are associated with the support. A Coptic recipe reported in a papyrus from the 6th or 7th century CE (contemporaneous with the date proposed for the codices from Apa Jeremiah on the basis of some coins found together with the manuscripts[189]) describes how the parchment surface is prepared with white lead and alum powder before it is used[190]. Although no aluminium was found on *Cpt*. 813, f. 3r, it is possible that white lead was used in this case to prepare the surface, and further analytical measurements on a higher number of leaves are needed to confirm this possibility.

[189] Thompson 1932, ix–x

[190] Crum 1905, 166–71. Warm thanks to Prof. Tonio Sebastian Richter for providing a meaningful insight into the terminology used in this recipe to describe the tools of the scribe and the chemical compounds

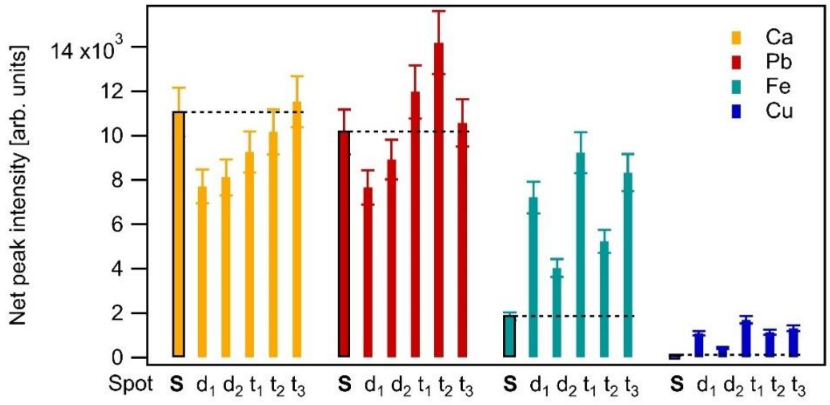

*Figure 24 XRF raw net peak intensities values of Ca, Pb, Fe and Cu collected on the parchment support (**S**), on the decoration (d_1 and d_2) and on the text (t_1, t_2 and t_3) of Dublin, Chester Beatty Library,* Cpt. *813, f. 3r. The horizontal dashed line marks the value of each element in the support. The analysis was performed using the Elio spectrometer.*

Figure 25 shows the fingerprints of the iron-gall inks found on the main text of the three codices and on the supralinear stroke of *Cpt.* 813, the decorations of *Cpt.* 813 and 814 and the page number of *Cpt.* 815. The bars show the median ratio of the intensity of manganese, copper and zinc to that of iron, while the error bars show the minimum and maximum ratio of each element.

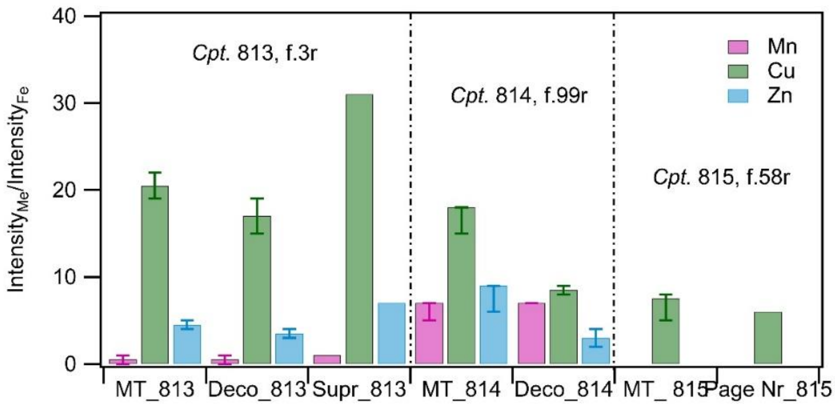

Figure 25 Fingerprint of the vitriolic components on main texts (MT), decorations (Deco), supralinear stroke (Supr) and page number (Page Nr) on Dublin, Chester Beatty Library, Cpt. *813, 814 and 815. The XRF analysis was performed using the Elio spectrometer.*

The comparison reveals that the three leaves were written using iron-gall inks containing different satellite elements. The ink on *Cpt*. 813, f. 3r contains copper and zinc, the ink on *Cpt*. 814, f. 99r is the only case in which a considerable amount of manganese is present in addition to copper and zinc, while the ink on *Cpt*. 815, f. 58r contains only copper. Furthermore, the comparison of the fingerprints of the inks used on *Cpt*. 813, f. 3r shows a different ratio of satellite elements to iron for the main text and the supralinear stroke. Similarly, two different fingerprints were highlighted for the main text and decoration on *Cpt*. 814, f. 99r. This indicates the use of different batches of ink, entailing that different writing phases were involved.

According to Thompson, the homogeneous script and format of these codices indicate that they were produced in a single scriptorium probably located inside the monastery itself. In addition, each codex was written, from beginning to end, by a different scribe[191]. Since only a few measurements were conducted on a single leaf from each codex, it is impossible to determine whether there is a correlation between the elemental composition of the ink and the scribe. However, it must be stressed that, apart from the codicological observations made by Thompson, there is no further evidence of the existence of an organised scriptorium inside the Monastery of Apa Jeremiah. For this reason, one should consider the possibility that the codices were written in different places by different scribes, which would more likely explain the use of different inks. If the hypothesis of white lead being used on codex *Cpt*. 813 was confirmed (and discarded for *Cpt* 814 and 815), this would be additional support for the suggestion that the codices were produced in different workshops, since it is unlikely that a single scriptorium would treat the surface of the codices produced in it in different ways.

In addition to producing data on the iron-gall inks, XRF analysis provided an insight into the elemental composition of the pigment used to dye the edge of the book holding codex *Cpt*. 814. The spectrum presented in Figure 26 shows that the pigment contains both sulphur (shown in the inset graph) and arsenic (main graph), suggesting that it may correspond to orpiment (As_2S_3) or realgar (As_4S_4), whose use in Egypt is documented from the Pharaonic period[192]. Arsenic-based yellow pigments, especially orpiment, were often used to substitute gold.

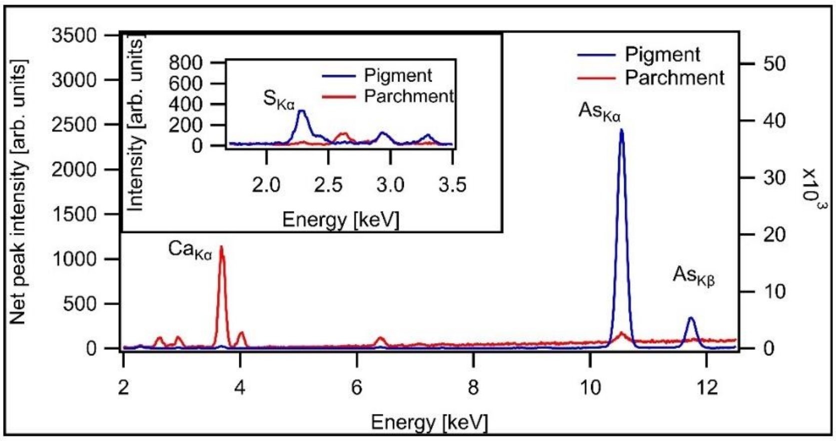

Figure 26 XRF spectra (Elio spectrometer) of parchment (scale on the left) and a coloured area (scale on the right) on the edge of the book holding Dublin, Chester Beatty Library, Cpt. *814, f. 3r. The inset shows the details for sulphur; the main graph the details for arsenic.*

4.2.5 The library of the cathedral church of Thi(ni)s

Corpus

At the Museo Egizio in Turin six different papyrus leaves were examined, belonging to four literary codices written in Sahidic Coptic and produced in Thi(ni)s. All the leaves showed a very simple layout where the main text had been written solely using black ink.

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[191] Thompson 1932, ix–x

[192] L. Lee and Quirke 2000; Daniels and Leach 2004; Di Stefano and Fuchs 2011

Turin, Museo Egizio, Codex II, Glass 18 had been treated with a transparent substance looking like gelatine; the use of gelatine films in the conservation of papyri is documented in 20th-century interventions[193]. This substance did not contain any metallic elements, and therefore it did not interact with XRF measurements. This same leaf displayed an intervention where a piece of different papyrus had been glued to the original support and overwritten. Table 5 describes the leaves which were analysed and the analytical techniques applied. All the analyses were carried out *in situ* with portable equipment.

Table 5. Description of the leaves from the library of the cathedral church of Thi(ni)s in the corpus, and the analytical techniques applied.

Shelfmark	CLM	Folio	Methods*	No. spots ink + supp.
Codex II	46	Glass 18	NIRR, XRF, FTIR	7 + 2
Codex IX	54	Glass 11	NIRR, XRF	2 + 1
		Provv. 8591		5 + 2
		Provv. 8592		5 + 2
Codex XIII	58	Glass 23	NIRR, XRF, Raman	6 + 2
Codex XV	60	Glass 1	NIRR, XRF	5 + 2

* The XRF equipment used for this analysis was the ArtTAX (Bruker Nano GmbH)

Results and discussion

The results obtained on the manuscripts from Thi(ni)s are partly discussed in an earlier publication (see the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use")[194]. Near-infrared reflectography showed that all the samples examined were written with iron-gall inks. Figure 27 shows the substantial change in opacity between the visible and near-infrared images, typical for this type of ink.

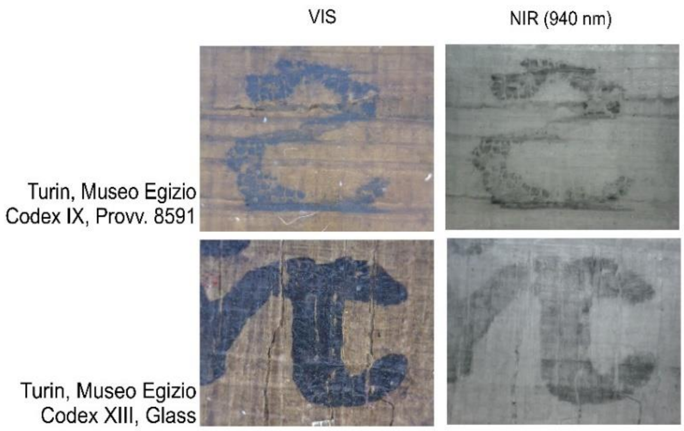

Figure 27 Visible and near-infrared micrographs (DinoLite, 50×) of an inked area on Turin, Museo Egizio, Codex IX, Provv. 8591 (top) and Codex XIII (bottom).

[193] Leach 2006
[194] Ghigo, Rabin, and Buzi 2020

This was a surprising result considering that the ink appears rather well preserved and does not display any trace of the corrosion which is often typical of iron-gall inks. In addition, the ink here possesses a brilliant black hue in visible light, and that is generally the case for carbon inks. Because of this, despite the significant change in opacity clearly indicating the iron-gallic nature of these inks, portable Raman spectroscopy (B&W Tek) was applied to gain further insights into their molecular structure. Unfortunately, this analysis gave no significant results due to the high fluorescence of the ink. Equally, DRIFTS analysis on Codex II, Glass 18 did not lead to any conclusions about the molecular structure of the gelatine.

Performing XRF on these codices was a rather challenging task. Because of the advanced state of degradation of the leaves, it was very difficult to choose the spots for analysis, since the black ink was barely visible due to the darkening of the support. Moreover, most of the ink was partially scraped off, making it difficult to get a good XRF signal and complicating the process of data treatment. In addition, the papyrus leaves were rather thick, and it was thus impossible to see through the folio and pick an inked area corresponding to a blank surface on the other side: it was necessary to copy the text of the manuscript on tracing paper, and then to overlap the two sides to find a suitable spot of ink and proceed to analysis.

The XRF analysis on the writing surface revealed a rather heterogeneous distribution of elements, as is normal for papyrus. This was particularly evident in the case of iron. Figure 28 shows the case of three line-scans of ten points each collected on different leaves of the same codex. They are respectively 2.16 mm, 1.98 mm and 1.71 mm long for Glass 11, Provv. 8591 and Provv. 8592. Despite the reduced length of the line-scan, the net peak intensity of iron varies significantly.

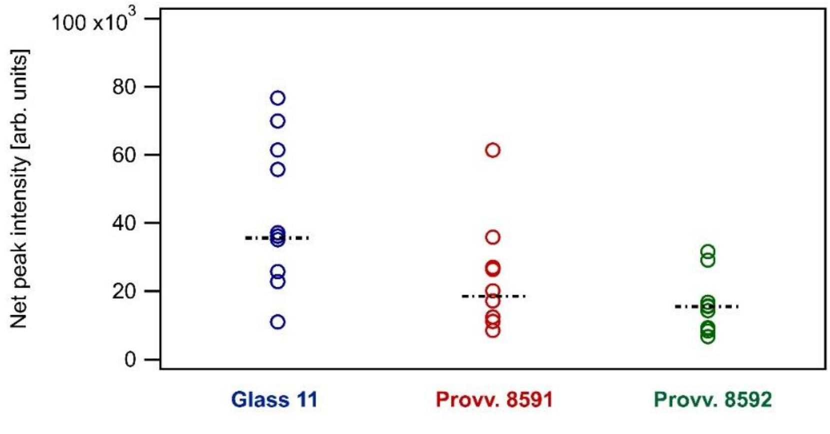

Figure 28 Individual values plot for Fe on Turin, Museo Egizio, Codex IX. Each dot represents the value of net peak intensity for each point in a line-scan of around 2 mm in length. The XRF measurement was performed using the ArtTAX spectrometer on three different leaves of the codex. The horizontal dashed line represents the median value.

The qualitative results obtained on the inks from these four codices revealed a rather simple elemental composition characterised mainly by the presence of iron, although lesser amounts of potassium and manganese were also detected. Figure 29 shows the case of an inked area on Codex II, where the peak at 6.4 keV corresponding to the Kα line of iron is much more intense in the inked area than in the support.

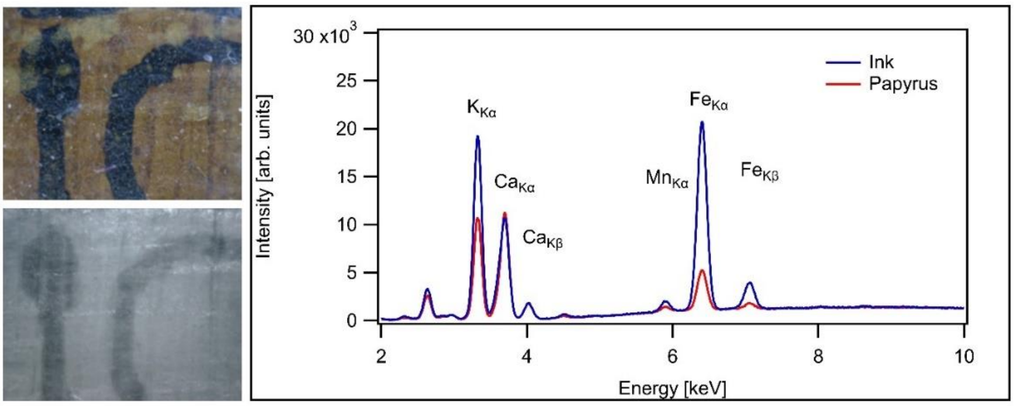

Figure 29 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (ArtTAX spectrometer) on Turin, Museo Egizio, Codex II, Glass 18.

The top right of the recto of Codex II, Glass 18 presents a "restoration" intervention, or perhaps just a correction, made by pasting a new piece of papyrus either over a *lacuna* or over some text that was to be corrected[195]. Figure 30 shows that the text on top of the pasted patch of papyrus was penned with an ink whose elemental composition is very similar to the one detected on all the other analysed spots, containing mainly iron. The difference observed in the amount of potassium and calcium cannot be considered as discriminant of a different type of ink, given that these elements are easily affected by matrix effects and variations in the amount detected can result from the uneven thickness of the trace of ink or of the papyrus. The fact that there is no substantial difference in the elemental composition of the ink used for the main text and for the patched piece of papyrus suggests that the latter may have been the result of a correction realised during the original production of the codex, rather than being a later intervention of restoration.

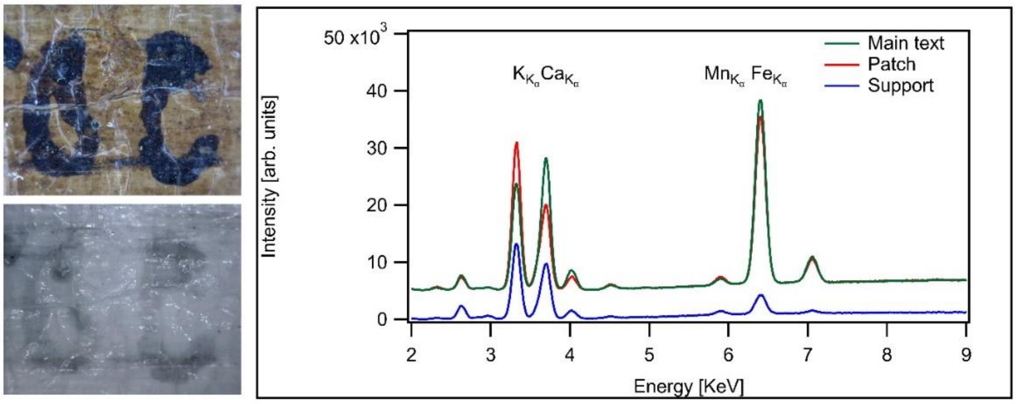

Figure 30 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (ArtTAX spectrometer) on Turin, Museo Egizio, Codex II, Glass 18. The spectrum of the support is in blue, the spectrum of the text written on a piece of patched papyrus is in red, and the spectrum of the text written on the rest of the leaf is in green.

To conclude, the leaves from the library of Thi(ni)s were all written using an ink whose elemental composition lacks the satellite elements – namely, copper and zinc – that are often attested by scientific analysis of inks based on vitriol[196]. As discussed in the article reproduced

[195] Buzi 2018b
[196] See, for instance, Hahn et al. 2004; Geissbühler et al. 2018; Aceto et al. 2017

in the appendix of this dissertation ("Black Egyptian inks in Late Antiquity: New insights on their manufacture and use", pp. 6–7), this could indicate the use of metallic iron rather than vitriol in the preparation of this ink[197]. Since only a few leaves from a reduced number of codices could be investigated, it is rather premature to claim that the scriptorium in Thi(ni)s systematically used the same type of ink to produce literary manuscripts. This hypothesis would seem to be compelling, since palaeographical and codicological studies have assessed that the codices were written over a limited span of time by a limited number of copyists[198], but further analysis is needed to confirm it.

4.2.6 Documents from the Monastery of Apa Apollo in Bawit

The intensive investigation of Coptic documentary papyri from Bawit started after evidence was found on a papyrus fragment from the Palau Ribes collection of an ink which contained copper. Figure 31 shows the results of the typological and elemental analysis on a spot of ink from Barcelona, Palau Ribes, Inv. 451. The line-scan acquired at the interface between non-inked and inked areas shows that copper is contained in the ink, while no trace of iron was found in the ink. This excludes the possibility that iron-gall ink was used to pen this document. The comparison between the visible and near-infrared micrographs shows a heterogeneous change in opacity: the ink appears more opaque on the top left and more transparent on the bottom right in the near-infrared region. This slight and diversified change in opacity may suggest that the ink contains some carbon, although it is difficult to draw an unequivocal conclusion. Moreover, its brownish colour under visible light, together with the fact that in some areas there is a greater change in opacity, may indicate that it contains tannins.

A similar type of ink – brownish in colour and containing copper but no iron – has been reported to have been found on some documentary texts written in Thebes during the 2nd and 3rd centuries BCE that are preserved at the Louvre[199]. The systematic investigation of documents from Bawit initially began in an attempt to find further evidence of this type of ink.

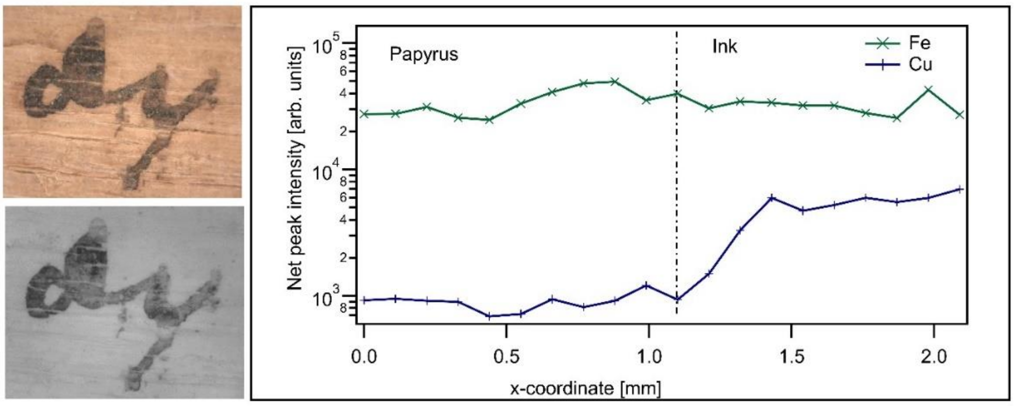

Figure 31 Near-infrared reflectography (DinoLite, 50×) and elemental intensity profiles of Fe and Cu (ArtTAX spectrometer) at the interface between inked and non-inked areas on Barcelona, Palau Ribes, Inv. 451.

[197] Ghigo, Rabin, and Buzi 2020
[198] Buzi et al. 2017
[199] Delange et al. 1990

Corpus

The investigation focused on Coptic documents written on papyrus and ostraca. Not all have yet been edited and published, and therefore in some cases we have limited information about their exact content. However, according to María Jesús Albarrán, the scholar currently studying these manuscripts, they all carry documentary texts and can be dated to the 7th or 8th century CE during the period of prosperity of the Monastery of Apa Apollo in Bawit[200]. The documents are nowadays preserved in two different institutions. In the Palau Ribes collection, the papyri are preserved in folders made of blotting paper, while at the Abbey of Montserrat they are kept between glass. All of them are of relatively small dimensions and present a very simple layout, and only black ink was used to write the text. Table 6 provides details of the specific manuscripts that were analysed; the information on the type of document has been extracted from the bibliography listed at the end of the table.

Table 6 Description of the papyri from the Monastery of Apa Apollo that have been analysed.

Shelfmark	Collection	Editor	Type of document
Inv. 39	Palau Ribes	M. J. Albarrán Martínez[a]	Agreement for loan of money
Inv. 40	Palau Ribes	A. Delattre[b]	Order payment for wine and fish
Inv. 41	Palau Ribes	S. J. Clackson[c]	Payment of oil
Inv. 352	Palau Ribes	M. J. Albarrán Martínez[d]	Payment of wine
Inv. 354	Palau Ribes	M. J. Albarrán Martínez, A. Delattre[e]	Loan of money
Inv. 367	Palau Ribes	J. V. Stolk[f]	Contract with witnesses
Inv. 371	Palau Ribes	R. Dekker[g]	Order for collection of taxes
Inv. 390	Palau Ribes	J. Delhez[h]	Accounts (twelve people beneficiaries of payment)
Inv. 409	Palau Ribes	A. Boles[i]	Order to open the gate
Inv. 438r	Palau Ribes	F. Gerardin[j]	Contract
Inv. 438v	Palau Ribes	F. Gerardin[j]	Accounts
Inv. 443	Palau Ribes	J. V. Stolk[k]	Contract with witnesses
O.Inv. 25	Palau Ribes	M. J. Albarrán Martínez[l]	Order to supply clover
O.Inv. 26	Palau Ribes	M. J. Albarrán Martínez[l]	Order to supply wheat
Inv. 37	Palau Ribes	-	-
Inv. 87	Palau Ribes	-	-
Inv. 357	Palau Ribes	-	-
Inv. 360	Palau Ribes	-	-
Inv. 376v	Palau Ribes	-	-
Inv. 384r	Palau Ribes	-	-
Inv. 392	Palau Ribes	-	-
Inv. 393	Palau Ribes	-	-
Inv. 399	Palau Ribes	-	-

[200] Personal communication with María Jesús Albarrán, July 2019

Shelfmark	Collection	Editor	Type of document
Inv. 401	Palau Ribes	-	-
Inv. 402	Palau Ribes	-	-
Inv. 404	Palau Ribes	-	-
Inv. 406r	Palau Ribes	-	-
Inv. 411	Palau Ribes	-	-
Inv. 433v	Palau Ribes	-	-
Inv. 434	Palau Ribes	-	-
Inv. 439	Palau Ribes	-	-
Inv. 454	Palau Ribes	-	-
Inv. 460	Palau Ribes	-	-
Inv. 227	Roca Puig	-	-
Inv. 345	Roca Puig	-	-
Inv. 521	Roca Puig	-	-
Inv. 557	Roca Puig	-	-
Inv. 570	Roca Puig	-	-
Inv. 636	Roca Puig	-	-
Inv. 670	Roca Puig	-	-
Inv. 715	Roca Puig	-	-

[a] Albarrán Martínez, María Jesús. 2017. "Rééditions. P. PalauRib.Copt 25–29." In *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:121–126

[b] Delattre, Alain. 2017. *Papyrus Coptes et Grecs du Monastère d'Apa Apollô de Baouît Conservés aux Musées Royaux d'Art et d'Histoire de Bruxelles*. Brussels: Académie Royale de Belgique, p. 219

[c] Clackson, Sarah J. 2008. *It Is Our Father Who Writes: Orders from the Monastery of Apollo at Bawit*. American Studies in Papyrology 43. Cincinnati: American Society of Papirology, pp. 90–91

[d] Albarrán Martínez, María Jesús. 2012. "A New Coptic Text from Bawit: P.PalauRib. Inv. 352." In *Actes du 26e Congrès International de Papyrologie, Genève 2010*, edited by Paul Schubert. Geneva: Droz, pp. 7–10

[e] Albarrán Martínez, María Jesús, and Alain Delattre. 2015. "Un Nouveau Contrat de Prêt Copte du Monastère d'Apa Apollô à Baouît." *Bulletin of the American Society of Papyrologists* 52:79–85

[f] Stolk, Joanne Vera. 2017. "7. Subscriptions to a Renunciation Contract." In *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:53–56

[g] Dekker, Renate. 2017. "16. A List of Officials." In *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:88–90

[h] Delhez, Julien. 2017. "12. Compte." In *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:75–79

[i] Boles, Ambrose. 2017. "Order to Open the Gate." In *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:101–102

[j] Gerardin, François. 2017. "9. Contrat de Cession d'un Travailleur pour le Chantier de Fustāt" and "13. Compte." In *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:64–64 and 80–81

[k] Stolk, Joanne Vera. 2017. "8. Subscriptions to a Lease Contract." In *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:57–60

[l] Albarrán Martínez, María Jesús. 2012. "The Coptic Ostraca of the Palau-Ribes Collection: New Perspectives and Edition." In *Coptic Society, Literature and Religion from Late Antiquity to Modern Times: Proceedings of the Tenth International Congress of Coptic Studies, Rome*, 2 edited by Paola Buzi, Alberto Camplani and Federico Contardi. Leuven: Peeters, pp. 1311–13

Results and discussion

Near-infrared reflectography showed that almost all the manuscripts from the Monastery of Apa Apollo that were analysed contain carbon. Only in three cases were there difficulties in interpretation and the presence of this material could not be unequivocally determined (Palau Ribes, Inv. 357, 399 and 401). In some cases, the examination of the papyri in visible light at a magnification of 50× revealed brownish halos around the letters indicating the presence of tannins. Figure 32 shows the results of the reflectographic analysis of two different documents. In the first (Palau Ribes, Inv. 39), no brownish halo is visible around the letter in visible light, and the ink maintains its opacity in the near-infrared region, indicating the presence of carbon. In the second case (Roca Puig, Inv. 227), a brownish halo is present around the letter under visible light and it disappears in the near-infrared region. This indicates the diffusion of tannins in the support. Furthermore, the ink maintains its opacity in the near-infrared region, revealing the presence of carbon.

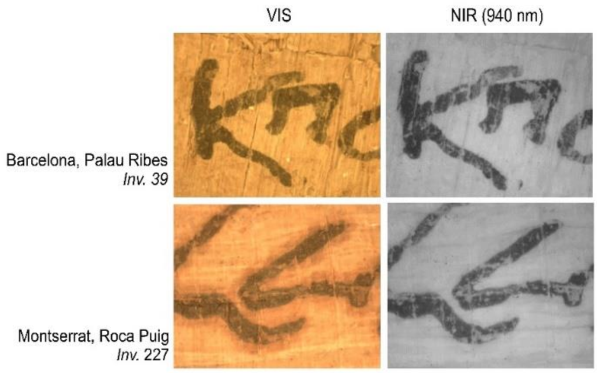

Figure 32 Visible and near -infrared micrographs (DinoLite, 50×) on Barcelona, Palau Ribes, Inv. 39 and Montserrat, Roca Puig, Inv. 227.

In addition, XRF analysis, performed on a limited number of documents, detected in some cases the presence of metallic elements. Iron was sometimes associated with carbon inks, while iron, copper and, in some cases, lead were found in substantial amounts in those inks that show the brownish halo around the letters. Table 7 presents the analytical techniques applied to each manuscript and the results obtained.

Table 7 Analytical techniques applied to the manuscripts from the Monastery of Apa Apollo, and the results obtained.

Shelfmark	Collection	Methods*	No. spots ink + supp.	Results
Inv. 39	Palau Ribes collection	NIRR, XRF	2 + 2	Carbon ink + Fe
Inv. 40	Palau Ribes collection	NIRR, XRF	2 + 2	Carbon ink + Fe
Inv. 41	Palau Ribes collection	NIRR	1	Carbon-based ink
Inv. 352	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 354	Palau Ribes collection	NIRR, XRF	3 + 3	Carbon ink + Fe
Inv. 367	Palau Ribes collection	NIRR, XRF	3 + 3	Carbon ink
Inv. 371	Palau Ribes collection	NIRR, XRF	5 + 5	Mixed ink
Inv. 390	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 409	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 438r/v	Palau Ribes collection	NIRR	2	Carbon-based ink

Shelfmark	Collection	Methods*	No. spots ink + supp.	Results
Inv. 443	Palau Ribes collection	NIRR	2	Carbon-based ink
O.Inv. 25	Palau Ribes collection	NIRR	1	Carbon-based ink
O.Inv. 26	Palau Ribes collection	NIRR	1	Carbon-based ink
Inv. 37	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 87	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 357	Palau Ribes collection	NIRR, XRF	4 + 4	Mixed ink(?)
Inv. 360	Palau Ribes collection	NIRR	1	Carbon-based ink
Inv. 376v	Palau Ribes collection	NIRR, XRF	3 + 3	Carbon ink
Inv. 384r	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 392	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 393	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 399	Palau Ribes collection	NIRR, XRF	3 + 3	Mixed ink(?)
Inv. 401	Palau Ribes collection	NIRR, XRF	3 + 3	Mixed ink(?)
Inv. 402	Palau Ribes collection	NIRR, XRF	3 + 3	Mixed ink
Inv. 404	Palau Ribes collection	NIRR	1	Carbon-based ink
Inv. 406r	Palau Ribes collection	NIRR, XRF	2 + 1	Carbon ink
Inv. 411	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 433v	Palau Ribes collection	NIRR	1	Carbon-based ink
Inv. 434	Palau Ribes collection	NIRR	2	Carbon-based ink
Inv. 439	Palau Ribes collection	NIRR	1	Carbon-based ink
Inv. 454	Palau Ribes collection	NIRR, XRF	2 + 2	Carbon ink
Inv. 460	Palau Ribes collection	NIRR, XRF	2 + 2	Carbon ink
Inv. 715	Roca Puig collection	NIRR, XRF	3 + 3	Carbon ink
Inv. 345	Roca Puig collection	NIRR, XRF	5 + 5	Mixed ink
Inv. 570	Roca Puig collection	NIRR, XRF	3 + 3	Carbon ink
Inv. 227	Roca Puig collection	NIRR, XRF	4 + 4	Mixed ink
Inv. 636	Roca Puig collection	NIRR, XRF	3 + 3	Carbon ink + Fe
Inv. 521	Roca Puig collection	NIRR, XRF	3 + 3	Carbon ink
Inv. 557	Roca Puig collection	NIRR, XRF	2 + 2	Carbon ink + Fe
Inv. 670	Roca Puig collection	NIRR, XRF	2 + 2	Carbon ink + Fe

* The XRF equipment used for this analysis was the Elio (Bruker Nano GmbH, formerly XG Lab)

To summarise the typologies of ink found on the documents from Bawit, we can distinguish five groups:

1. Carbon-based inks. These appear black in visible light and show no change in opacity under near-infrared light (Figure 33). No signs of corrosion are present. XRF was not applied to these inks, therefore it was not possible to verify their elemental composition.

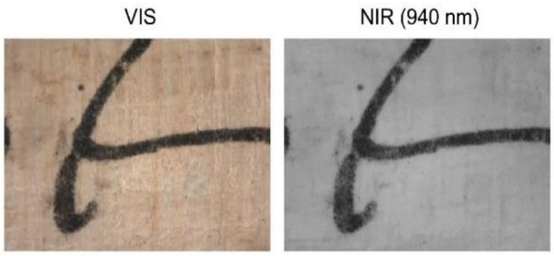

Figure 33 Visible and near-infrared micrographs (DinoLite, 50×) on Barcelona, Palau Ribes, Inv. 41.

2. Carbon inks. These are black in visible light and show no change in opacity under near-infrared light. XRF analysis did not detect the significant presence of any metallic element (Figure 34).

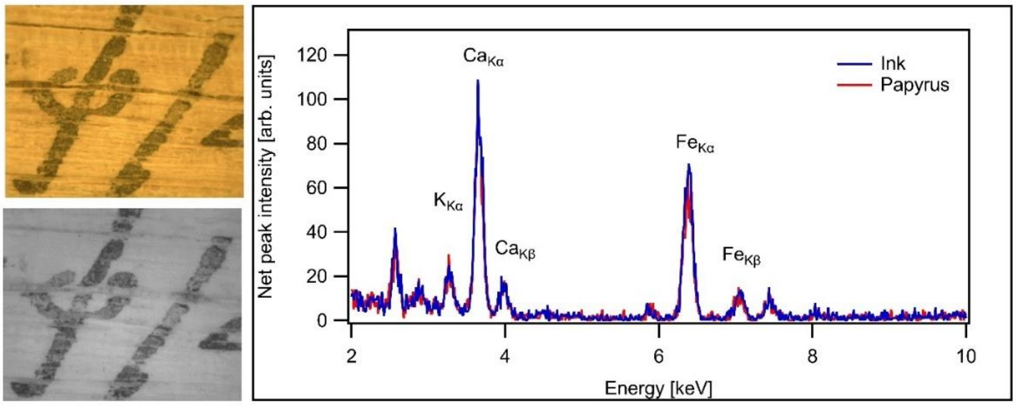

Figure 34 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (Elio spectrometer) of inked and non-inked areas on Barcelona, Palau Ribes, Inv. 376.

3. Carbon inks containing iron. They appear black in visible light and show no change in opacity if illuminated with near-infrared light. XRF analysis detected a higher intensity in the inked areas of the peak at 6.4 keV, corresponding to iron (Figure 35). The heterogeneity of the level of iron contained in the support precluded the calculation of the amount of iron present in the ink on the basis of the few analytical spots that were collected. Therefore, without further investigation, one can only speculate about the reason behind the presence of this metal. On the one hand, it is possible that carbon was mixed with iron-gall ink, although the fact that sulphur was not systematically detected in these cases nor was there a brownish halo around the letters would seem to suggest otherwise. On the other hand, it could be that the iron that was detected is the result of contamination caused by the writing tools or by metallic pots where the inks were mixed or stored.

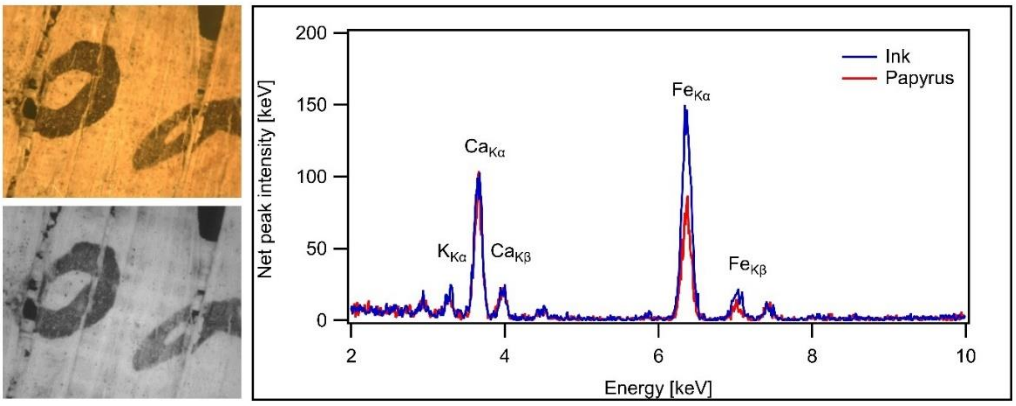

Figure 35 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (Elio spectrometer) of a spot of ink and the papyrus on Montserrat, Roca Puig, Inv. 636.

4. Mixed inks. The four fragments presenting this type of ink are of a black colour in visible light with a more or less evident brownish halo around the trace of each letter, indicating the presence of tannins. The ink showed no change in opacity when illuminated with near-infrared light, attesting the presence of carbon. Moreover, XRF detected an increase in the intensities of iron, copper and, in some cases, lead associated with the inked areas. Figure 36 shows the net peak intensities measured for iron (turquoise), copper (blue) and lead (red) on three different inked areas for each one of the four manuscripts. The grey bars represent the intensity of the elements in non-inked areas measured in proximity of each inked area; so the intensity of the element that is associated with the ink can be seen by looking at the height by which the coloured column extends beyond its associated grey column. Due to the heterogeneity of the distribution of iron in the papyrus, it is not possible to calculate the amount of iron in the ink on the basis of the few analytical spots measured, however the results provide an indication. It can be observed that only for Roca Puig, Inv. 227 is the relative intensity of copper to iron similar to what was found in the iron-gall inks examined during this investigation: the peak of copper tends to be lower than that of iron (the early Christian manuscripts presented in § 4.2.3 or the codices from Thi(ni)s presented in § 4.2.5 may serve as examples). For the other manuscripts, the relative intensities of iron to copper are very different and in two cases lead is also present. For Roca Puig, Inv. 345 the intensity of the peaks of iron associated with the ink is consistently lower than the intensity of the peaks of copper. On Palau Ribes, Inv. 402 the peak of lead is consistently higher than the peak of iron associated with the ink, while on Palau Ribes, Inv. 371 it seems roughly as high. While the presence of iron and copper can be associated with iron-gall inks, the lead probably has a different origin; in particular, carbon inks containing lead have been previously reported[201]. Since these inks show a rather complex chemical composition, a very different type of investigation is required to identify the metallic compounds and unequivocally cast light on their nature.

[201] Brun et al. 2016

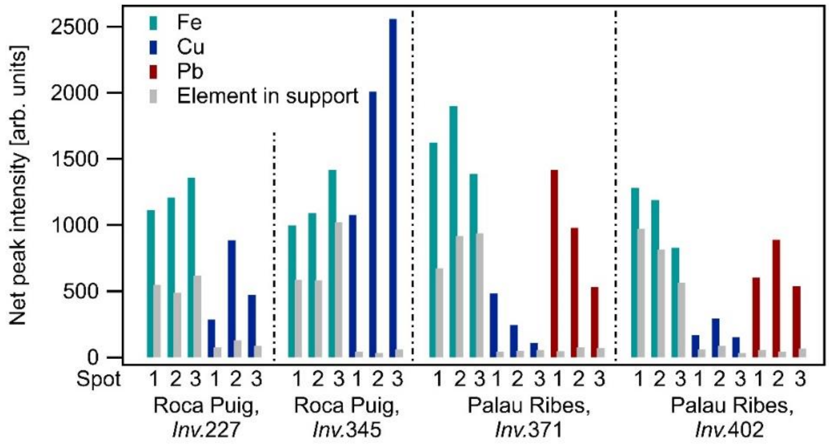

Figure 36. XRF raw net peak intensities of different elements measured on three inked and non-inked areas per manuscript (spots 1, 2 and 3). The analysis on Montserrat, Roca Puig, Inv. 227 and 345 and Barcelona, Palau Ribes, Inv. 371 and 402 was performed using the Elio spectrometer[202].

5. Mixed inks(?). In three cases the analytical results did not offer an unequivocal answer in identifying the type of ink. On one hand, XRF revealed the presence of significant amount of metals, while on the other, the results of NIRR are rather difficult to interpret. Figure 37 shows visible and near-infrared images from these documents. On Palau Ribes, Inv. 357 the colour of the ink in visible light is rather heterogeneous, appearing black or brownish for the left letter and black for the right letter. The near-infrared micrograph shows that the letter K appears darker and more substantial on the right; and lighter and more meagre on the left, corresponding to those areas where the ink appears rather brownish in visible light. However, the letter on the right maintains a certain level of opacity. This makes one wonder if it is just because of the state of conservation of the manuscript that carbon could not be clearly detected. The superficial layer of carbon pigment may have been affected from abrasion, with the small amount of carbon that has survived deterioration being insufficient to be detected using near-infrared reflectography at 940 nm. In a similar fashion, near-infrared reflectography of Palau Ribes, Inv. 399 and 401 does not provide an unequivocal answer. In these ambiguous cases, infrared reflectography performed above 1510 nm should be applied, to detect any trace of carbon.

[202] The graph does not show the error bars relative to the experimental error. This is generally set at 10%, but the heterogeneity of the papyrus surface introduces an additional error that is hard to determine due to the different thickness and morphology of the leaves

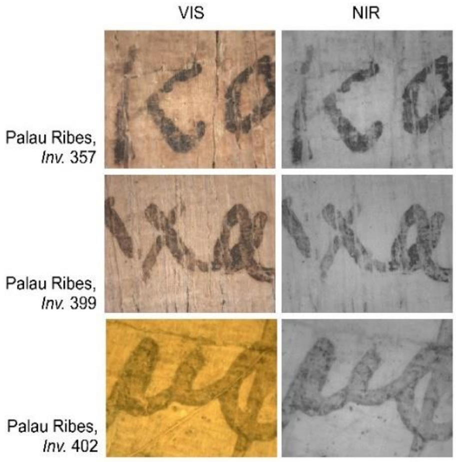

Figure 37 Visible and near-infrared micrographs (DinoLite, 50×) of three documents from the Palau Ribes collection.

On one hand, the fact that carbon cannot be clearly detected and that the brownish halo indicating the presence of tannins is not visible around the letters seem to indicate that these inks are different from the mixed inks of the previous group. On the other, because carbon may have been removed by abrasion and since inks containing tannins do not always show a brownish halo (for example, the inks of the papyrus codices from Thi(ni)s in § 4.2.5) this possibility cannot be completely ruled out. In addition, Figure 38 shows that the variety of the relative intensities of iron, copper and lead is similar to that observed for the mixed inks from the previous group.

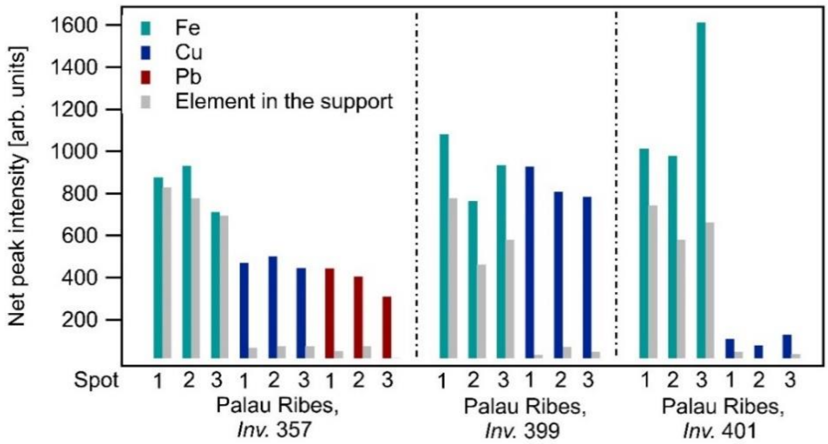

Figure 38 XRF raw net peak intensities of different elements measured on three inked and non-inked areas per manuscript (spots 1, 2 and 3). The analysis on Barcelona, Palau Ribes, Inv. 357, 399 and 401 was performed using the Elio spectrometer[203].

To conclude, the analysis carried out on the documents from Bawit showed a complex reality attesting that carbon was often mixed with other ingredients to produce ink, and that different types of writing media were in use in the monastery around the 7th and 8th centuries CE. The great variety of types of ink found is not surprising. As Delattre describes in his

[203] The graph does not show the error bars relative to the experimental error. This is generally set at 10%. However, the heterogeneity of the papyrus surface introduces an additional error that is hard to determine due to the different thickness and morphology of the leaves.

doctoral dissertation, the analysis of the numerous papyri from Bawit that have survived reveals that the Monastery of Apa Apollo was characterised by a complex and articulated administration system[204]. Therefore, it is not difficult to imagine that offices dedicated to different tasks may have used different types of ink. The scarcity of information regarding the content of the texts examined did not make it possible to observe the existence of any covariance between the type of ink and the type of document. It is to be hoped that future textual analysis will provide new insights into the nature of these documents, giving new meaning to the analytical results presented here.

4.2.7 The White Monastery library

Corpus

Literary codices on parchment written in Sahidic Coptic that formed part of the White Monastery library are nowadays spread over many different institutions within and outside Europe. The present investigation included 22 different codicological units preserved in three different institutions.

The codices of the White Monastery were investigated primarily to explore qualitative aspects of the composition of the inks. Therefore, a thorough investigation of the writing phases involved in the production of the individual codices was not performed. Table 8 reports the list of manuscripts that form part of the corpus. Note that some of the leaves present coloured decoration in tones of yellow, red and green adorning the margins and the letters.

Table 8 Description of the manuscripts from the White Monastery that were analysed, and the techniques used.

Shelfmark	CLM	Collection	No. spots ink[a] + supp.	Methods
Ms.or.fol. 1348, ff. 1–3	502	Berlin, Staatsbibliothek	12 + 7	NIRR, XRF*
Ms.or.fol 1349, f. 1	496	Berlin, Staatsbibliothek	6	NIRR
Ms.or.fol. 1350, f. 1	264	Berlin, Staatsbibliothek	5 + 4	NIRR, XRF*
Ms.or.fol. 1350, f. 3	576	Berlin, Staatsbibliothek	5 + 4	NIRR, XRF*
Ms.or.fol. 1605, f. 1	427	Berlin, Staatsbibliothek	7 + 2	NIRR, XRF*
Ms.or.fol. 1605, f. 2	430	Berlin, Staatsbibliothek	5 + 4	NIRR, XRF*
Ms.or.fol. 1605, f. 3	547	Berlin, Staatsbibliothek	8 + 3	NIRR, XRF*
Ms.or.fol. 1605, f. 6	476	Berlin, Staatsbibliothek	7 + 4	NIRR, XRF*
Ms.or.fol. 1606, f. 3	555	Berlin, Staatsbibliothek	3 + 3	NIRR, XRF*
Ms.or.fol. 1607, ff. 1–2	343	Berlin, Staatsbibliothek	9 + 6	NIRR, XRF*
Ms.or.fol. 1607, ff. 9–10	400	Berlin, Staatsbibliothek	5 + 5	NIRR, XRF*
Ms.or.fol. 1608, f. 3	375	Berlin, Staatsbibliothek	8 + 4	NIRR, XRF*
Ms.or.fol. 1609, ff. 1–2	3350	Berlin, Staatsbibliothek	9 + 6	NIRR, XRF*
Ms.or.fol. 1609, f. 3	283	Berlin, Staatsbibliothek	8 + 2	NIRR, XRF*
Ms.or.fol. 1609, f. 4	1572	Berlin, Staatsbibliothek	5 + 3	NIRR, XRF*
Ms.or.fol 1610	5608	Berlin, Staatsbibliothek	9 (ff. 1–4)	NIRR
Ms.or.fol. 1611, f. 1	1710	Berlin, Staatsbibliothek	7 + 4	NIRR, XRF*

[204] Delattre 2007, 66–72

Shelfmark	**CLM**	**Collection**	**No. spots** ink[a] + supp.	**Methods**
Ms.or.fol. 1612, ff. 1–4	278	Berlin, Staatsbibliothek	5 + 5 (ff. 1-3)	NIRR, XRF*
Ms.or.fol. 1613, f. 1	346	Berlin, Staatsbibliothek	6 + 4	NIRR, XRF*
Ms.or.fol. 1614, f. 1	325	Berlin, Staatsbibliothek	7 + 4	NIRR, XRF*
Borg.copt. 109 *Cass*. 16.57	480	Berlin, Staatsbibliothek	4 + 2 (f. 2)	NIRR, XRF**
Borg.copt. 109 *Cass*. 26.131	314	Berlin, Staatsbibliothek	7 + 6 (ff. 2–3)	NIRR, XRF**
Borg.copt. 109 *Cass*. 29.141	589	Berlin, Staatsbibliothek	5 + 1 (f. 9)	NIRR, XRF*
Borg.copt. 109 *Cass*. 29.166	538	Berlin, Staatsbibliothek	7 + 6 (ff. 1–2)	NIRR, XRF**
Or. 1699 M1–M2***	511	Berlin, Staatsbibliothek	10 + 4	NIRR, XRF**

[a] The spots collected on the ink include black ink as well as red, yellow and green pigments
* The XRF equipment used for this analysis was the ArtTAX (Bruker Nano GmbH)
** The XRF equipment used for this analysis was the Elio (Bruker Nano GmbH, formerly XG Lab)
*** Warm thanks are due to Olivier Bonnerot for performing the analysis on this codicological unit

Results ad discussion

Black inks found on the main text of the leaves

The results obtained on the black inks of the codices from the White Monastery library have been thoroughly discussed in a dedicated article (see the appendix "Gaining perspective on the materiality of manuscripts: The role of archaeometry in the study of the inks from the White Monastery codices")[205]. There, the possibility of a correlation between the composition of the iron-gall inks and the place of production of the codices was explored. In fact, we learn from the colophons that some of the codices were produced outside the monastery and donated to this institution at a later time (see § 1.2.2.2). Figure 39 aims at offering an alternative representation of the results reported in the article. The Venn diagram shows that one group of iron-gall inks contains iron, while another group contains in addition copper and sometimes a lesser amount of zinc. The four codicological units reported in bold are the only manuscripts whose place of production is known (or believed) to be the area of the Fayyum, far from Sohag where the White Monastery was settled. Interestingly, the inks of these four manuscripts show a similar composition, containing iron and lacking copper and zinc. The dedicated publication discusses in detail these results and addresses the implication they could have in the study of the White Monastery codices.

[205] Ghigo and Rabin 2020

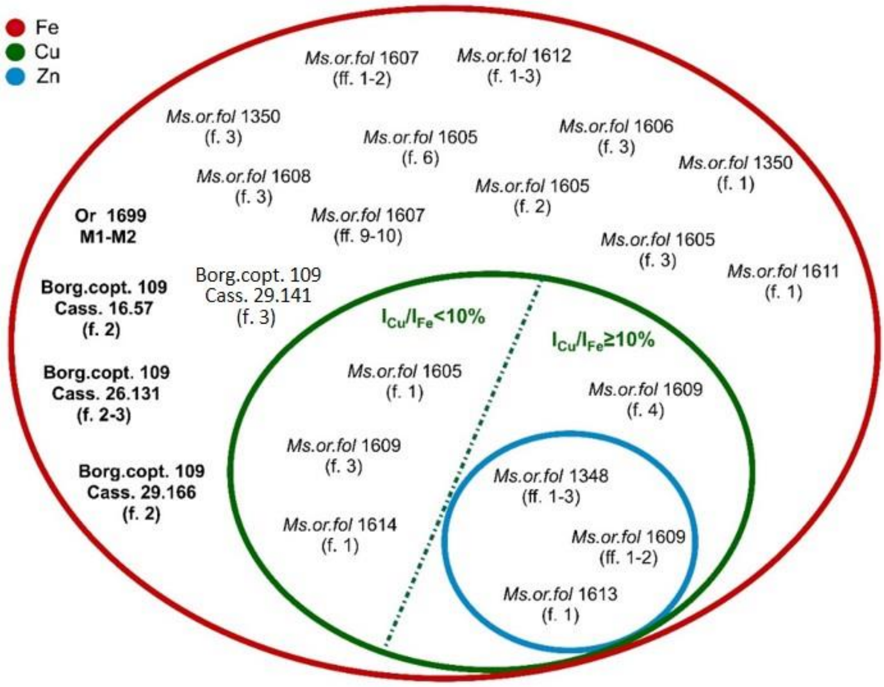

Figure 39 Venn diagram of the vitriolic components found in the inks from the library of the White Monastery. The manuscripts in bold are believed to have been produced in the Fayyum.

Of the inks, the one found on *Ms.or.fol*. 1613, f. 1 represented a peculiar case. Figure 40 shows that the peak at 8.0 keV, corresponding to copper, is more intense that the peak of iron at 6.4 keV. In addition, the visible micrographs show that the ink has flaked in some areas, leaving an unusual greenish halo on the parchment.

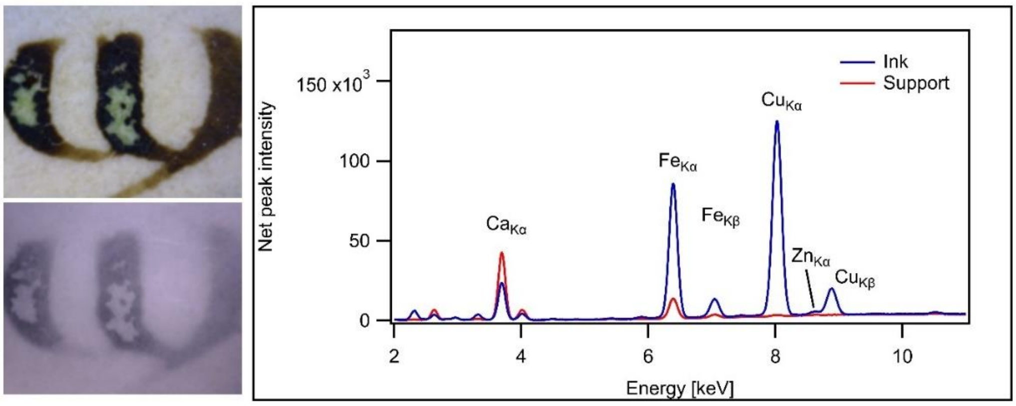

Figure 40 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra of an inked area on Berlin, Staatsbibliothek, Ms.or.fol. *1613, f. 1.*

In an attempt to find an explanation for this unusual green halo, it is worth mentioning that Pliny reports the adulteration of *aeruginis* (copper acetate, a green pigment nowadays known as verdigris) using *atramentum sutorium* (shoemaker's black)[206] which he equates to *chalcanthon*[207], a copper-based substance whose composition in Antiquity is unknown. Rabin pointed out that to serve its purpose as a shoe blackener, *atramentum sutorium* must have contained iron as well, and she suggested that this misconception regarding the nature of

[206] Pliny. *Naturalis Historia* 34.26
[207] Pliny. *Naturalis Historia* 34.32

copper- and iron-based substances may have impacted the diffusion and use of iron-gall inks[208] (see § 2.2.1). The blackest iron-gall ink is made using pure iron(II) sulphate, which is green in colour. On the other hand, copper sulphate is blue. However, a mixture of *atramentum sutorium*, probably containing both copper and iron, and verdigris would look greenish. This explains Pliny reporting that the former was used to adulterate the latter. Because of its greenish colour, such a mixture may have been mistaken for iron(II) sulphate, and therefore used to prepare ink. The resulting writing medium would have contained iron in addition to a fair quantity of copper coming both from the verdigris and from the *atramentum sutorium*.

Marginal notes

In the analysis of these manuscripts, the marginal notes were sometimes found to be written with a different type of ink from the one used on the main text, suggesting that they had been added in a different phase. For example, this is the case with *Ms.or.fol* 1606, f. 3. While the main text ink is an iron-gall ink, Figure 41 shows that the ink of the marginal note maintains its opacity in the near-infrared region, which is typical of carbon ink. In addition, XRF revealed that the intensity of the Kα peak of iron at 6.4 keV is much higher in the inked area than in the support, and lower amounts of copper and zinc are contained in the ink as well. Therefore, this is an example of mixed ink, most likely prepared by mixing carbon and iron-gall ink.

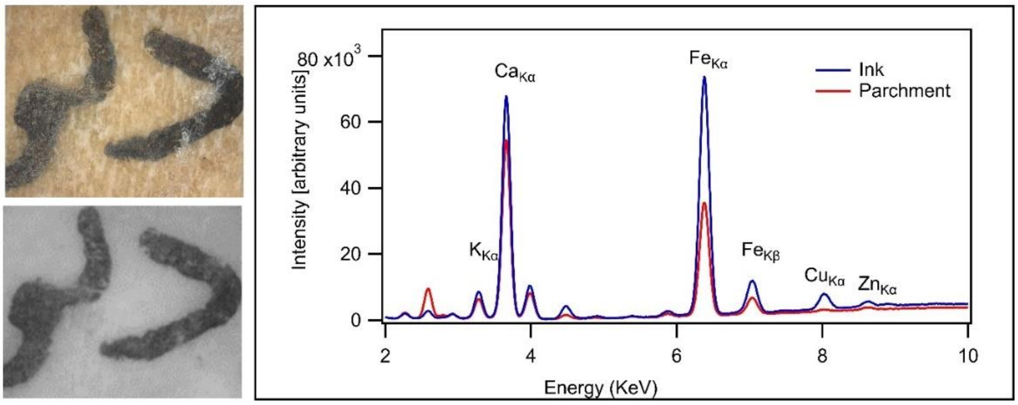

Figure 41 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (ArtTAX spectrometer) on the marginal note found on f. 3v of Berlin, Staatsbibliothek, Ms.or.fol. *1606.*

Coloured pigments

The XRF analysis of red, green and yellow pigments found on a number of the leaves allowed them to be identified in some cases. Figure 42 shows the analysis of a red ink found in the decoration of a capital letter on Berlin, Staatsbibliothek, *Ms.or.fol*. 1605, f. 3. The elemental analysis reveals that it contains both mercury (Lα and Lβ lines at 9.9 and 11.8 keV) and lead (Lα and Lβ lines at 10.4 and 12.6 keV). This suggests that minium may have been used to adulterate cinnabar, as Pliny describes in his treatise[209].

[208] Rabin 2017

[209] Pliny. *Naturalis Historia*, 33.40

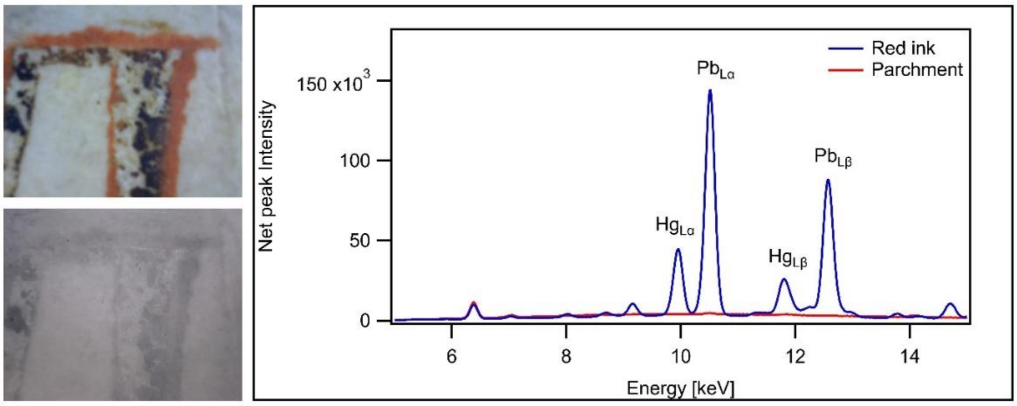

Figure 42 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (ArtTAX spectrometer) on Berlin, Staatsbibliothek, Ms.or.fol. *1605, f. 3.*

Table 9 reports the elemental results obtained on each leaf containing coloured pigments. Overall, the pigments found on the leaves of the codices from the White Monastery offered no surprises: the elements detected suggest the use of pgments documented in Egypt since at least the Greco-Roman period[210].

Table 9. Results of the elemental analysis of the coloured pigments from manuscripts of the White Monastery.

Shelfmark	**Results of the elemental analysis***			**Pigments**
	Red	**Green**	**Yellow**	
Ms.or.fol. 1348, ff. 1–3	Pb	Cu	-	Minium, copper-based green
Ms.or.fol. 1605, f. 1	Pb	-	-	Minium
Ms.or.fol. 1605, f. 3	Pb + Hg (mixture)	Cu	As	Minium + cinnabar (mixture), copper-based green, orpiment/realgar
Ms.or.fol. 1605, f. 6	Pb	-	-	Minium
Ms.or.fol. 1607, ff. 1–2	Pb	-	-	Minium
Ms.or.fol. 1608, f. 3	Pb	Cu	-	Minium, copper-based green
Ms.or.fol. 1609, ff. 1–2	Pb	-	-	Minium
Ms.or.fol. 1609, f. 3	Pb	Cu	As	Minium, copper-based green, orpiment/realgar
Ms.or.fol. 1611, f. 1	Pb	-	As	Minium, orpiment/realgar
Ms.or.fol. 1614, f. 1	Pb	-	-	Minimum
Borg.copt. 109 *Cass*. 26.131	Pb	-	-	Minimum

* The XRF equipment used for this analysis was the ArtTAX (Bruker Nano GmbH)

210 L. Lee and Quirke 2000; Di Stefano and Fuchs 2011; Daniels and Leach 2004; Ahmed Afifi 2011

4.2.8 The library of the Monastery of Saint Macarius[211]

Corpus

At the Vatican Library, the investigation focused on parchment leaves from eight different literary codices written in Bohairic Coptic that were produced in the Monastery of Saint Macarius. Of these, four leaves from four different codicological units were investigated exclusively to gain insight into the coloured pigments (*Vat.copt*. 58^2, f. 10r; 68^2, f. 16r; 68^3, f. 30r; 68^4, f. 33r). The remaining leaves come from four codices characterised by a rather complex layout, where the original parts – composed of the main text, the titles and the colophons – were later complemented by several marginal annotations written in different languages. In addition, coloured geometrical patterns and drawings decorate some of the leaves, and in some cases these have been traced on top of existing text. Of these four codices, *Vat.copt*. 1 represents the most complex case, since some extra leaves were added to the original leaves in a second phase of production; and then a marginal translation in Arabic was later written all along the codex, covering the new added leaves as well as the original folios.

Due to time restrictions, it was not possible to systematically investigate all the inks from the text, the decorations and the marginalia to gain a thorough understanding of the different writing phases involved in the production and use of the codices. Consequently, the results presented here will discuss qualitative aspects of the inks rather than semi-quantitative data. Table 10 describes the leaves that were analysed using NIRR, XRF (Elio Bruker Nano GmbH, formerly XG Lab) and FORS (applied only to the coloured pigments).

Table 10 Description of the leaves from the library of the Monastery of Saint Macarius that were analysed.

Shelfmark	CLM	Part of the text	Leaves	Ink spots	Support Spots
Vat.copt. 1	70				6
Original leaves		Main text, titles, colophon	ff. 157r, 166r, 225r	10	
		Arabic translation	ff. 157r, 225r	4	
		Marginal note (Coptic)	f. 65v	1	
		Marginal note (Coptic)	f. 157r	2	
		Decoration (coloured)	f. 66r, 97v, 225v	11	
Added leaves		Main text	f. 1r	3	2
		Arabic translation	f. 1r	2	
		Decoration (black)	f. 1r	1	
Vat.copt. 57	72	Main text, titles, colophon, correction	ff. 1r, 16r, 74r, 179r, 184r, 230v, 256v	36	7
		Marginal notes (Arabic)	ff. 179r, 230v	2	
		Marginal note (Coptic)	f. 74r	1	
		Marginal note (Coptic)	f. 256v	1	

[211] Warm thanks are due to Ira Rabin, Oliver Hahn and Carsten Wintermann for performing the XRF and FORS analyses on these codices

Shelfmark	CLM	Part of the text	Leaves	Ink spots	Support Spots
		Page number	f. 256v	1	
		Decoration (black)	f. 230v	1	
		Decoration (coloured)	ff. 1r, 74r, 179r, 256v	9	
Vat.copt. 58[9]	81	Main text, titles, colophon	ff. 123r, 132r, 138v, 150v	19	4
		Marginal note (Coptic)	f. 123r	1	
		Marginal note (Coptic)	f. 132r	1	
		Marginal note (Arabic)	f. 132r	1	
		Decoration (coloured)	f. 123r	4	
Vat.copt. 68[1]	147	Main text, colophon	ff. 5r, 15r	10	2
Vat.copt. 58[2]	74	Decoration (coloured)	f. 10r	5	1
Vat.copt. 68[2]	148	Decoration (coloured)	f. 16r	6	1
Vat.copt. 68[3]	149	Decoration (coloured)	f. 30r	1	1
Vat.copt. 68[4]	150	Decoration (coloured)	f. 33r	4	1

Results and discussion

Black inks

The results obtained on the manuscripts from the library of the Monastery of Saint Macarius were reported in a chapter in the book *Detecting early medieval Coptic literature in Dayr al-Anbā Maqār*, where the analysis performed on *Vat.copt*. 57 was presented in detail and the variety of types of ink found on the four codices was introduced (see the appendix "Archaeometric study of inks from Coptic manuscripts in the collection of the Apostolic Vatican Library")[212].

Figure 43 offers a graphic representation of the inks found on *Vat.copt*. 1. It can be observed that the type of ink used for the main text, titles and colophon (MT) of the original leaves is different from the type of ink on the added leaves. In addition, the translation in Arabic on the original leaves was written with the same type of ink that was used for the main text and decoration on the added leaves. This suggests that the Arabic translation found along the whole codex could have been written at the time when the new leaves were added. However, an accurate study of the different writing phases is needed to confirm this possibility. It is worth mentioning that variable amounts of lead were found in some of the inked areas of the main text and black decoration on the added leaf, as well as in some parts of the Arabic translation. However, given that the codex presents an extensive rubrication and numerous decorations made with a lead-based red pigment (see Table 11), the analysis of a

[212] Ghigo and Rabin 2019

higher number of spots is needed to establish whether this element is associated to the black ink or if it results from scattered particles of red ink over the surface of the leaves.

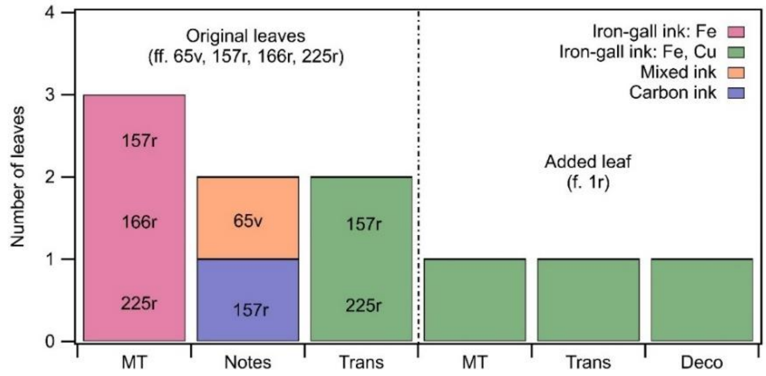

Figure 43 Graphic representation of the different types of black ink found on the leaves of Rome, Biblioteca Apostolica Vaticana, Vat.copt. *1. On the* x-axis*, MT indicates the main text, titles and colophon; Notes refers to the marginal notes in Coptic; Trans is the Arabic translation; and Deco indicates the decorations.*

The leaves that were studied from the codices *Vat.copt*. 57 (Figure 44) and *Vat.copt*. 58 (Figure 45) showed a similar situation, revealing the presence of a variety of inks that were used on the codices in different moments, while folios 5r and 15r of *Vat.copt*. 68 showed a rather simple structure, where the main text and colophon had been traced with an iron-gall ink containing iron.

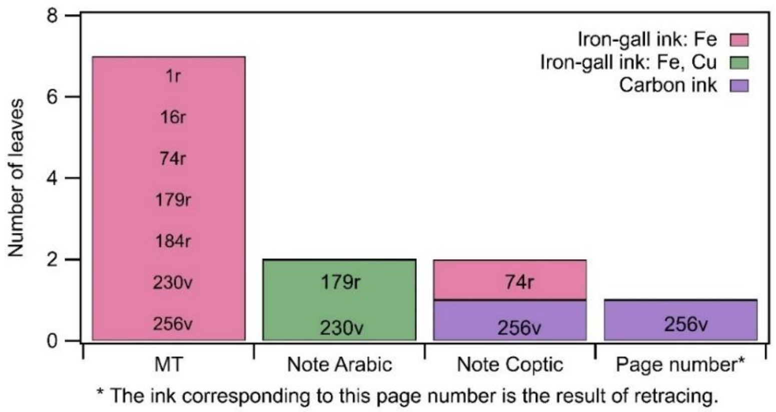

Figure 44 Graphic representation of the different types of ink found on the leaves of Rome, Biblioteca Apostolica Vaticana, Vat.copt. *57. On the* x-axis*, MT indicates the main text, titles and colophon.*

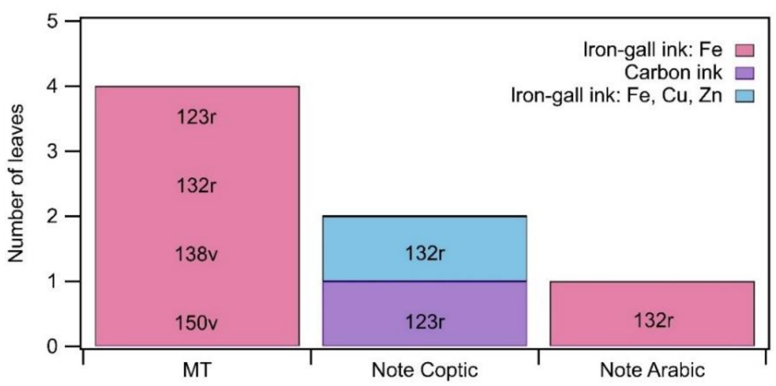

Figure 45 Graphic representation of the different types of ink found on the leaves of Rome, Biblioteca Apostolica Vaticana, Vat.copt. *58. On the* x-axis*, MT indicates the main text, titles and colophon.*

Despite the number of different black inks found on these leaves, it is important to notice that the original parts of the four codices (main text, titles and colophon) were written with iron-gall ink containing only iron. This suggests that the scriptorium of the Monastery of Saint Macarius may have systematically used the same type of ink to write codices during a certain phase of its library (9th–10th centuries CE). However, since only a few leaves from a small number of codices were investigated, further analysis is needed to confirm this hypothesis.

Coloured pigments

In some cases it was possible to identify the coloured pigments on these manuscripts using XRF and FORS analysis, although FORS analysis rarely produced conclusive spectra. In fact, the decoration of these codices consists of geometrical patterns of different colours rather close to each other, meaning that the coloured areas that were investigated were often smaller than the diameter of the probe and more than one colour was measured at the same time. In addition, the coloured areas investigated resulted sometimes from mixtures of different pigments or from thin layers of different pigments overlapping each other. This precluded the possibility of clearly identifying them. Table 11 describes the results that were obtained.

Table 11. Results of the elemental analysis on the coloured pigments in manuscripts from the library of the Monastery of Saint Macarius.

Shelfmark	**Leaf**	**Elemental results***			**Pigments**
		Red	**Green**	**Yellow**	
Vat.copt. 1	66r	Pb, Hg	Cu	-	Minium, cinnabar; copper-based green
	97v	Pb, Hg	-	-	Minium, cinnabar
	225v	Pb, Hg	Cu	-	Minium, cinnabar; copper-based green
Vat.copt. 57	1r	Fe, Pb, Hg, As	-	-	Ochre, minium, cinnabar, orpiment/realgar
	74r	Pb, Hg	Cu	-	Minium, cinnabar; copper-based green
	179r	Fe	Cu	As	Ochre; copper-based green; orpiment/realgar
	256v	-	Cu	-	Copper-based green
Vat.copt. 58^2	10r	Pb	Cu	As	Minium; copper-based green; orpiment/realgar
Vat.copt. 68^2	16r	Pb, Fe	Cu	As	Minium, ochre; copper-based green; orpiment/realgar
Vat.copt. 68^3	30r	Pb + Hg (mixture)	-	-	Minium + cinnabar (mixture, probably adulteration of cinnabar)[213]
Vat.copt. 68^4	33r	Pb, Fe	Cu	As	Minium, ochre; copper-based green; orpiment/realgar

* The XRF equipment used for this analysis was the Elio (Bruker Nano GmbH, formerly XG Lab)

[213] Pliny. *Naturalis Historia*, 33.40

Figure 46 and Figure 47 show the complementary results obtained using XRF and FORS on the red pigments of some of the leaves. In the first case, XRF reveals the presence of a considerable amount of mercury. FORS confirms this result, revealing that the red strokes were traced using cinnabar (HgS). In the second case, XRF reveals the presence in the ink of a significant quantity of iron. FORS confirms this result, revealing that the red strokes were traced using red ochre (mainly composed of hematite, Fe_2O_3). The results show that the coloured palette in use at the Monastery of Saint Macarius was similar to the one used at the White Monastery.

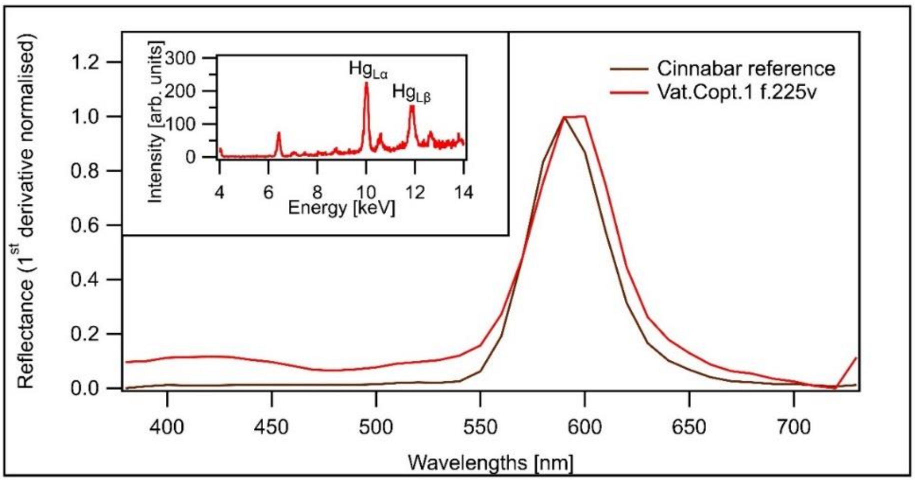

Figure 46 FORS and XRF spectra (inset, obtained with the Elio spectrometer) of a trace of red ink on Rome, Biblioteca Apostolica Vaticana, Vat.copt. *1, f. 225v.*

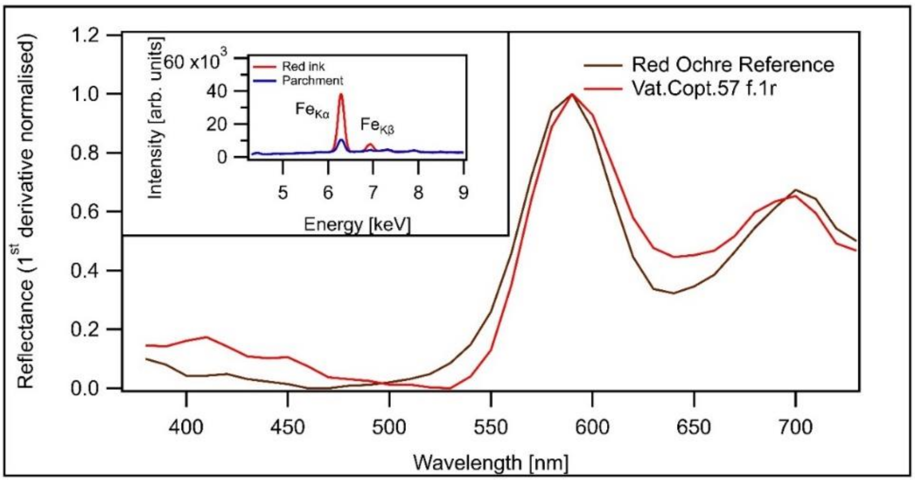

Figure 47 FORS and XRF spectra (inset, obtained with the Elio spectrometer) of a trace of red ink on Rome, Biblioteca Apostolica Vaticana, Vat.copt. *57, f. 1r.*

4.2.9 The Roca Puig and Palau Ribes collections

Corpus

The corpus of manuscripts analysed at the Palau Ribes and Roca Puig collections is very heterogeneous and includes both literary and documentary manuscripts. The time span covered goes from the 3rd century BCE up to the 12th century CE, although the chronological distribution of the manuscripts that were analysed is not even, and most of them were produced between the 2nd and the 8th centuries CE.

In total, it was possible to examine fragments and leaves preserved under 53 different inventory numbers, corresponding to 52 manuscripts. Almost all of them are papyrus leaves, with the exceptions of Barcelona, Palau Ribes Inv. 181–183 and Inv. 60, which are parchment manuscripts, and Barcelona, Palau Ribes, Inv. 388, a paper codex. All the manuscripts in the corpus were written exclusively using black inks, except for Montserrat, Roca Puig, Inv. 498, which was penned in red ink. Traces of red ink were also found on Barcelona, Palau Ribes, Inv. 388, but unfortunately it was not possible to analyse the elemental composition of the inks on this manuscript. The layout of the manuscripts is rather simple, with each constituted solely by the main text; evidence of a marginal note was found only on Barcelona, Palau Ribes, Inv. 73 (225r).

Results and discussion

Table 12 reports the information on each manuscript, along with the results of the typological and elemental analysis. The information about date and provenance was extracted from the bibliography listed at the end of the table.

Table 12. Description of the manuscripts from the Roca Puig and Palau Ribes collections that have been analysed, and the results obtained.

Shelfmark	Collection	Type of text	Edition	Language	Place	Date	Methods	No. spots ink+supp.	Results
Inv. 46	Roca Puig	Literary	Torallas, Worp[a]	Greek	?	251–300 BCE	NIRR, XRF*	3 + 1	Carbon ink + Fe
Inv. 47	Roca Puig	Literary	Torallas, Worp	Greek	?	251–300 BCE	NIRR, XRF*	3 + 1	Carbon ink + Fe
Inv. 172	Palau Ribes	Documentary	De Frutos, Torallas[b]	Greek	Oxyrhynchus?	186 BCE	NIRR	4	Carbon-based ink
Inv. 252	Roca Puig	Documentary	Unpublished[c]	Greek	Fayyum	183 BCE	NIRR, XRF*	1 + 1	Carbon ink
Inv. 1015	Roca Puig	Documentary	Torallas, Worp	Greek	Krokodilopolis (Arsin.)	182–81 BCE	NIRR	2	Carbon-based ink
Inv. 718–792	Roca Puig	Documentary	Torallas, Worp	Greek	Soknopaiou Nesos	37–69 CE	NIRR	2	Carbon-based ink
Inv. 258	Roca Puig	Documentary	Torallas, Worp	Greek	Oxyrhynchus	49–54 CE	NIRR	2	Carbon-based ink
Inv. 158	Palau Ribes	Documentary	Daris[d]	Greek	Oxyrhynchus	81–82 CE	NIRR, XRF**	3 + 1	Carbon ink
Inv. 66	Palau Ribes	Documentary	Daris	Greek	?	1–100 CE	NIRR, XRF**	3 + 1	Carbon ink
Inv. 127	Palau Ribes	Literary	O'Callaghan[e]	Greek	?	101–200 CE	NIRR	1	Carbon-based ink
Inv. 147	Palau Ribes	Literary	O'Callaghan	Greek	?	101–200 CE	NIRR	1	Carbon-based ink
Inv. 164	Palau Ribes	Literary	O'Callaghan	Greek	?	101–200 CE	NIRR	1	Carbon-based ink
Inv. 328	Roca Puig	Documentary	Torallas, Worp	Greek	Bubastos	141–42 CE	NIRR, XRF**	3 + 1	Carbon ink
Inv. 159	Palau Ribes	Documentary	Daris	Greek	Soknopaiou Nesos	157 CE	NIRR, XRF**	3 + 1	Carbon ink
Inv. 812	Roca Puig	Documentary	Torallas, Worp	Greek	?	161–69 CE	NIRR, XRF**	3 + 1	Carbon ink + Fe
Inv. 2	Palau Ribes	Documentary	Daris	Greek	?	101–200 CE	NIRR	2	Carbon-based ink
Inv. 57	Palau Ribes	Documentary	Daris	Greek	?	101–200 CE	NIRR		Carbon-based ink
Inv. 125	Palau Ribes	Documentary	Daris	Greek	?	101–200 CE	NIRR, XRF**	3 + 1	Carbon ink + Fe
Inv. 150	Palau Ribes	Documentary	Daris	Greek	Oxyrhynchus	101–200 CE	NIRR	2	Carbon-based ink
Inv. 157	Palau Ribes	Documentary	Daris	Greek	?	101–200 CE	NIRR	1	Carbon-based ink
Inv. 162	Palau Ribes	Documentary	Daris	Greek	?	101–200 CE	NIRR	1	Carbon-based ink
Inv. 189	Palau Ribes	Documentary	Daris	Greek	?	101–200 CE	NIRR	1	Carbon-based ink
Inv. 8	Palau Ribes	Documentary	Daris	Greek	Oxyrhynchus	245–46 CE	NIRR, XRF**	3 + 1	Carbon ink + Fe, Pb
Inv. 223	Roca Puig	Documentary	Torallas, Worp	Greek	Oxyrhynchus?	336–37 CE	NIRR	2	Carbon-based ink
Inv. 194	Roca Puig	Documentary	Torallas, Worp	Greek and Latin	Alexandria	378–79 CE	NIRR, XRF**	3 + 2	Carbon ink
Inv. 28	Palau Ribes	Documentary	Daris	Greek	Oxyrhynchus	301–400 CE	NIRR	1	Carbon-based ink
Inv. 308	Roca Puig	Documentary	Torallas, Worp	Greek	Oxyrhynchus	419 CE	NIRR, XRF**	3 + 1	Carbon ink

Shelfmark	Collection	Type of text	Edition	Language	Place	Date	Methods	No. spots ink+supp.	Results
Inv. 239	Palau Ribes	Documentary	Daris	Greek	Oxyrhynchus?	431 CE	NIRR, XRF**	3 + 1	Carbon ink
Inv. 97	Palau Ribes	Documentary	Daris	Greek	Oxyrhynchus	475–76 CE	NIRR, XRF **	3 + 1	Carbon ink + Fe
Inv. 4	Palau Ribes	Literary	O'Callaghan	Greek	?	401–500 CE	NIRR	1	Iron-gall ink
Inv. 31	Palau Ribes	Literary	O'Callaghan	Greek	?	401–500 CE	NIRR	1	Iron-gall ink
Inv. 60	Palau Ribes	Literary	O'Callaghan	Greek	?	401–500 CE	NIRR	1	Iron-gall ink
Inv. 65	Roca Puig	Literary	Torallas, Worp	Greek	?	401–600 CE	NIRR, XRF**	3 + 1	Iron-gall ink: Fe, Cu, Zn
Inv. 72	Palau Ribes	Literary	O'Callaghan	Greek	?	401–500 CE	NIRR	1	Iron-gall ink
Inv. 73 (225r) Main text	Palau Ribes	Literary	O'Callaghan	Greek	?	401–500 CE	NIRR, XRF**	4 + 1	Iron-gall ink: Fe
Inv. 73 (225r) Marginalia	Palau Ribes	Literary	O'Callaghan	Greek	?	401–500 CE	NIRR, XRF**	1 + 1	Carbon-based ink
Inv. 181–183 (CLM 3956)	Palau Ribes	Literary	Orsini[f]	Coptic	?	451–500 CE	NIRR	1	Iron-gall ink
Inv. 33	Palau Ribes	Literary	O'Callaghan	Greek	?	401–600 CE	NIRR	2	Iron-gall ink
Inv. 347	Roca Puig	Literary	Albarrán[g]	Coptic	?	401–600 CE	NIRR, XRF**	3 + 1	Iron-gall ink: Fe
Inv. 367	Roca Puig	Literary	Albarrán	Coptic	?	401–600 CE	NIRR, XRF**	3 + 1	Iron-gall ink: Fe
Inv. 174v	Palau Ribes	Documentary	Daris	Greek	?	401–600 CE	NIRR	1	Carbon-based ink
Inv. 233	Palau Ribes	Documentary	Daris	Greek	Oxyrhynchus	401–500 CE	NIRR	1	Carbon-based ink
Inv. 70	Palau Ribes	Documentary	Daris	Greek	Aphrodites Kome	501–600 CE	NIRR	1	Carbon-based ink
Inv. 241	Palau Ribes	Documentary	Daris	Greek	Aphrodites Kome	501–600 CE	NIRR	1	Carbon-based ink
Inv. 243	Palau Ribes	Documentary	Daris	Greek	Hermoupolis Nomos	501–600 CE	NIRR	1	Carbon-based ink
Inv. 90 (CLM 6299)	Palau Ribes	Literary	Boud'hors[h]	Coptic	Bawit?	501–700 CE	NIRR	1	Iron-gall ink
Inv. 134 (CLM 6300)	Palau Ribes	Literary	Boud'hors	Coptic	Bawit?	501–700 CE	NIRR	1	Iron-gall ink
Inv. 427 (CLM 6298)	Palau Ribes	Literary	Boud'hors	Coptic	Bawit?	501–700 CE	NIRR	2	Iron-gall ink
Inv. 6	Palau Ribes	Literary	Bartina[i]	Coptic	?	601–700 CE	NIRR, XRF**	3 + 1	Iron-gall ink: Fe, Cu
Inv. 14	Palau Ribes	Documentary	Daris	Greek	?	601–700 CE	NIRR, XRF**	3 + 1	Carbon ink
Inv. 498	Roca Puig	Documentary	Torallas, Worp	Greek	Hermopolite	729 CE	NIRR, XRF**	3 + 1	Red ink, iron-based

Shelfmark	Collection	Type of text	Edition	Language	Place	Date	Methods	No. spots ink+supp.	Results
Inv. 53	Palau Ribes	Literary	Bartina[j]	Coptic	?	701–800 CE	NIRR	1	Iron-gall ink
Inv. 51	Palau Ribes	Documentary	Albarrán[k]	Coptic	?	701–800 CE	NIRR	1	Carbon-based ink
Inv. 388	Palau Ribes	Literary	Carlig[l]	Coptic	?	1001–1200 CE	NIRR	2	Carbon-based ink

[a] Torallas Tovar, Sofía, and Klaas Anthony Worp. 2014. *Greek Papyri from Montserrat (P.Monts.Roca IV)*. Barcelona: PAMSA

[b] De Frutos García, Alba, and Sofía Torallas Tovar. 2017. "New Fragments of the Amnesty Decree of October 9, 186 BCE." *Bulletin of the American Society of Papyrologists* 54:45–57

[c] Personal communication with Alba de Frutos García, January 2019

[d] All the papyri edited and published by Sergio Daris are found in: Daris, Sergio. 1995. *Papiri Documentari Greci del Fondo Palau-Ribes*. Barcelona: Institut de Teología Fonamental, with the exception of:
Inv. 158: Daris, Sergio. 1986. "Papiri Palau Ribes." *Aegyptus* 66:105–40
Inv. 70: Daris, Sergio. 1982. "P. Palau Rib. Inv. 172 e 70." *Studia Papyrologica* 21:73–86
Inv. 233 and 243: Daris, Sergio. 1996. "Due Note a Papiri Palau Ribes." *Emerita* 64:289–94

[e] O'Callaghan, José. 1993. *Papiros Literarios Griegos del Fondo Palau Ribes*. Barcelona: Seminari de Papirologia

[f] Orsini, Pasquale. 2008. "La Maiuscola Biblica Copta." *Segno e Testo* (Università degli Studi di Cassino) 6:121–50 (pp. 134–35)

[g] Albarrán Martínez, María Jesús. 2015. "Las Actas del Concilio de Éfeso del Año 431." In *La Mano del Escriba: Recorrido por los Tesoros Manuscritos de la Abadía de Montserrat*, edited by Sofía Torallas Tovar, 101–13. Barcelona: PAMSA

[h] Boud'hors, Anne. Forthcoming. *Réflexions sur les Conditions d'Existence d'une Bibliothèque à Baouit*

[i] Bartina, Sebastian. 1970. "Un Nuevo Papiro Copto de Proverbios 15,27–16,8 (PPalau Rib. inv. 6)." *Studia Papirologica* 9:39–49

[j] Bartina, Sebastian. 1970. "A New Sahidic Papyrus of the Gospel of Saint John. PPalau Ribes. Inv. 53." *American Studies in Papyrology* 7:23–28

[k] Albarrán Martínez, María Jesús. 2017. "Rééditions. P. PalauRib.Copt 25-29." *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:121–126

[l] Carlig, Nathan. 2017. "IV Rois 15, 26-34; 18, 30-33; 18, 37-19, 2." In *Coptica Barcinonensia: Textes et Documents de la 5e Université d'Été de Papyrologie Copte*, edited by María Jesus Albarrán Martínez, Anne Boud'hors and Alain Delattre. Special issue, *Journal of Coptic Studies* 19:21–28

* The XRF equipment used for this analysis was the ArtTAX (Bruker Nano GmbH)

** The XRF equipment used for this analysis was the ArtTAX (Bruker Nano GmbH) and Elio (Bruker Nano GmbH, formerly XG Lab)

The analysis of the manuscripts from the Palau Ribes and Roca Puig collections was crucial in discovering the existence of a difference in the types of ink used to write documentary and literary texts: the former were mainly written with carbon-based ink, while the latter were produced with iron-gall ink. This trend is discussed in a recent article, where the results obtained on the literary and documentary manuscripts dated to between the 2nd and the 8th centuries are reported (see the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use")[214]. Following the analyses at the Palau Ribes and Roca Puig collections, Anne Boud'hors identified the papyrus fragments Barcelona, Palau Ribes, Inv. 90, 134 and 427 as probably being among the earliest literary texts known thus far from the Monastery of Apa Apollo in Bawit – this site was previously known for the discovery of numerous documentary papyri (see § 1.2.2.3). Interestingly, these three papyrus fragments were written in iron-gall ink, in contrast with most of the documentary texts from the same site whose main ingredient was carbon. The fact that in the very same institution there might have been a difference in the type of ink used to write documentary texts versus literary texts stimulates further reflection on the understanding that the scribes had regarding the use of different writing materials. Further discussion on this matter will be presented in a dedicated article[215].

The results from manuscripts examined with both NIRR and XRF revealed in some cases the presence of carbon inks containing metals. In § 2.2.1 such inks were presented, explaining that their existence has been recorded from the last centuries before the Common Era onwards[216]. In recent times, these inks have attracted the attention of scholars and scientists, who generally believed that they may be evidence of mixed inks that were intentionally prepared by blending metallic salts and carbon, and that they perhaps represent an intermediate step towards the introduction of iron-gall ink. In previous literature, there were only reports of carbon inks containing either copper[217] or lead[218], whereas the present investigation has revealed evidence of carbon inks containing iron on manuscripts dating as far back as the early Ptolemaic period (3rd century BCE) in the case of Montserrat, Roca Puig, Inv. 46 and 47. It is worth noting that a study of some documentary papyri from Hermoupolis dated to the 1st and 2nd centuries CE carried out in parallel to the current research has revealed further evidence of carbon inks containing iron[219]. Figure 48 shows the analysis of Montserrat, Roca Puig, Inv. 47, where the near-infrared reflectography reveals the presence of carbon, while XRF reveals a significant presence of iron in the ink.

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214 Ghigo, Rabin, and Buzi 2020

215 Ghigo and Albarrán Martínez forthcoming

216 Nir-El and Broshi 1996; Christiansen, Cotte, et al. 2017; Christiansen, Buti, et al. 2017; Brun et al. 2016

217 Nir-El and Broshi 1996; Christiansen, Cotte, et al. 2017

218 Brun et al. 2016

219 This information is courtesy of Oliver Hahn and Ira Rabin, who recently performed a systematic study of the papyri preserved in the Biblioteca Laurenziana and the Istituto Vitelli in Florence

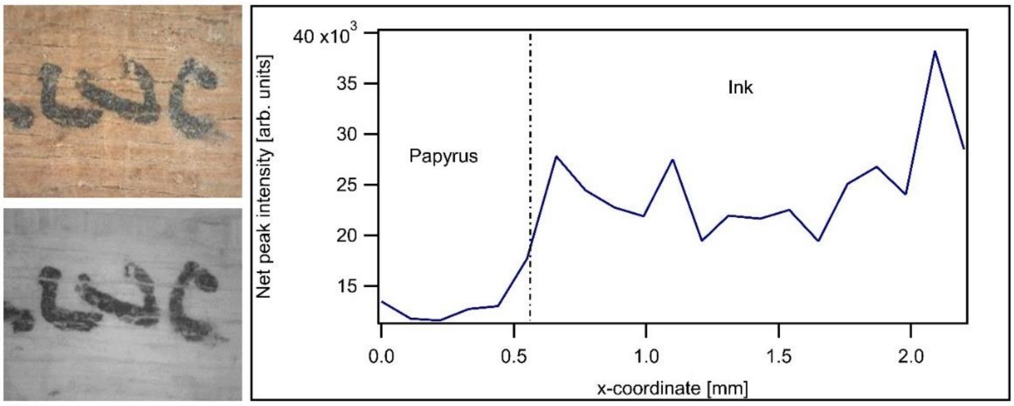

Figure 48 Visible and near-infrared micrographs (DinoLite, 50×) and XRF intensity profile of Fe (ArtTAX spectrometer) at the interface between inked and non-inked areas on Montserrat, Roca Puig, Inv. 47.

Further examples of carbon ink containing iron were found in the current research on manuscripts dating to the first centuries of the Common Era. This is the case for Montserrat, Roca Puig, Inv. 812, which dates to 161–169 CE (Figure 49), and Barcelona, Roca Puig, Inv. 8, which dates to 245–246 CE. Interestingly, the latter contains lead as well as iron, in lesser amounts (Figure 50). The heterogeneous distribution of iron characteristic of papyrus precluded in these cases a calculation of the amount of iron associated with the ink based on the few analytical spots collected. The examination of a higher number of spots or the application of imaging X-ray spectrometry is required to establish the consistent presence of iron and lead in these inks. If it is indeed consistently present, a different type of investigation will be needed to identify the iron and lead compounds and thus to cast light on the nature of these inks.

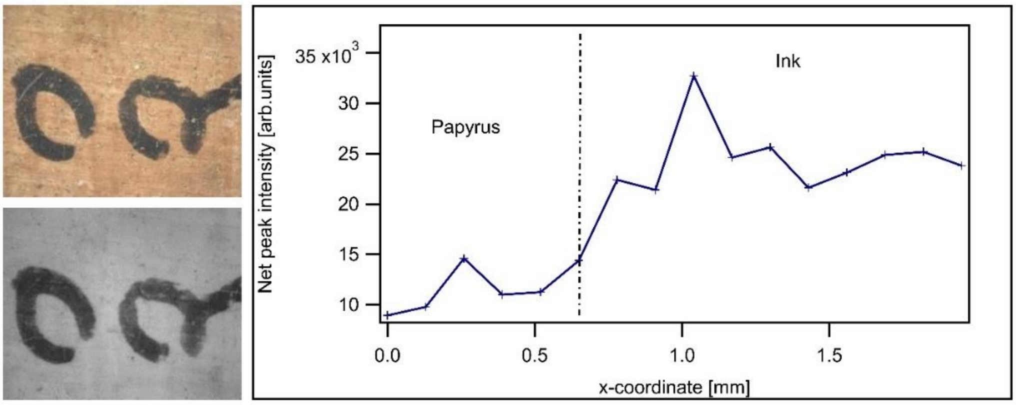

Figure 49 Visible and near-infrared micrographs (DinoLite, 50×) and XRF intensity profile of Fe (ArtTAX spectrometer) at the interface between inked and non-inked areas on Montserrat, Roca Puig, Inv. 812.

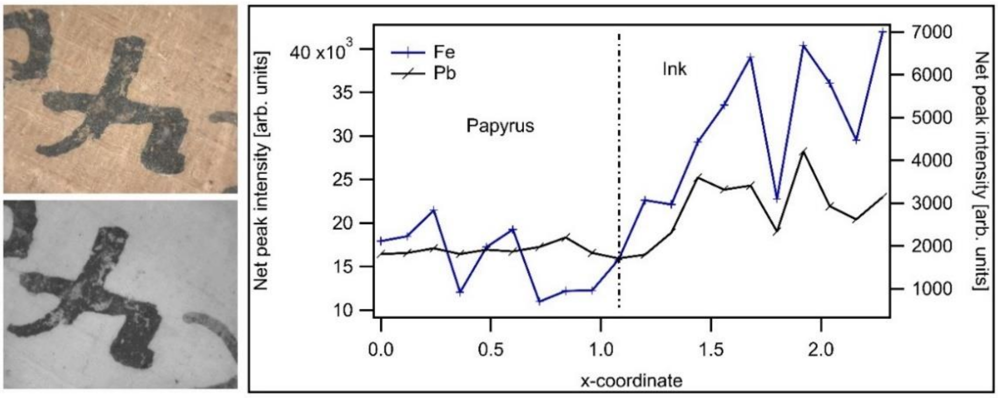

Figure 50 Visible and near-infrared micrographs (DinoLite, 50×) and XRF intensity profiles (ArtTAX) of Fe, following the scale on the left, and Pb, following the scale on the right, at the interface between inked and non-inked areas on Barcelona, Palau Ribes, Inv. 8.

As well as finding carbon inks, the analysis of this corpus revealed the presence of iron-gall inks containing different satellite elements on manuscripts dating from the 5th century CE onwards. Figure 51 and Figure 52 show the cases of Montserrat, Roca Puig, Inv. 65 and Barcelona, Palau Ribes, Inv. 6. Both inks show the presence of a variety of satellite elements together with sulphur, indicating the use of vitriol.

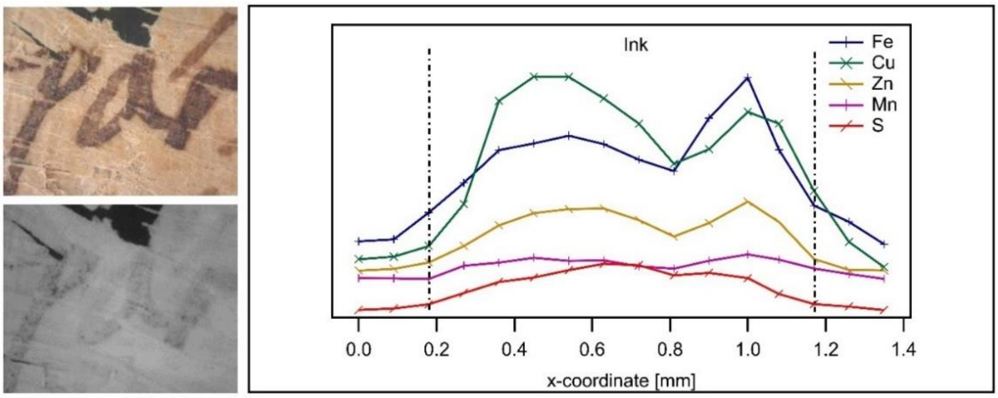

Figure 51 Visible and near-infrared micrographs (DinoLite, 50×) and XRF intensity profiles of different elements (ArtTAX spectrometer) collected along a line connecting non-inked and inked areas on Montserrat, Roca Puig, Inv. 65. The graph is shown for qualitative purposes only, and the different profiles are therefore represented in offset and no scale of intensity is reported.

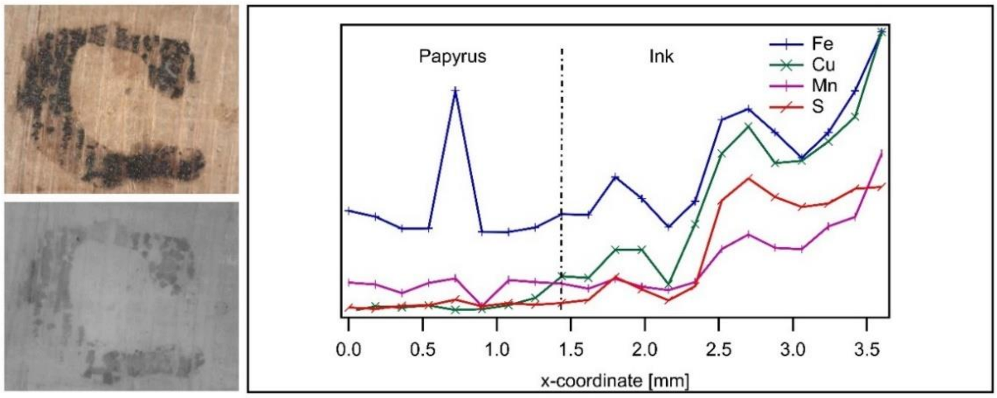

Figure 52 Visible and near-infrared micrographs (DinoLite, 50×) and XRF intensity profiles of different elements (ArtTAX spectrometer) collected along a line connecting non-inked and inked areas on Barcelona, Palau Ribes, Inv. 6. The graph is shown for qualitative purposes only, and the different profiles are therefore represented in offset and no scale of intensity is reported.

4.2.10 The Michaelides collection[220]

Corpus

At the Cambridge University Library, the investigation focused on Coptic literary texts from the Michaelides collection. In total 2 papyri, 13 parchment and 4 paper fragments were examined. Their palaeographical and codicological features have not yet been examined, and thus no information is presently available about their dates or places of production (see § 1.2.2.7).

The fragments are written using mainly black ink, with only two manuscripts showing traces of red ink as well (*Michael*. 1114 and 1166), while in one case the state of conservation of the manuscript was so poor that it was difficult to identify the colour of the ink (*Michael*. 834/E). The manuscript *Michael*. 918 is an example of a palimpsest: on one side the text was erased (or had faded due to deterioration) and a new text was traced over it. Unfortunately, the state of conservation of these manuscripts is quite poor. They are often very small and the edges have deteriorated substantially; the text is in some cases only barely visible. Owing to this, it was extremely difficult to select suitable inked areas for analysis, and sometimes very challenging to ensure a proper representation of the sample. Therefore, semi-quantitative data on this collection did not lead to meaningful conclusions.

Table 13 describes the leaves in the corpus and the analytical techniques applied to them.

Table 13. Description of the leaves from the Michaelides collection that have been analysed, and the techniques applied.

Shelfmark	CLM	Support	Methods*	Colour ink	No. spots ink+supp.
Michael. 1112	2853	Papyrus	NIRR	Black	8
Michael. 834/E	-	Papyrus	NIRR	Red?	4
Michael. 918	1551	Paper	NIRR, XRF	Black	3 + 1
Michael. 1154	4225	Paper	NIRR, XRF	Black	5 + 1
Michael. 1114	4224	Paper	NIRR, XRF	Black	4 + 1
				Red	5 + 1
Michael. 1166	2747	Paper	NIRR, XRF	Black	3 + 1
				Red	2 + 1
Michael. 1235	2936	Parchment	NIRR, XRF	Black	3 + 1
Michael. 1259	2748	Parchment	NIRR, XRF	Black	3 + 1
Michael. 37/4	4221	Parchment	NIRR, XRF	Black	3 + 1
Michael. 37/6	4220	Parchment	NIRR, XRF	Black	3 + 1
Michael. 37/7	2086	Parchment	NIRR, XRF	Black	2 + 1
Michael. Q120	4226	Parchment	NIRR, XRF	Black	2 + 1
Michael. Q121	2523	Parchment	NIRR, XRF	Black	2 + 1
Michael. Q122	1553	Parchment	NIRR, XRF	Black	3 + 1
Michael. Q123	2749	Parchment	NIRR, XRF	Black	2 + 1
Michael. Q125	2109	Parchment	NIRR, XRF	Black	3 + 1
Michael. Q127	1563	Parchment	NIRR, XRF	Black	2 + 1
Michael. Q129	1569	Parchment	NIRR, XRF	Black	3 + 1

[220] Warm thanks are due to Olivier Bonnerot for performing the analysis on this group of fragments

Shelfmark	**CLM**	**Support**	**Methods***	**Colour ink**	**No. spots** ink+supp.
Michael. Q130	1573	Parchment	NIRR, XRF	Black	2 + 1

* The XRF equipment used for this analysis was the Elio (Bruker Nano GmbH, formerly XG Lab)

Results and discussion

Near-infrared reflectography and XRF analysis allowed for the identification of different types of black inks in these documents. Figure 53 shows the distribution among the fragments that were analysed with both techniques.

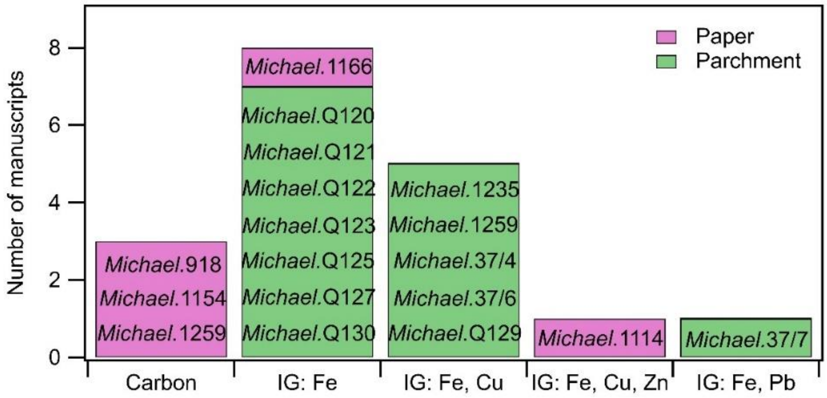

Figure 53 Distribution of different types of black inks found on the fragments examined with NIRR and XRF in the Michaelides collection.

It is worth mentioning that the carbon ink used to trace the drawing representing the *scriptio superior* of the palimpsest *Michael*. 918 was found to contain lead. The presence of lead in carbon inks has been attested on papyrus fragments from Herculaneum and from Hermoupolis[221]. However, its origin remains presently unknown.

The fragment *Michael*. 37/4 is worth further discussion. Three different spots were measured on this manuscript, and the results are displayed in Figure 54, Figure 55 and Figure 56. Near-infrared reflectography shows that on two of the three spots (Figure 54 and Figure 56, corresponding to spots A and C) the ink disappears completely at 940 nm, typical for plant inks. Furthermore, the XRF spectra of these spots show no trace of iron or any other metallic element. In contrast, the ink of the third spot (Figure 55, corresponding to spot B) changes its opacity in the near-infrared region but remains partly visible, which is typical for iron-gall ink. XRF analysis confirmed this result – the intensity of the Kα line of iron at 6.4 keV is about four times higher in the ink than in the support, and a lesser amount of copper is present.

[221] Brun et al. 2016; Maltomini et al. forthcoming

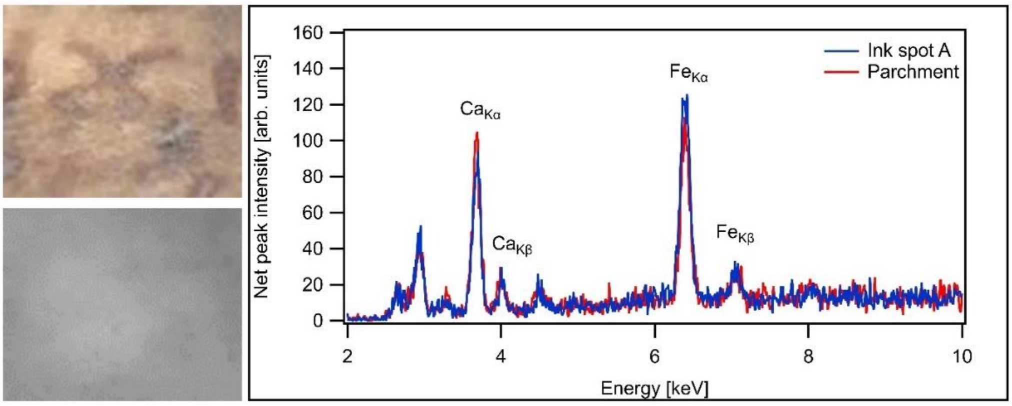

Figure 54 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (Elio spectrometer) of inked and non-inked areas on Cambridge University Library, Michael. *37/4.*

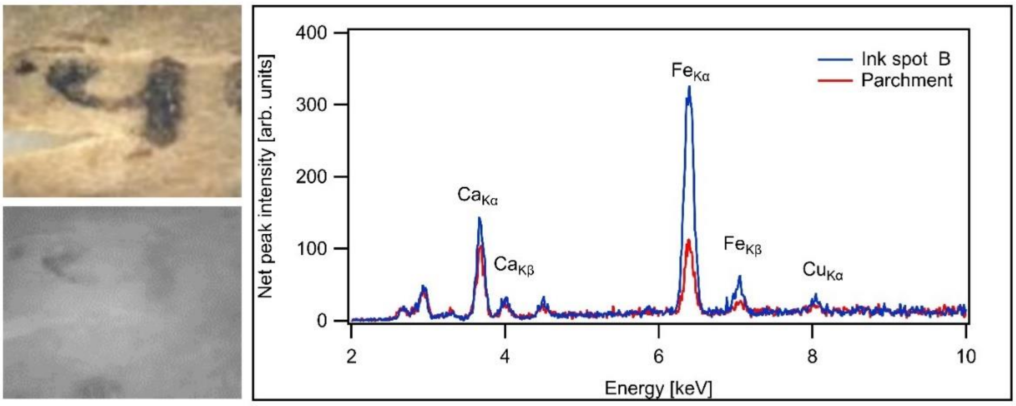

Figure 55 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (Elio spectrometer) of inked and non-inked areas on Cambridge University Library, Michael. *37/4.*

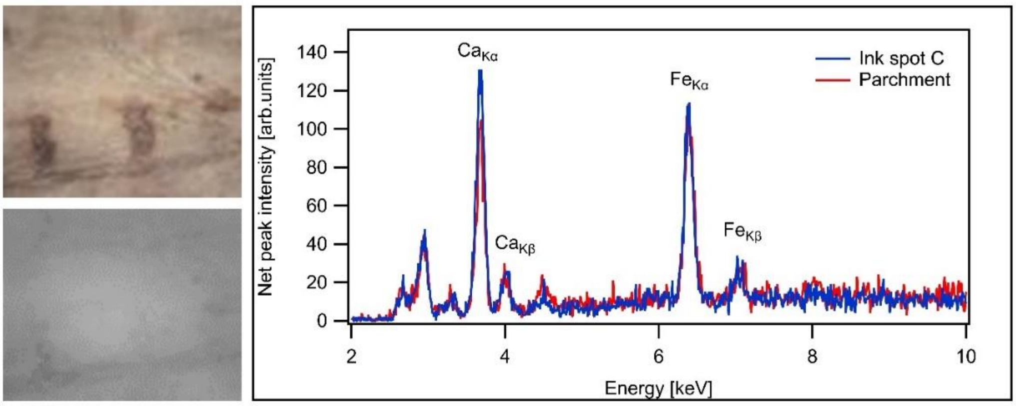

Figure 56 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (Elio spectrometer) of inked and non-inked areas on Cambridge University Library, Michael. *37/4.*

Figure 57 shows that *Michael*. 37/4 is characterised by a marked difference in the level of deterioration along an imaginary line that vertically crosses the text. The left part of the recto, where spot A is located, corresponds to the right part of the verso, where spot C is located, and this part of the manuscript presents a poor state of conservation, where most of the ink seems to have faded. In contrast, on the right part of the recto, corresponding to the left part of the verso, where spot B was collected, the conservation state appears to be better. This suggests that at spots A and C it was not possible to detect iron because deterioration processes have caused the loss of the superficial layer that would have been rich in this element. A similar situation was also found on *Michael*. 37/6.

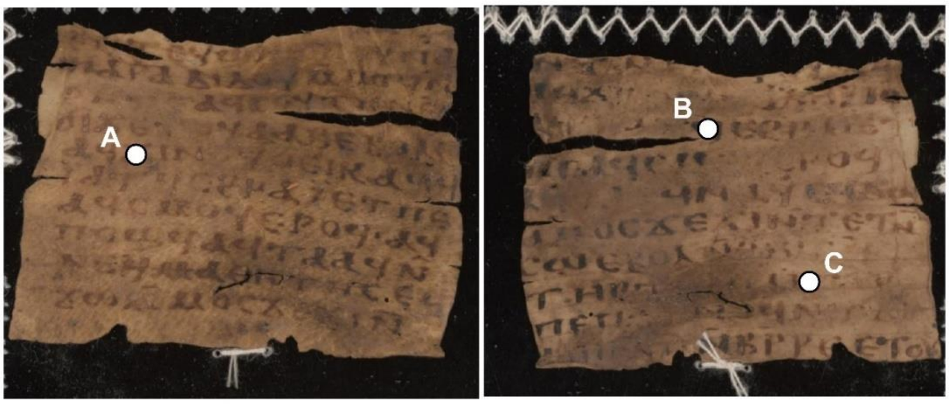

Figure 57 Cambridge University Library, Michael. *37/4 recto (left) and verso (right). The spots of analysis are marked in white. © Cambridge University Library*[222].

Michael. 37/7 represents another interesting case. Figure 58 shows that XRF analysis detected, besides iron, a considerable quantity of lead. Unfortunately, the poor state of conservation of this fragmentary part of a parchment leaf made it possible to analyse only two spots on this manuscript: lead was found on both, suggesting that it is indeed associated with the ink. This is the only case of an iron-gall ink containing lead that was found during the present investigation.

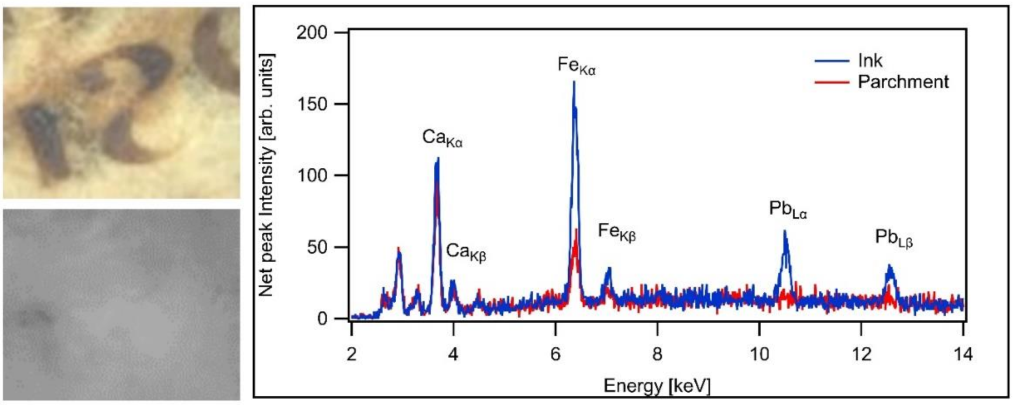

Figure 58 Visible and near-infrared micrographs (DinoLite, 50×) and XRF spectra (Elio spectrometer) of inked and non-inked areas on Cambridge University Library, Michael. *37/7.*

The elemental analysis of the red inks found on *Michael*. 1114 and *Michael*. 1166 showed that their composition was different. Figure 59 shows intense peaks at 10.5 and 12.6 keV, corresponding to the lines Lα and Lβ of lead. This suggests that the pigment used on *Michael*. 1114 is minium (Pb_3O_4). In contrast, the high peaks at 9.9 and 11.8 keV visible in Figure 60 correspond to the lines Lα and Lβ of mercury and indicate the use of cinnabar (HgS) on *Michael*. 1166. In both cases, the peak of iron is more intense in the inked area than in the support; however, because only a limited number of measurements were collected on the support, it is

[222] I thank the Syndics of the Cambridge University Library for their kind permission to reproduce the images of the manuscript presented here

not possible to establish if this indicates the use of an iron-based pigment mixed with cinnabar and minium, or if it is due to the heterogeneity of the iron contained in the paper support.

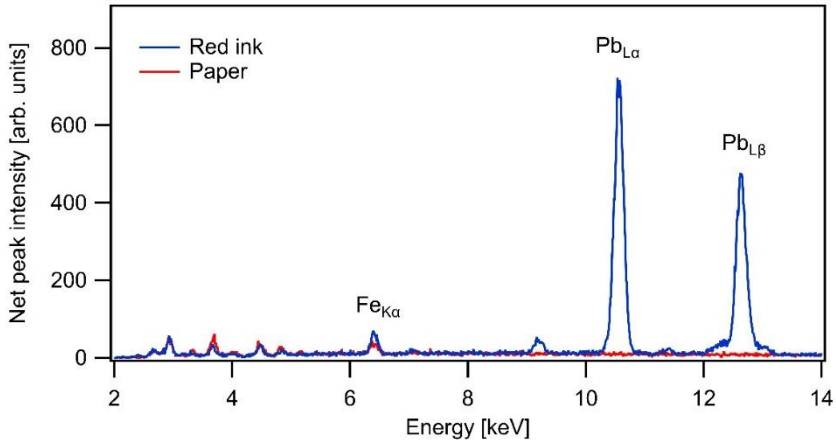

Figure 59 XRF spectra (Elio spectrometer) of the support and a red inked area on Cambridge University Library, Michael. *1114.*

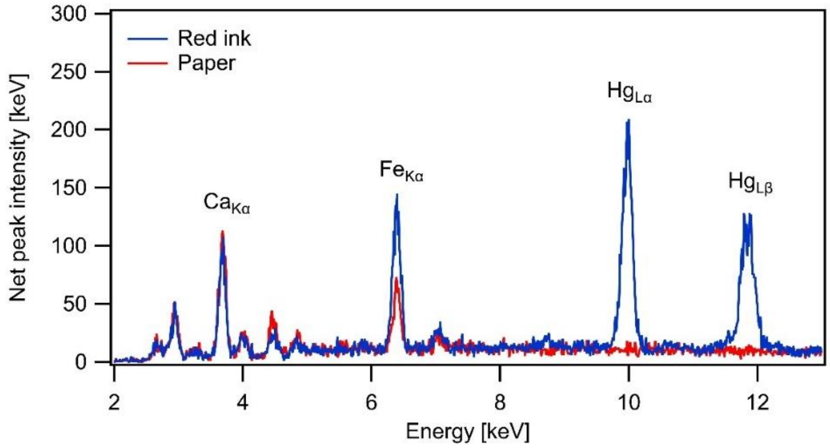

Figure 60 XRF spectra (Elio spectrometer) of the support and a red inked area on Cambridge University Library, Michael. *1166.*

5 Conclusions and outlook

This investigation initially began with the purpose of providing insights into the materiality of Coptic literary manuscripts, through a systematic scientific study of the writing media used between the 3rd and the 12th centuries CE over a large geographic area, including the whole of Egypt and northern Nubia.

The main goal was to explore the variety of inks used over the relevant time span and to investigate possible distribution patterns related to the chronology and/or geography of the manuscripts examined. The results would have laid the foundation for a geo-chronological map describing the history of writing media in Egypt. In the process of doing this, the investigation was expected to find some of the first examples of iron-gall ink since this type of in had previously been reported on a Coptic codex dated to the 4th century CE[223]. Furthermore, it aimed at exploring other aspects of the materiality of manuscripts: for instance, the possible connection between the type of ink and the type of support that has been previously suggested in the literature[224].

The initial focus on Coptic literature was later expanded to include literary texts in Greek and Latin, as well as documentary texts in Greek, Latin and Coptic. On one hand, this granted access to a number of manuscripts that inherently display the information on date and provenance needed for building a geo-chronological map. On the other, it allowed the results obtained from Coptic literature to be considered in a broader context reflecting the complex multilingual environment which characterised Egypt during Late Antiquity[225].

The manuscripts that were analysed date between the 3rd century BCE and the 12th century CE, with the bulk unevenly distributed between the 2nd century CE and the 11th century CE. Unfortunately, almost 50% of manuscripts are of unknown provenance, since this is not displayed in the documents themselves nor can it be deduced from the historical contexts of the documents using traditional approaches. The majority of the remaining manuscripts are either documentary texts from Bawit or Oxyrhynchus, or literary texts from the Monastery of Saint Macarius, the cathedral church of Thi(ni)s or the Monastery of Apa Jeremiah. Only in rare cases it was possible to examine manuscripts produced in different areas during the same period, especially for literary texts. Therefore, the influence of geography on the manufacture of inks could only be partially explored.

[223] Ghigo et al. 2018
[224] Macarthur 1995
[225] Buzi 2018a; Camplani 2015a; Choat 2009; Bagnall 1993, 230–60

5.1 Clusters of manuscripts

The results demonstrate that ink manufacture in Egypt between the 3rd century BCE and the 12th century CE shows great diversity. By cross-linking the information available on the historical context and textual genre of each manuscript with the results of the material analysis it was possible to establish different clusters, where each cluster is defined as a group of manuscripts having in common the type of ink used, the period of production, the type of text and, in some cases, the place of origin. These clusters were created exclusively on the basis of the inks originally used to produce a manuscript, excluding inks from marginalia that were added in other phases of the history of the document. It must be stressed, however, that the clusters listed below neither contain all the manuscripts investigated in this work nor aim at providing an exhaustive report on the materials used in the manufacture of inks in Egypt. Rather, they outline a foundation for future research.

- Cluster A gathers literary papyri produced between the end of the 4th century CE and the beginning of the 5th century CE (see § 4.2.3). These were written using iron-gall inks containing a noticeable amount of copper (IG: Fe, Cu). The manuscripts belonging to this cluster include: Montserrat, Roca Puig, Codex Miscellaneus (with the exception of its final section); Montserrat, Roca Puig, Inv. 14 (CLM 1206); Rome, Biblioteca Apostolica Vaticana, *Pap.copt*. 9 (CLM 6295); and Dublin, Chester Beatty Library, *Cpt*. 2020 (CLM 38). The first two were produced in the area around Panopolis[226], while the provenance for the last two manuscripts is debated, although the area of Panopolis has been proposed as a possibility[227].
- Cluster B collects literary papyri from the library of the cathedral church of Thi(ni)s, in the south of Egypt, produced around the 7th or 8th century CE[228]. These were written using iron-gall inks containing mainly iron (IG: Fe); no trace of copper or zinc was found (see § 4.2.5).
- Cluster C gathers literary parchment leaves written with a type of ink similar to the one found on the leaves from cluster B (IG: Fe). However, the manuscripts were in this case produced in the north of Egypt between the 9th century CE and the 11th century CE. This cluster includes the codices from the Monastery of Saint Macarius[229] (see § 4.2.8) and the codices produced in the area of Fayyum that were later donated to the library of the White Monastery (see § 4.2.7)[230].
- Cluster D includes almost 90% of the documentary texts on papyrus and ostraca produced between the 2nd century BCE and the 8th century CE in different areas of Egypt. These were found to be written using carbon or carbon-based inks (C, C-based).

[226] Fernández and Torallas Tovar 2010; Torallas Tovar 2018
[227] For further discussion on this matter, see Nongbri 2018, 162
[228] Buzi 2018b; Orlandi 1974
[229] Buzi 2019b
[230] Buzi 2014

Unfortunately, it was not possible to perform XRF analysis on all the documents included in this group. Nevertheless, it is interesting to notice that, despite having been produced in different places and different time periods, the majority of documentary manuscripts that were examined in this research were written using inks containing carbon (see § 4.2.6 and § 4.2.9).

- Cluster E contains documentary papyri issued in Bawit around the 7th or 8th century CE that were found to contain a high amount of carbon and fair quantities of metals such as iron, copper and lead. In addition, these papyri show a brownish halo around the trace of ink, indicating the presence of tannins. The inks of these manuscripts are classified as mixed inks (M) and are among the few examples of such that have been attested so far being used for the main text of manuscripts.

5.2 The correlation of type of ink with language, support and textual genre

5.2.1 Language

Figure 11 shows that the period between the 4th and the 6th centuries is when the most information was collected on manuscripts written in different languages. In fact, scarce information was collected on manuscripts from the 3rd century, and before that Coptic still had not emerged as a language. On the other hand, the fact that the manuscripts dating from the 7th century onwards that were investigated are written almost exclusively Coptic reflects specific choices. For the group of manuscripts dated to between the 4th and 6th centuries no correlation was found between the type of ink and the language of the document. Greek, Latin and Coptic manuscripts were all written using a variety of inks. The relationship among the different languages spoken in Egypt during Late Antiquity is a very complex topic that has often attracted the attention of scholars[231]. From the latest studies, it is clear that it is extremely difficult to set precise borders to describe the use and jurisdiction of each language. The Codex Miscellaneus, being the product of a religious environment and carrying texts in both Greek and Latin may well serve as an example. Despite the differences in content and language of sections A to G, palaeographic studies suggest that this was all written by the same person[232]. Archaeometric analysis revealed that the literary sections of the codex (A to F) had been written in different phases, but with the same type of ink (see the appendix "Between literary and documentary practices: The Montserrat Codex Miscellaneus and the material investigation of its inks")[233]. Like other examples, this small codex shows that the absence of strict functional distinctions in the use of different languages seems to be reflected in the inks used, and there is no correlation of ink type with one or another language.

[231] Buzi 2018a; Camplani 2015a; Bagnall 1993; Camplani forthcoming
[232] Ghigo and Torallas Tovar 2020; Ammirati 2015a, 59; Ammirati 2015b, 16–18
[233] Ghigo and Torallas Tovar 2020

5.2.2 Support

The results show that, for the most part, the type of ink used was independent of the writing support. In contrast to what previous literature has suggested[234], no correlation was found between the use of iron-gall ink and parchment. The papyrus codices written in iron-gall ink corresponding to clusters A and B serve as good examples of this.

Both carbon and iron-gall inks have been found on papyrus, parchment and paper, while the use of mixed inks has been documented on papyrus and parchment. However, it should be stressed that the use of carbon ink and of mixed ink on literary parchment codices was rare and restricted to marginal notes (carbon: Rome, Biblioteca Apostolica Vaticana, *Vat.copt*. 1, f. 157; Cambridge University Library, *Michael*. 1259; mixed: Berlin, Saatsbibliothek, *Ms.or.fol*. 1605, f. 6 and 1606, f. 3). Nevertheless, one should be cautious in drawing conclusions: the fact that carbon and mixed inks were rarely observed on literary parchment leaves may reflect a correlation between the type of ink and the genre of text rather than between the type of ink and the writing support; this connection is thoroughly discussed in the following section.

5.2.3 Textual genre

This study revealed further analytical evidence of the use of iron-gall ink during the first centuries of the Common Era. The manuscripts in cluster A show that Berlin, Staatsbibliothek, *Ms.or.oct.* 987, dated to the 4th century and written with an iron-gall ink[235], is not an isolated example of the use of this type of ink in this period. Moreover, the results obtained across all the literary papyri from the 4th or 5th century CE (§ 4.2.3) show the use of iron-gall ink on six out of nine manuscripts: Rome, Biblioteca Apostolica Vaticana, *Pap.copt*. 9 (CLM 6295); Montserrat, Roca Puig, Inv. 14 (CLM 1206) and Codex Miscellaneus; Berlin, Staatsbibliothek, *Ms.or.fol*. 3065 (CLM 24); Dublin, Chester Beatty Library *Cpt*. 2020 (CLM 38) and *Pma* B (CLM 174). This suggests that this type of ink may have been commonly in use from the end of the 4th century CE onwards. It is worth stressing that, while in two cases the iron-gall ink may have been mixed with carbon (CLM 6295 and the Codex Miscellaneus), the results show the use of pure iron-gall inks on at least three manuscripts (CLM 1206, CLM 24 and CLM 38).

A look at the manuscript clusters reveals that iron-gall ink was extensively used in literary manuscripts (clusters A, B and C), but that, in contrast, most documentary texts were written using carbon and carbon-based inks (cluster D). Figure 61 shows the distribution of the different types of ink on all the literary and documentary texts examined during this investigation. Iron-gall ink dominates in the pie chart of literary texts produced between the 3rd century BCE and the 12th century CE. This type of ink was found on almost 90% of the literary manuscripts, while it was never found on documentary texts, at least not until the 8th century CE, when the most recent documentary manuscripts in the corpus were written.

[234] Macarthur 1995
[235] Ghigo et al. 2018

Similarly, carbon and carbon-based inks (the latter referring to those inks whose elemental composition was not established, see § 4.2.1) dominate in the pie chart of the documentary texts and were found on almost 90% of documentary manuscripts produced between the 2nd century BCE and the 8th century CE, while they occur on a limited number of literary manuscripts. Although this correlation is significant, it must be stressed that not only is the period covered in these two graphs different, but the distribution of manuscripts along this time span is uneven. In addition, a substantial number of documentary manuscripts analysed was produced roughly at the same time and in the same place (it is the case of the documents from Bawit dated to between the 7th and 8th centuries). For the sake of clarity, Figure 62 reports the chronological distribution of literary and documentary manuscripts (in blue and orange, respectively).

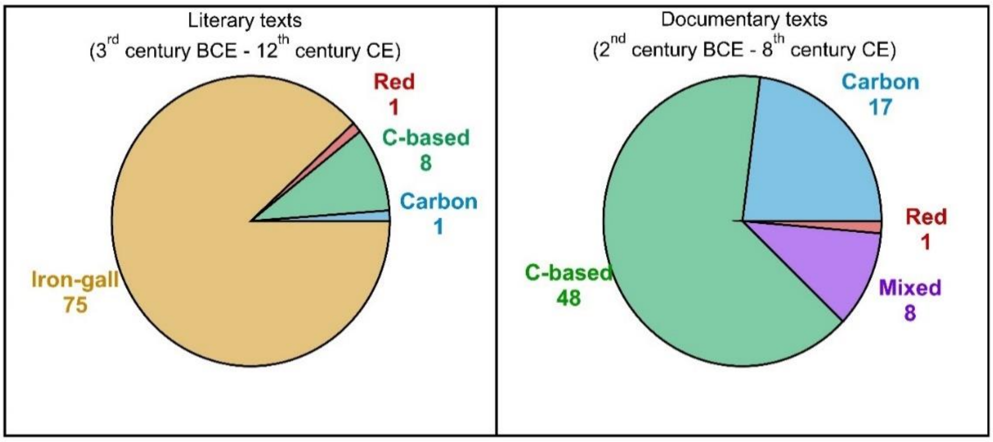

Figure 61 Distribution of different types of inks in literary and documentary[236] texts across the entire corpus of manuscripts. Montserrat, Roca Puig, Codex Miscellaneus is counted as both a literary and a documentary text.

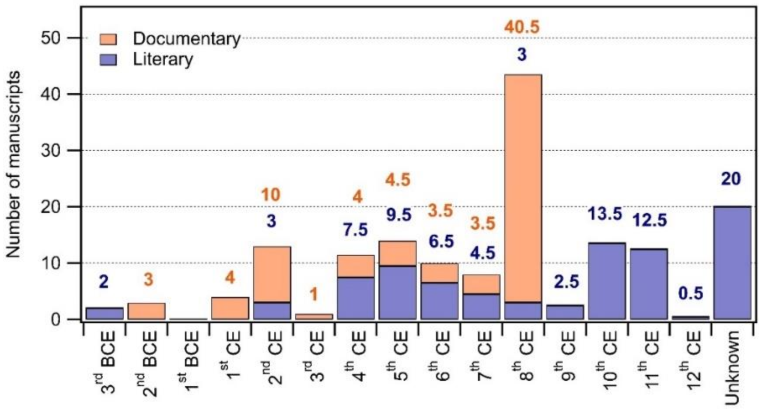

Figure 62 Chronological distribution of the manuscripts according to their genre. Where a manuscript is known to date to one of two centuries, the count is given as 0.5 in each of the two adjacent centuries. Montserrat, Roca Puig, Codex Miscellaneus is counted as both a literary and a documentary text.

The correlation between the type of ink and the genre of manuscript can be seen even on the leaves of the Codex Miscellaneus of Montserrat. The codex is divided into seven textual

236 In four cases (Barcelona, Palau Ribes Inv. 357, 399, 401, 451) it was not possible to uncontroversially identify the inks as mixed, probably due to their poor conservation state (see § 4.2.6).

units: sections A to F carry literary texts, while section G displays a list of Greek words connected to the practice of stenography, typical of an environment where documentary texts were produced. The examination of one leaf from each textual section revealed that the literary texts are written in iron-gall ink while the list of Greek words is written in carbon ink (see the appendix "Between literary and documentary practices: The Montserrat Codex Miscellaneus and the material investigation of its inks")[237].

This correlation was also observed on manuscripts probably produced in the same place and within a relatively short time span: it is the case for the documentary and literary texts produced between the 7th and 8th centuries CE in the monastery of Apa Apollo in Bawit. However, while it was possible to examine a substantial number of documents from this monastery (§ 4.2.6), only three fragments of papyrus carrying literary texts were analysed (§ 4.2.9): Palau Ribes, Inv. 90 (CLM 6299), Inv. 134 (CLM 6300) and Inv. 427 (CLM 6298). Palaeographical and codicological studies suggest that these fragments might be among the first literary texts from the Monastery of Apa Apollo known to the scientific community[238]. Therefore, further investigation on literary texts from Bawit is needed to establish whether iron-gall ink was systematically used in the scriptorium of the monastery.

Another matter altogether is understanding the reason why such difference in the writing media used for documentary and literary texts might have existed even within the same institution. Previous studies on manuscripts from Bawit pointed out that the support of documents issued for internal purposes was frequently reused[239]. A dedicated publication will explore the possible connection between this phenomenon and the fact that many documents from this site were found to be written with carbon-based inks[240].

The results obtained during this investigation seem to suggest that the transition between carbon ink and iron-gall ink happened at first in environments where literary texts were produced. However, this is a rather surprising result, since studies performed on different groups of documentary texts from the 4th or 3rd century BCE onwards have revealed the use of different types of mixed inks, which are believed to be a crucial step in the transition between carbon ink and iron-gall ink[241]. If iron-gall inks were increasingly used from the end of the 4th century BCE onwards, it is likely that this type of ink appeared at an earlier point in time and then gradually spread. The fact that mixed inks have been found as far back as the Hellenistic period may suggest that the quest for the earliest evidence of iron-gall ink should be carried out by examining manuscripts produced prior to the Coptic period.

237 Ghigo and Torallas Tovar 2020

238 Boud'hors in press

239 Clackson 2008; Delattre 2007

240 Ghigo and Albarrán Martínez forthcoming

241 Delange et al. 1990; Rabin, Wintermann, and Hahn 2019. In addition, in an investigation parallel to this one, evidence of mixed inks was found on some documentary texts from Elephantini and carbon inks containing metals were found on documentary texts from Hermoupolis

5.3 Comparing the inks of different literary scriptoria

It is generally assumed that a particular scriptorium made consistent use of the same type of ink, at least in a specific phase of its library, since it is likely that an institution acquired the inks, or the ingredients to prepare them, from the same place over a certain period of time. The results obtained for the papyrus codices from Thi(ni)s and for the parchment codices from the Monastery of Saint Macarius seem to corroborate this hypothesis, since in each case the manuscripts were written using the same type of iron-gall ink. In contrast, the study of the parchment codices from the Monastery of Apa Jeremiah revealed the use of different types of iron-gall ink. However, it must be stressed that the assumption that these latter codices were produced in the same place is based only on the codicological analysis of Thompson, who states that the homogeneous format and scripts of the codices are proof that they were produced in one and the same scriptorium, probably inside the monastery itself[242]. In any case, since only a few leaves from a limited number of codicological units were examined (four from Thi(ni)s, four from Saint Macarius and three from Apa Jeremiah) further investigation is needed to cast more light on ink usage (and manufacturing?) inside Egyptian scriptoria.

The codices from the library of the Monastery of Saint Macarius and some of the codices from the White Monastery library, originally produced in Touton or attributed more generally to the area of the Fayyum, are grouped together in cluster C. They were produced between the 9th and 11th centuries CE and although they originated from different scriptoria, they were written with the same type of ink: iron-gall ink with no satellite elements. The map in Figure 63 shows the location of the institutions mentioned. Scant information is available on the place of production of many of the codices of the White Monastery library, but it is definitively known that some of the codices were produced in a professional scriptorium in Touton and later donated to the monastery in a gesture intended to save the souls of the donors[243]. The examination of leaves from codices originally produced in Touton or in the area of Fayyum more generally (Cambridge University Library, *Or*. 1699 (CLM 511); Rome, Biblioteca Apostolica Vaticana, *Borg.copt*. 109 *Cass*. 26.131 (CLM 314), 109 *Cass*. 16.57 (CLM 480) and 109 *Cass*. 29.166 (CLM 538)) revealed that they were written with iron-gall inks containing only iron, in contrast with the iron-gall inks containing other satellite elements found on some other codicological units whose place of production is unknown (see § 4.2.7 and the appendix "Gaining perspective into the materiality of manuscripts: The contribution of archaeometry in the study of the inks from the White Monastery codices")[244]. Therefore, the codices from the White Monastery prove that different types of iron-gall ink were in use in Egypt between the 9th and 11th centuries CE. However, further analytical investigation on a substantial number of manuscripts is needed to establish if iron-gall inks with no satellite elements may have been characteristic in this period of the area of Lower Egypt, where the Monastery of Saint Macarius, Touton and the area of Fayyum are located.

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242 Thompson 1932, ix–x
243 Nakano 2006
244 Ghigo and Rabin 2020

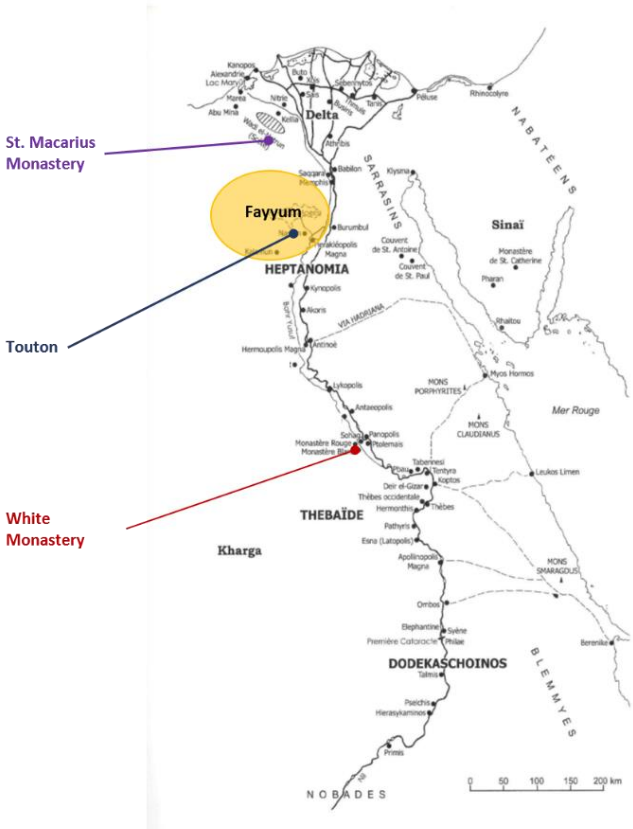

Figure 63 Location of the Monastery of Saint Macarius, Touton, the area of Fayyum and the White Monastery. The map of Egypt used to create this distribution has been extracted from: E. Wipszycka, Moines et communautés monastiques en Égypte, *Warwsaw 2009 [*Journal of Juristic Papyrology, *Supplement XI], fig. 1.*

5.4 Impact of the results on the current data treatment process and analytical protocol

From a strictly analytical point of view, this investigation of Egyptian inks from Late Antiquity pointed out the limitations in the use of the fingerprint model when applied to the study of manuscripts on papyrus (see § 3.2.3.2). Although for inks on papyrus is rather challenging to obtain satisfactory semi-quantitative results, this research also showed that in some cases the fingerprint model applied to papyrus codices still provides a meaningful insight, as in the case for the Codex Miscellaneus (see the appendix "Between literary and documentary practices: the Montserrat Codex Miscellaneus and the material investigation of its inks")[245].

In addition, it underlined the difficulties that are encountered in identifying and characterising mixed inks using the current protocol. This matter has been thoroughly addressed in a dedicated publication (see the appendix "The quest for the mixed inks")[246]. In order to reach unequivocal results for manuscripts, this dissertation has suggested the implementation of a micro-invasive analytical technique that can be applied *in situ*.

[245] Ghigo and Torallas Tovar 2020
[246] Colini et al. 2018

Atmospheric solids analysis probe mass spectroscopy was proven to be successful in detecting the presence of tannins in mixed inks. Potentially, this technique could also distinguish between several families of tannins (condensed versus hydrolysable), thus refining the characterisation of inks. In addition, it could be employed to identify the binders or other additional organic compounds present in the ink (see the appendix "Black Egyptian inks in Late Antiquity: New insights on their manufacture and use")[247]. Furthermore, the use of infrared reflectography performed above 1500 nm would allow for the identification of carbon even when small quantities are added to other ingredients. The use of such reflectography has been considered in the past, but only recently have developments introduced transportable equipment. For this reason, the analytical protocol originally adopted near-infrared reflectography performed at 940 nm instead, which was commercially available on small devices.

Despite the limitations, in several cases it was possible to identify mixed inks. Evidence of them was noted in the marginal notes of some literary parchment codices dating to the 10th or 11th century CE – Berlin Staatsbibliothek, *Ms.or.fol.* 1605, f. 6 (CLM 476) and 1606, f. 3 (CLM 555) – as well as in the main text of some of the documentary papyri from Bawit dating to the 7th or 8th century CE – Barcelona, Palau Ribes, Inv. 371 and 402; and Montserrat, Roca Puig, Inv. 375 and 227. Further investigation is needed to provide clear insights into the role that mixed inks may have played in the transition between carbon ink and iron-gall ink. In this regard, the present investigation highlighted two manuscripts dating to the end of the 4th century CE whose inks may be a mixture of iron-gall and carbon: Montserrat, Roca Puig, Codex Miscellaneus and Rome, Biblioteca Apostolica Vaticana, *Pap.copt.* 9 (CLM 6295). Once the proposed analytical techniques are implemented in the current protocol, these manuscripts could represent a valid starting point for investigation. In addition, evidence of carbon inks containing iron has been revealed as far back as the Ptolemaic period (Montserrat, Roca Puig, Inv. 46 and 47) and further examples have been reported in manuscripts from the 2nd and 3rd centuries CE (Montserrat, Roca Puig, Inv. 812 and Barcelona, Palau Ribes, Inv. 8, respectively). The identification of the metallic compounds contained in these inks may provide an insight into whether particular inks are carbon inks that contain metals as a result of contamination or are mixed inks prepared intentionally by the addition of metallic salts.

5.5 Dissemination of the results

With the purpose of providing the scientific and scholar community with free access to the research reported here, the results obtained on Coptic literary manuscripts have been entered into the online *Archaeological Atlas of Coptic Literature*. The black inks of main text, titles and marginalia of each codicological unit are divided according to their elemental composition and described using the categories introduced in § 4.2.2. The pictures obtained through reflectography and the spectra deriving from the elemental analysis are attached to the records

[247] Ghigo, Rabin, and Buzi 2020

of each manuscript, while further relevant information on the elemental composition is reported in the notes, where necessary. Since the two routine methods (NIRR and XRF) were not applied to all the manuscripts examined, a note warns the user of the atlas if a particular codicological unit has only been partially investigated.

It must be stressed that the categories used in the atlas to describe the inks do not aim to give an exhaustive indication of their composition, but are rather intended to be a partial classification that allows for the comparison of inks produced over a large geographical area and time span. The results presented in the *Archaeological Atlas* enable the user to visualise the different types of ink on the map, according to where the manuscripts were produced, stored or discovered. In this way, the technology used in the production of different types of inks can be tracked and studied. Far from being exhaustive, this graphic representation aims at nothing more than being an initial cornerstone. Future investigation is needed to make this nucleus develop into a map which outlines the technological evolution of writing media.

5.6 Outlook

Because of the variety of inks examined in this dissertation, the results that have been obtained will encourage further investigation of the materials used in the manufacture of writing media, in order to create a geo-chronological map displaying their evolution. The data collected are far from providing a thorough description of all the areas touched upon in this investigation, and further research is needed to understand in depth the distribution of different ink compositions as well as the existence and articulation of a commercial trade in the ingredients.

Future investigation should focus on the in-depth examination of shorter time spans and analyse literary and documentary manuscripts produced in different areas. The transition between iron-gall ink and carbon ink could potentially be employed as a *terminus ante/post quem* to complement information on the dating of a manuscript. To try to find the earliest evidence of iron-gall ink, future research should focus on manuscripts produced before the Coptic period and consider possible biases between literary and documentary texts.

In parallel with such investigations, scientific research should focus on implementing in the analytical protocol techniques that could provide unequivocal results on mixed inks, such as those that have been proposed here. A systematic study on mock samples using ASAP-MS is needed to address the effects of the ionisation condition on the detection of different compounds. This would lead to a better understanding of the potential of this technique in detecting different types of polyphenolic molecules and might allow to refine the classification of writing media.

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Theophilus. *De Diversis Artibus*, 1.40

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APPENDIX

Contributions published before the defence of this dissertation

Article

The Quest for the Mixed Inks

Claudia Colini, Oliver Hahn, Olivier Bonnerot, Simon Steger, Zina Cohen, Tea Ghigo, Thomas Christiansen, Marina Bicchieri, Paola Biocca, Myriam Krutzsch, and Ira Rabin | Hamburg, Berlin, Paris, Rome, Turin

In this article, we would like to share our observations concerning the inks produced by intentionally mixing soot or charcoal with tannin extracts or iron-gall ink. Aside from Zerdoun's mention in her outstanding review of written sources, *Les encres noires au Moyen-Âge*[1], this ink category has received little if any attention from scholars and scientists. And yet, if analytically attested, the use of such inks could serve as an additional category to classify and distinguish the writing inks on the historical socio-geographic map of the writing inks we are trying to build.

In the collection of recipes from Arabic sources that one of us investigated, we found that explicit recipes for mixed inks constitute some 20% of the collection[2]. It would be extremely interesting and important for our enterprise to obtain a chronological and geographic attribution of the recipes from the Orient, beyond those of Dioscorides[3] and Philo of Byzantium[4]. However, the overall scarcity of copies per treatise and the young age of the manuscripts make it difficult for the current state of the art to understand when and where a certain formula was introduced and changes were made. In addition, we observed that the transmission of recipes from one treatise to another is massive, but at the same time extremely fluid, since small but mostly reasonable changes are introduced every time, often resulting in modifications to the formulas (concerning the quantities, ingredients, or technique employed). Although great respect was accorded to the authors, especially if they were eminent figures, their texts and words were not untouchable and unchangeable. This 'active' transmission[5] suggests at the same time a living tradition with practical applications, as otherwise there wouldn't be the need to change the content and the formulas, but only the form. For this reason, a more detailed study not only of the origin, but also of the transmission of these texts[6] will contribute to establishing a chronology of the modifications of the single recipes, which will be useful when comparing with specific manuscripts.

Mixed inks appear also in the Jewish sources associated with the Jewish Diaspora in the Orient. The best-known among these recipes was suggested in the twelfth century by Maimonides, a Jewish philosopher from Spain and Egypt, for inscribing phylacteries.[7] It is very similar to the one attributed to Ibn Muqla, a famous calligrapher from the Abbasid period.[8] However, Maimonides argued against the practice of adding iron-gall ink to carbon, another popular mixed ink. It is also interesting to notice that none of the five Maimonides autographs we analyzed contained inks that followed his recipe. Analysis of the codices in the Jewish National Library in Jerusalem (Heb. 5703_2) and the Bodleian Library in Oxford (Huntington 80, fol. 165r, signature) revealed that these manuscripts were written using pure iron-gall inks. But the letter preserved in Cambridge University Library (T-S 12.192) was penned in carbon ink. Most interestingly, the manuscript containing 'The guide for the perplexed' (T-S 10 Ka 4.1) displayed both carbon and iron-gall ink on different pages and corrections both written by Maimonides himself.

These results correlate well with the study of the inks used in the legal documents found in the Cairo Genizah, which stated that both ink types were employed in mediaeval Fustat.[9]

In our study of the inks of the manuscripts produced in the Diaspora, we have found indication that Jews used the same

[1] Zerdoun 1983.

[2] Colini to be published in the PhD thesis 2018.

[3] *Materia Medica* V.181; Zerdoun 1983, 80.

[4] Zerdoun 1983, 92.

[5] Meaning the copyist's deliberate intervention in the text; Varvaro 1970, 87.

[6] Few contributions started a research in this sense: Zakī 2011, Fani 2013, Raggetti 2016.

[7] Zerdoun 1983, 111.

[8] Zerdoun 1983, 124; Schopen 2006, 130.

[9] Cohen, PhD thesis to be published in 2019.

writing materials as their non-Jewish neighbors.[10] Therefore, the Jewish records might be an excellent source for studies of the technology that corresponds to the place and time of the source. In this respect, it is interesting to compare the ink of Rashi (Rabbi Salomon ben Isaac), a Jewish author who lived in Northern France in the eleventh century, with the commentaries of Maimonides. In the Orient, Maimonides was familiar with the palette of all possible inks: carbon, plant, iron-gall, and mixtures of carbon inks with plant or iron-gall inks. In contrast, the arguments of Rashi allow us to conclude that mostly plant and maybe iron-gall ink were in use in northern Europe during the eleventh century. It is noteworthy that mixtures of carbon and iron-gall ink were found in some drawings of German artists in the fifteenth and sixteenth centuries.

The wealth of recipes for the black mixed inks in the Orient, on the one hand, and the absence of analytical evidence of their existence, on the other, raises two questions:

1. Is there a simple method for recognizing these inks?
2. Why would one use a mixture of two black inks?

Let us start by looking at the methods employed in the ink studies. Raman spectroscopy has been extensively used to identify materials such as pigments in paintings and archeological artefacts.[11] Generally, Raman spectroscopy probes the change in the wavelength of light that occurs when a light beam interacts with molecular vibrations (Raman scattering). Reliable Raman identification of mediaeval black inks started to emerge during the past decade[12] and shows that soot, logwood, and iron-gall inks have characteristic Raman spectra that provide a recognition pattern.[13] Therefore, Raman spectroscopy presents the cleanest and the most straightforward method to identify carbon and iron-gall inks and is therefore well suited to document a mixture of both. In the example below, mixed carbon and iron-gall inks were found in addition to the pure iron-gall inks of the main text of a Syriac manuscript (a sacred text, fourteenth century). The amount of added carbon was variable: ink A in Fig.1 contains less carbon than ink B, so that the features related to iron-gall (blue

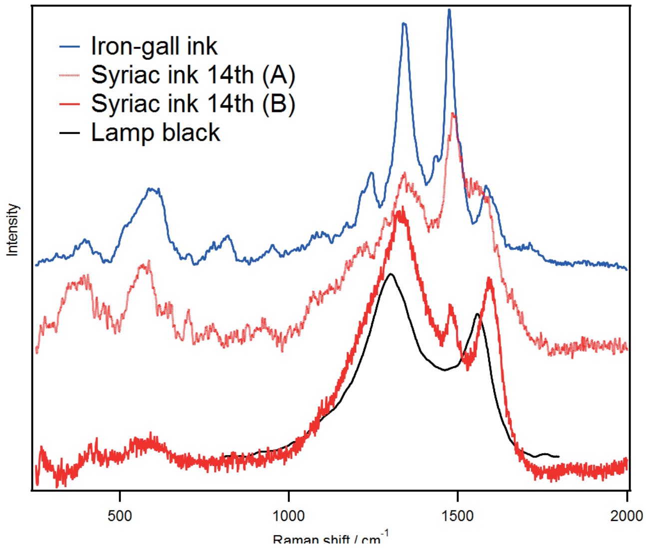

Fig.1: Raman spectra of Syriac inks (red), 14th century. The spectra of a standard laboratory sample of iron-gall ink (blue) and lamp-black ink (black) are reported for comparison. The spectra are stacked for the sake of the presentation.

curve) are more evident in spectrum A, whereas spectrum B look similar to the carbon ink (black). The Raman peak at about 577 cm^{-1} and the XRF control test on both inks confirmed the presence of iron in the ink.

Unfortunately, despite the recent development of portable Raman spectrometers, black ink analysis using Raman technique still often requires a bench instrument or the extraction of samples in addition to trained personnel.

Furthermore, Raman measurements on plant inks, i.e., inks based on tannin but not containing metals, yield no conclusive spectra with lasers in the VIS wavelength range whereas better results can be obtained by exciting the sample with a laser in the near-infrared.[14] In many cases strong fluorescence (= emission of light after excitation) of organic molecules considerably disturbs the spectrum. To overcome this difficulty, it has become customary to use Surface-Enhanced-Raman-Spectroscopy (SERS) in studies of modern paints and dyes.[15] SERS is a powerful technique in which the Raman scattering of molecules is enhanced by several orders of magnitude (up to a factor of 10^{11}) due to their adsorption by plasmonic metal surfaces (e.g. gold or silver nanoparticles) or nanostructures.[16] The simultaneous quenching of fluorescence allows measurements of strongly

[10] Rabin et al. 2014

[11] Smith and Clark 2004; Vandenabeele et al. 2007.

[12] Lee et al. 2008.

[13] Bicchieri et al. 2008.

[14] Bicchieri t al. 2017.

[15] Pozzi and Leona 2015.

[16] Schlücker 2014; Pozzi and Leona 2015; Lee and Meisel 1982.

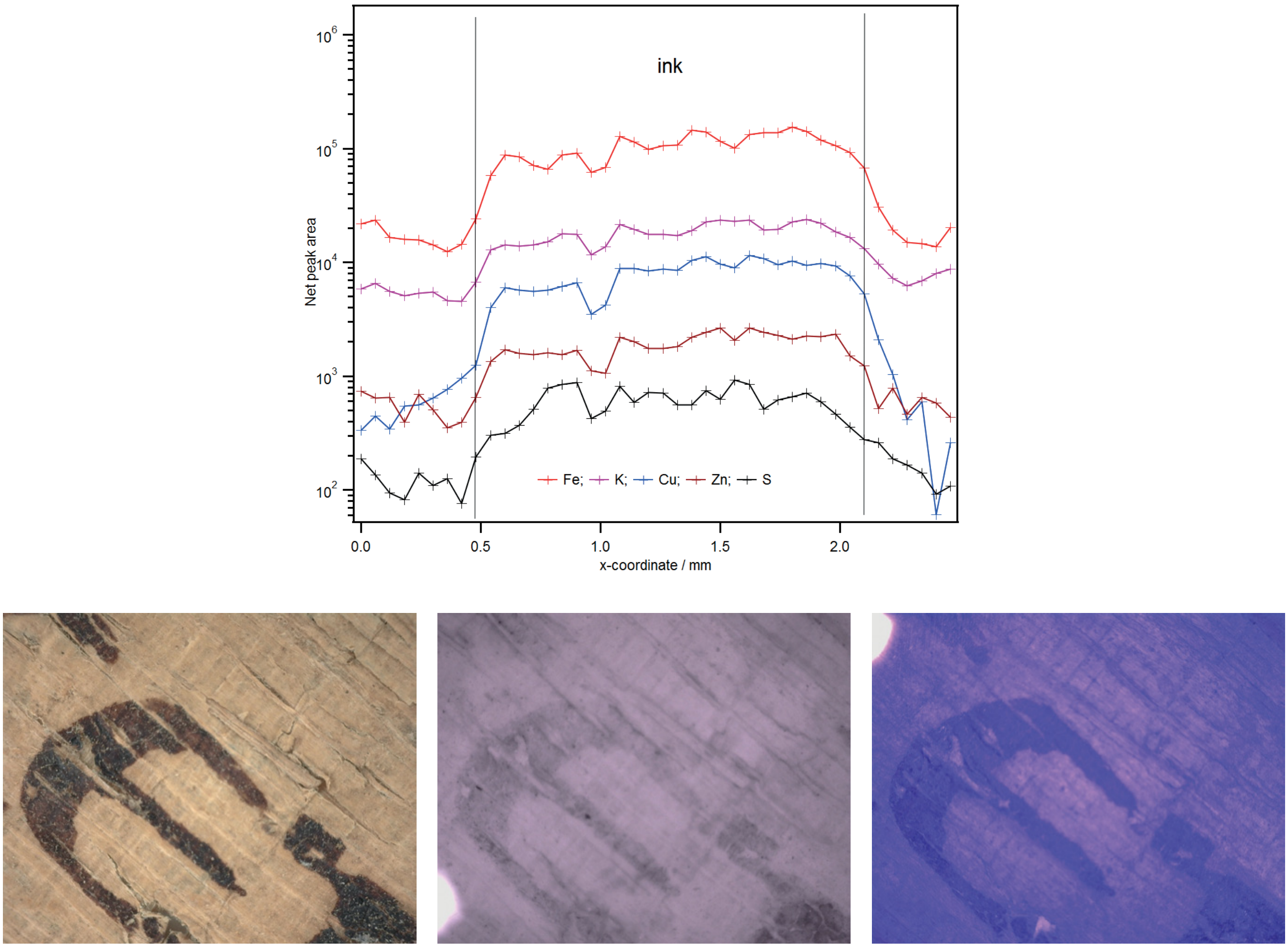

Fig. 2: Sahidic papyrus fragment Ms. Thompson HT 110.1. Fig. 2a (top): Intensities of the ink components extracted from an XRF line scan across the letter shown in the bottom images. Figs 2b, 2c and 2d (bottom): micrographs under white (left), near-infrared light (middle), and ultraviolet light (right).

fluorescent materials as well. Many different procedures for synthesizing and modifying SERS substrates have been described to optimize SERS for different kind of materials.[17] SERS is a micro-invasive technique that, depending on the selected substrate, requires a certain amount of sample. Attempts have been made, for cultural heritage purposes, to reduce the sample amount to a minimum and to optimize it.[18] In the case of tannin and iron gall ink, our first SERS tryouts yielded positive results. However, an optimized substrate and procedure for SERS on tannins and mixed inks need still to be defined. This means that, for the time being, we cannot use Raman technique to detect mixed inks on a large scale in situ and have to find a simpler way to conduct a primary classification similar to the one adopted in our ink test protocol.[19]

In short, we use the comparison of the images recorded under white and near-infrared light to quickly classify the inks by type (carbon, plant, or iron-gall). The simplicity of the test encouraged many codicologists and paleographers to adopt our methodology and share with us the results of their own field studies. As a result, a considerable number of papyri from the turn of the era started undergoing routine reflectographic checks in various collections. The knowledge of the ink type helps select which inks to study more closely. In such cases, following the reflectographic screening, we perform X-ray fluorescence analysis (XRF) on selected inks to determine their elemental composition and, in the case of the iron-gall inks, their fingerprint.[20] For the carbon inks,

[17] Pozzi and Leona 2015; Fan et al. 2011; Le Ru and Etchegoin 2009.

[18] e.g. Pozzi and Leona 2015; Lofrumento et al. 2012; Gomez and Lazzari 2014.

[19] e.g. Ghigo et al., present volume.

[20] Hahn et al. 2004; Rabin 2014.

we have used XRF to identify trace elements that could indicate characteristic contaminations. It was XRF analysis of the carbon inks that led to a successful identification of metals whose amounts hinted at intentional admixture rather than unintentional contamination.[21] In general, NIR reflectography is a quick and perfect method when dealing with an ink of a pure class, since carbon, plant, and iron-gall inks have very distinct optical properties. However, no unequivocal identification of mixed inks seems possible, since a considerable amount of carbon ink should mask the presence of any other component when illuminated with NIR light. On the other hand, tannin's property of quenching fluorescence and enhancing the contrast between a fluorescing background and the text makes UV reflectography a fine tool for identifying tannins or tracking the texts written with inks containing tannins. Since tannin solution deeply penetrates the substrate, it stays in it even if the text is removed from the surface. Therefore, the contrast enhancement achieved by UV light illumination has been widely used to recover lost writing done in iron-gall ink.[22] In the example below, we analyzed the ink in the Sahidic papyrus fragment from Cambridge University Library (Ms. Thompson HT 110.1). In the top part of Fig. 2, we present the individual intensities of the elemental components resulting from a line scan across a heterogeneously degraded letter shown in the three bottom images. Note that the curve form of each element in the graphics follows that of iron, the main component of iron-gall ink, revealing the composition of the ink. Iron, copper, and zinc represent the vitriol used in the recipe, sulfur indicates that the ink indeed contained vitriol, i.e., a mixture of metallic sulfates, and potassium is strongly associated with the tannins and gum arabic that was traditionally used as a binder. The varying thickness and degradation of the ink are reflected by the variability of the signal for iron and its satellites within the inked area. The changes in the opacity of the iron-gall inks can be seen in the bottom part of the same picture. Here the left, middle, and right images present micrographs taken under white, near-infrared (NIR), and ultraviolet (UV) light, respectively. The text penned in iron-gall ink that is perfectly visible under normal illumination becomes almost transparent when illuminated with NIR light, but regains its opacity under UV light. The latter picture shows the presence of tannin in the iron-gall ink.

We hope that tannins or the carbon/plant or carbon/iron-gall inks would be also detectable if they suffered damage and have been partially removed from the surface. Meanwhile, we started employing XRF for a routine screening of carbon inks to identify metals in metal-containing carbon inks. The fragment below is part of a demotic text concerning dream divination. It comes from Tebtynis and dates to c. 100–200 CE. It derives from clandestine excavations and was acquired by the Carlsberg Foundation on the antiquities markets of Cairo sometime between 1931 and 1938.[23]

The images in the top row of Fig. 3 show that there is no change in the opacity and intensity of the black color when the illumination is switched to NIR, proving the carboniferous nature of the ink. At the same time, the images in the bottom row show that the distributions of Ca and Fe correlate with the text, suggesting their presence in the ink. Strictly speaking, the presence of iron can't be considered unequivocal proof of iron-gall ink, since iron could have wandered into the ink as unintentional contamination. Here, however, ink contains also the element Ca, which has been detected many times in iron-gall inks. Therefore, we can assume here that we are dealing here with a mixed carbon and iron-gall ink, even though no Raman test for an unequivocal identification of iron-gall ink has been conducted.

The very early date of this ink correlates well with the detection of iron-gall ink coeval with the Coptic codex.[24] Therefore, we can assume that iron-gall ink was indeed in use in Egypt as early as the third century CE. However, it is not clear whether the production technology was always based on vitriol. In our example above, no copper, zinc, or other common iron satellites from vitriol could be detected. It is possible that metallic iron from nails was used: when soaked for a prolonged time in vinegar, the oxidation will result in the production of iron ions ready to react with tannins. We find that some of the oldest recipes in the Arabic collection prescribe using iron filings with or without acid.[25]

After establishing that the scarcity of analytical evidence results from the difficulties of unequivocal identification, we are left with a historical question of the emergence of the

[21] Nir-El and Broshi 1996; Brun et al., 2016; Christiansen et al., 2017; Rabin 2017.

[22] Rabin et al. 2015.

[23] Christiansen et al. 2017.

[24] Ghigo et al., present volume.

[25] Schopen 2006, 98–101, 124–125.

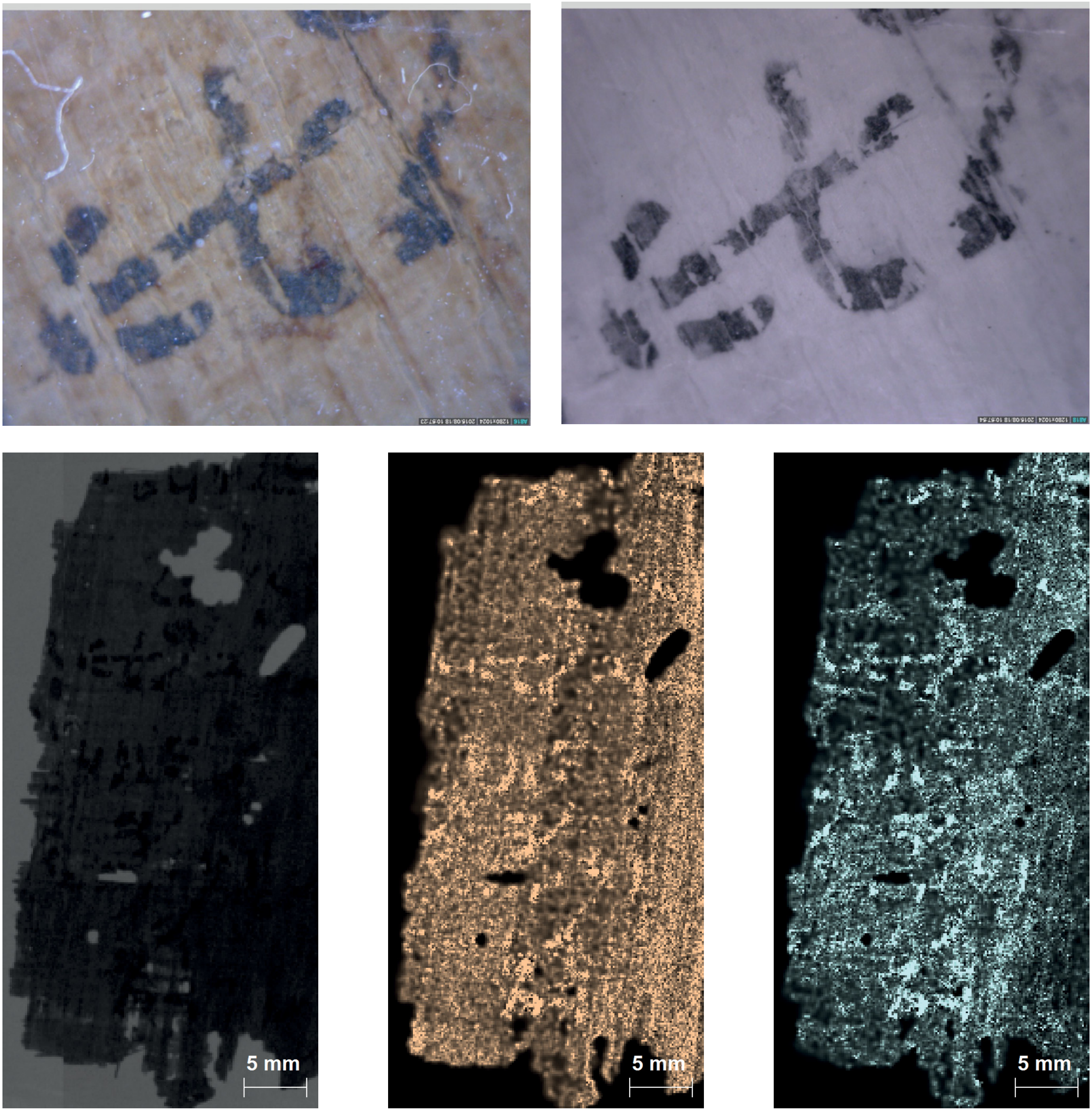

Fig. 3: Images of the papyrus P. Carlsberg 649. Top: micrographs under white (left) and near-infrared light (right). Bottom: visual image (left), calcium (middle) and iron (right) maps of the fragment.

mixed inks. The very early appearance of iron-gall inks and a high number of papyri inscribed with this ink overturn the generally accepted opinion that iron-gall ink accompanied the change of the substrate from papyrus to skin-based writing surfaces.[26] Moreover, thousands of the Dead Sea Scroll fragments inscribed with carbon inks speak strongly against this theory.

We believe that the explanation can be found in the entry 'Atramentum' of the very first encyclopedia preserved in the Western world: *Natural History* of Pliny (35.25). He recounts a number of ways to obtain black writing inks, where salts or dried leaves could be used in addition to soot. In other words, in the late Roman period, inks produced according to different recipes were in use. Given that Pliny mentions blue vitriol (copper sulfate) as 'shoemaker black' (34.123), it is rather obvious that the Romans had not yet arrived

[26] Diringer 1982, 551.

at the understanding that only green vitriol (iron sulfate) reacts with tannins to produce black substance. It is highly probable that early iron-gall ink was brown like tannin inks, so that carbon was added to obtain black ink. Alternatively, expensive carbon ink could have been adulterated by adding various dark liquids.

In any case, once we are aware of the existence of the mixed inks, we will be able to develop a suitable method for detecting them.

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Article

An Attempt at a Systematic Study of Inks from Coptic Manuscripts

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Introduction

When it comes to Egyptian writing and drawing materials, it is surprising to realize how much information we have on pigments compared with the little we know about inks.

It is well documented that throughout Antiquity, ancient Egyptians used mostly carbon inks as a writing material.[1] In Late Antiquity, some metals started to be added to carbon-based inks. We have records of five manuscripts from the Dead Sea Scrolls collection whose carbon inks were found to contain copper.[2] Also, lead was recently found as an additive in carbon inks on a charred fragment from Herculaneum.[3] Furthermore, the earliest evidence of iron-gall ink was found in the Book of Proverbs (Codex Ms. Berol. orient. oct. 987) dating to the third fourth centuries CE.[4] It has been suggested that along with carbon and iron-gall inks, there is no reason to think that purely tannin inks were not also in use in Egypt.[5] However, so far, we just have evidence of a copper-tannin ink identified in a number of documents from Egypt in the first third centuries BCE.[6]

In an attempt to fill this gap in this extremely fragmented scenario during our studies of the socio-geographic history of inks, we arrived at the conclusion that the continuous production of Coptic manuscripts from Late Antiquity to the Middle Ages offers a unique opportunity for the historical study of inks across a large geographic area. Few analyses with specific reference to Coptic Egypt have been conducted so far. Among them, we can list the study of a fragment of parchment purchased in Cairo in the mid-1970s. This revealed that the two sides of the document had been inscribed with iron-gall inks that differ in their metal salts composition, suggesting that the same manuscript may have been inscribed by more than one person or by the same person but at different times.[7] A previous study of Coptic inks and pigments laid on a variety of supports dating from the sixth to the eighth centuries, pointed out that carbon ink was used on pottery while iron-gall inks were used on parchment.[8]

Aim of the project

The studies presented so far are just sporadic pieces of investigation into the history of writing materials in Egypt. For this reason, thanks to the collaboration with the ERC project 'PAThs' (www.paths.uniroma1.it) based at the Sapienza University of Rome and within the activities of a PhD research dedicated to this topic, we created a new project focused entirely on the analysis of Coptic inks. Pigments and dyes, if present in the manuscripts, will also be investigated.

This study of Coptic codices will address primarily the history of the development of inks. As stated above, we have record of different kinds of inks used in Coptic fragments, but we still do not know if this difference is due to an evolution of materials and methods during the Coptic period or to a regional arrangement of the writing materials, which seems to be very possible considering that the Coptic language experienced a regional fragmentation into various dialects throughout its history.[9] We hope that systematic study will be able to unequivocally address the validity of MacArthur's suggestion that the choice of ink type might

[1] e.g. Lucas 1962.

[2] Nir-El and Broshi 1996.

[3] Brun et al. 2016.

[4] Rabin and Krutzsch 2016 (unpublished lecture).

[5] Buzi and Emmel 2015.

[6] Delange et al. 1990.

[7] Rabin et al. 2012.

[8] MacArthur 1995.

[9] Buzi 2015.

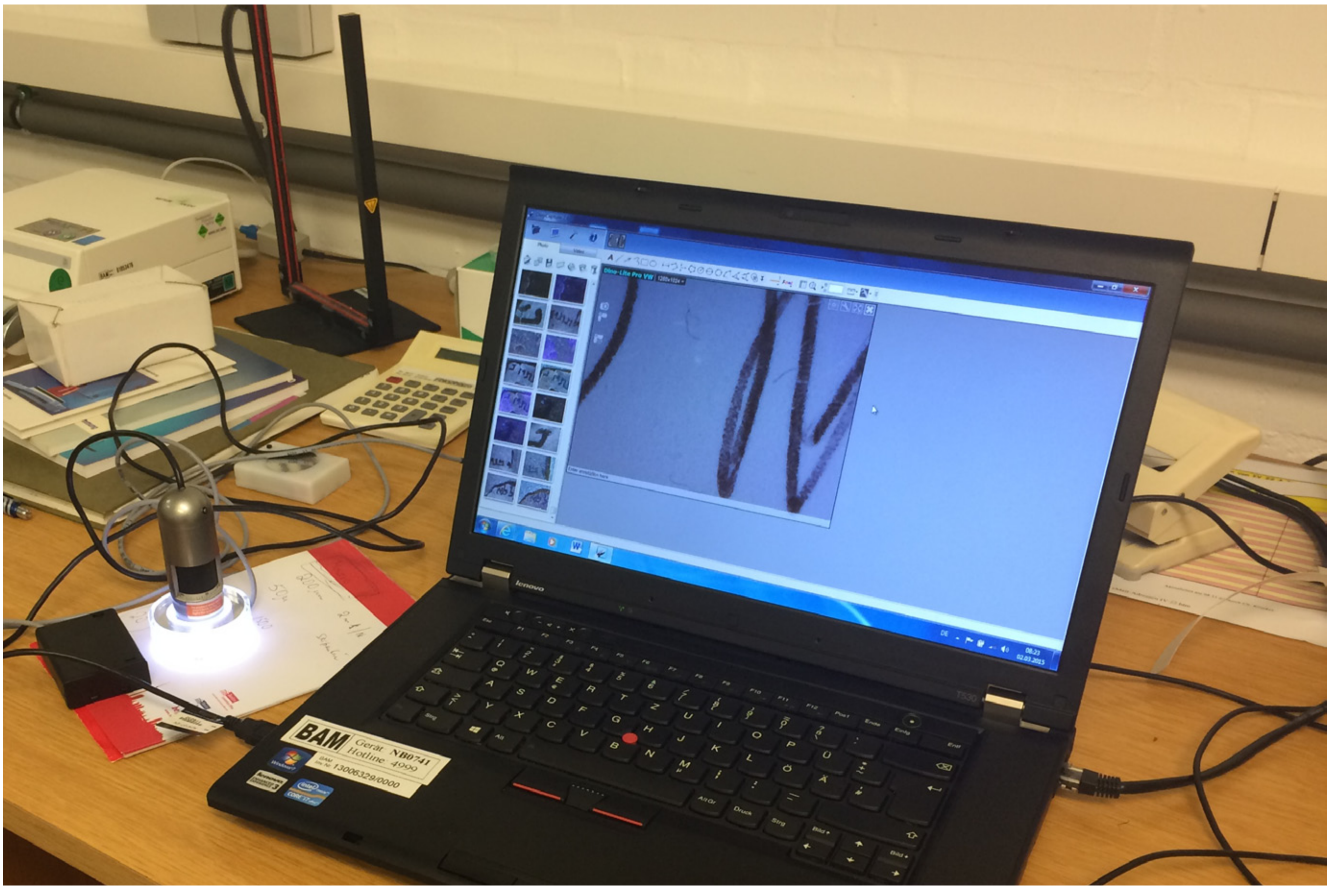

Fig. 1: DinoLite microscope, AD413T-12V.

have depended on the writing surface.[10] Therefore, the study will include the detailed description and characterization of the writing surfaces parchment and papyrus. Of course, it is also possible that more than one of the conditions presented above coexisted in the same temporal and spatial context, thus making the results of this study even more important.

Aside from the study of the history of writing materials, this investigation may make a valuable contribution to Coptic paleography and codicology. As already demonstrated in a previous study,[11] a correct scientific approach to the study of writing materials makes it possible not only to distinguish among different types of inks, but also, in the case of iron-gall inks, to distinguish among different types of materials used in the preparation of the inks. This information, if complemented by additional paleographical and codicological expertise, might lead to some interesting considerations regarding the persons and phases involved in the production of a specific codex.

Finally, the ink production recipe revealed by scientific methods can be used as a geochronological marker, making it possible to lay a first foundation stone for an inks database. This could help to date, localize, or provide new elements for understanding the typology and dating of some other Coptic scripts, thus completing dating results obtained so far from paleographic and textual methods.

Corpus

The full corpus of the documents covering a broad time span is still to be defined and adjusted in accordance with the results obtained in the course of work. In any case, we are going to work with the texts whose codicological and paleographical aspects have been properly studied in the frame of the PATHs project.

Our first analysis deals with the manuscripts that very likely originate in the cathedral of Thi(ni)s, nowadays Girga, located not far from Abydos. The library of Thi(ni)s is indeed a crucial and transitional instance in the history of Coptic manuscripts, which saw the creation of new codicological and palaeographical features, on the one hand, and the

[10] MacArthur 1995.

[11] Rabin et al. 2012; Buzi 2016.

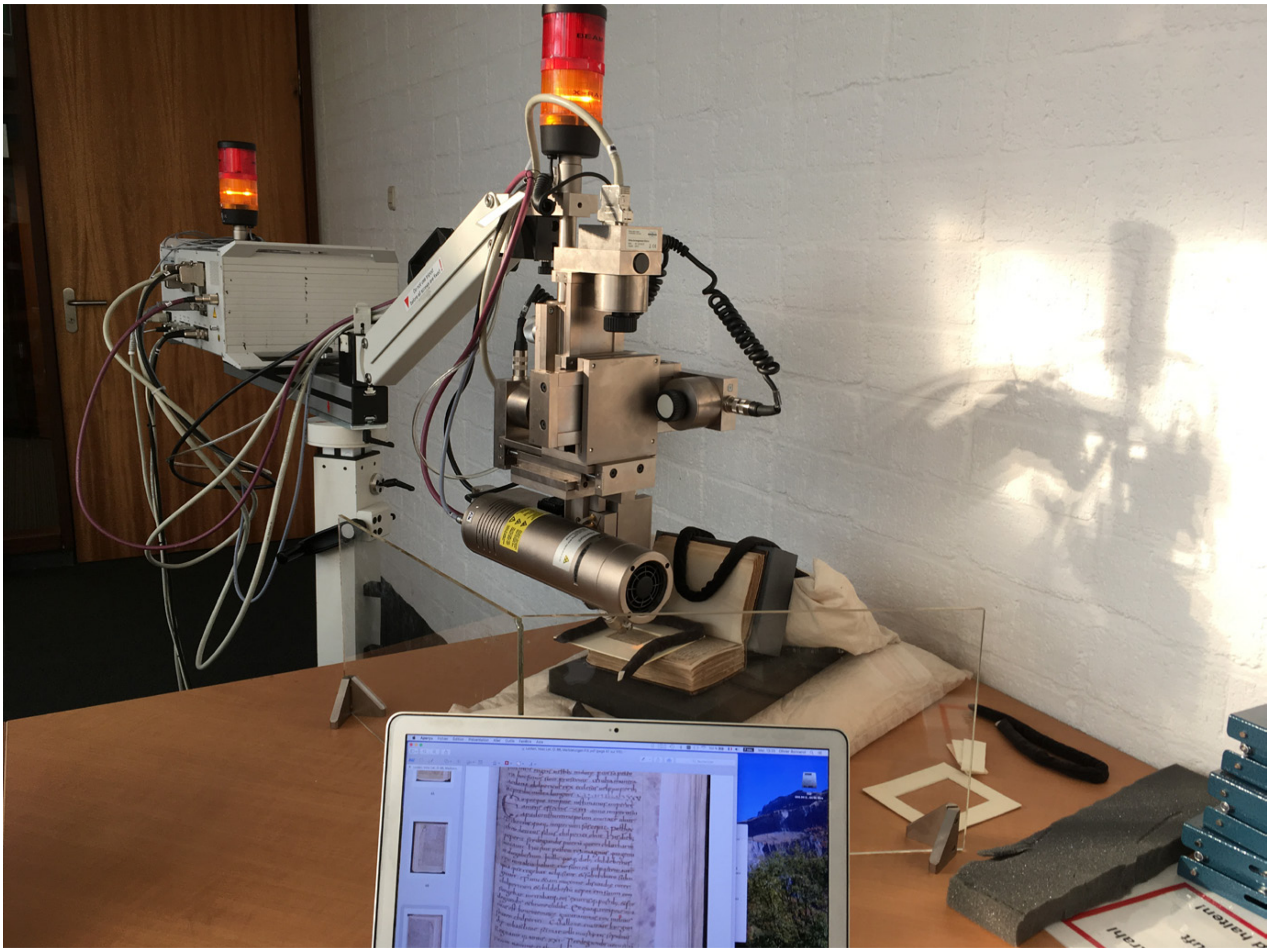

Fig. 2: ARTAX Bruker Nano GmbH.

progressive emergence of multiple-text codices, on the other. This explains the great importance of acquiring information concerning the material aspects of these codices. Besides, the fact that the manuscripts in question were very likely manufactured in a limited span of time and were written by a limited number of copyists made the study of the library of Thi(ni)s the first choice in our corpus.

The other collection to be analyzed includes fragments from the White Monastery in Sohag (Upper Egypt). Under the leadership of Shenoute (approximately 348–465/66 CE), the confederation of monasteries coordinated by the White Monastery became one of the most important centers of Coptic literary production. Its library (dating back to the ninth–eleventh centuries) is nowadays preserved in several collections all over the world, because the codices were dismembered and ended up in different places[12] such as the Staatsbibliothek zu Berlin (State Library Berlin)and the Bibliothèque nationale de France (National Library of France) in Paris.

Furthermore, we will work also on some manuscripts from the Michaelides collection. George Michaelides, a Greek collector who died in 1873, possessed a fine collection of manuscripts. The Cambridge University Library acquired part of this collection between 1976 and 1979, including some texts in Coptic. According to Michaelides, the texts date to the period between the sixth and ninth centuries and originate in the Fayyum region.[13]

Growing recognition of the importance of the material studies of the manuscripts, coupled with the development of the non-invasive protocols, encouraged many renowned institutions to give us access to their collections. We have already carried out analysis at the Egyptian Museum in Turin, at the State Library Berlin, and at the Cambridge University Library. During the first year of the project, we

[12] Buzi 2016.

[13] Clackson 1993.

plan on performing the analysis also at the Apostolic Vatican Library in Rome and at the National Library in Paris. Finally, the Bodmer Library in Cologne has also expressed its interest in cooperating with the project.

Experimental protocol and equipment

Our standard protocol for ink analysis consists of a primary screening to determine the type of the ink and a subsequent in-depth analysis using several spectroscopic techniques: XRF, FTIR, and Raman .[14]

The primary screening is carried out by means of NIR reflectography. Strictly speaking, optical differences between carbon, plant, and iron-gall inks are best recognized by comparing their response to the infrared light: carbon ink has a deep black colour, iron-gall ink becomes transparent above 1200 nm, and plant ink disappears at about 750 nm. We have simplified the analysis using a small USB microscope (with the built-in NIR (940 nm) and UV (390 nm) LED in addition to an external white light source. Working at 940 nm, we determine the ink typology by observing the changes in the opacity of the ink. Here, carbon-based inks show no change in their opacity when illuminated with NIR wavelengths, while the opacity of iron-gall inks changes considerably, and plant inks become transparent.[15] The in-depth investigation includes micro-XRF analysis to obtain the contribution of the inorganic components of the ink. In the case of iron-gall inks, we establish the fingerprints, i. e., the characteristic ratios of the vitriolic components of the ink.[16] Finally, in specific cases that may require more insight and further investigation, we perform FTIR spectroscopy to collect information on the chemical composition of the binders and Raman spectroscopy to determine the co-presence of carbon and iron-gall ink.

First results

The evidence of the earliest iron-gall ink we have ever measured comes from the Book of Proverbs kept at the Staatsbibliothek in Berlin (Ms. Berol. orient. oct. 987).

The single-layer Book of Proverbs codex consists of forty bifolia and three single folios that were cut to shape from three papyrus rolls. As Hugo Ibscher[17] has already determined, the rolls were previously halved in height. The dimensions of the folios are about 13 cm (height) × 29 cm (width), while the inner double folios are up to 4 cm narrower because this was the only way the form of the book block could be shaped in a unified way. If the double folios, detached from the codex, are laid beside each other individually in the sequence of the pages in the codex, the work method of cutting the sheets to shape from the roll becomes recognizable. The course of the fibers on the recto side shows that the double sheets were cut from the roll from right to left.

It is difficult to examine the material quality and technical details of the papyrus, because the codex was embedded in chiffon silk in 1958 and 1959. It is nonetheless possible to determine that the papyrus material is of low quality and poor structure. The quality difference between the recto and the verso is obvious. Thus, many verso sides display conspicuously dark, very coarse fiber strands. Six double folios (fols 2, 4, 12, 21, 30, and 40) have patches; here, too, these are on the verso side.

An examination of the codex showed that two-thirds of the double sheets display two sheet glue bonds each; one-third have only one-sheet glue bond; and one double sheet has no glue bond. The sheet glue bonds are manufactory glue bonds[18] of the common Type II. As could be expected, the left sheets lie over the right sheets. The sequence of the sheets thus corresponds with the direction of the script. The width of the glue bonds varies between 2 and 3 cm; it reaches 3.5 cm in three cases and even 4 cm in one case. Precisely the width of the sheet glue bonds can indicate the time of the production of the papyrus material placing it in in Roman or even Byzantine times.

Figures 3a and 3b show the reflectographic images and the XRF spectra. The observed loss of opacity when the illumination is changed from the white (Fig. 3a left) to the NIR light (Fig. 3a right) indicates that the ink belongs to the iron-gall type. In Fig. 3b, we observe that the peaks corresponding to iron (Fe), copper (Cu), and potassium (K) grow considerably in the spectrum of the inks as compared with that of the underlying writing surface papyrus. A constant ratio between copper and iron, found throughout the ink of the manuscript, delivers a decisive proof that we are dealing with iron-gall ink.

[14] Rabin et al. 2012.

[15] Mrusek et al. 1995.

[16] Hahn 2010; Rabin 2012.

[17] Ibscher 1958.

[18] Krutzsch 2017.

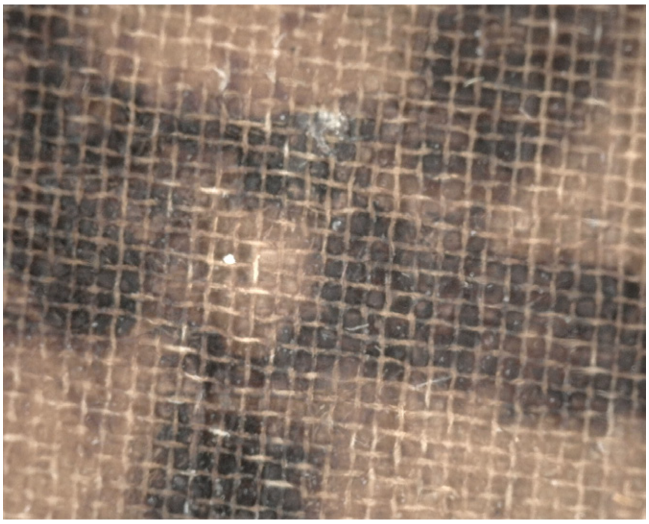

Fig. 3a: VIS images of a black ink from the Book of Proverbs.

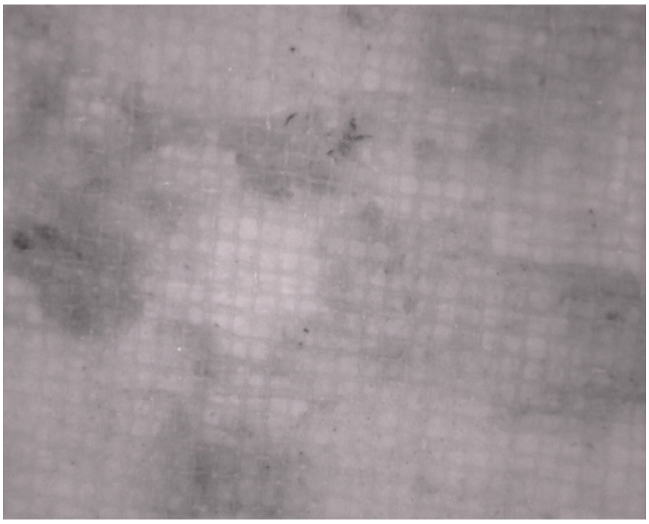

Fig. 3b: NIR images of a black ink from the Book of Proverbs.

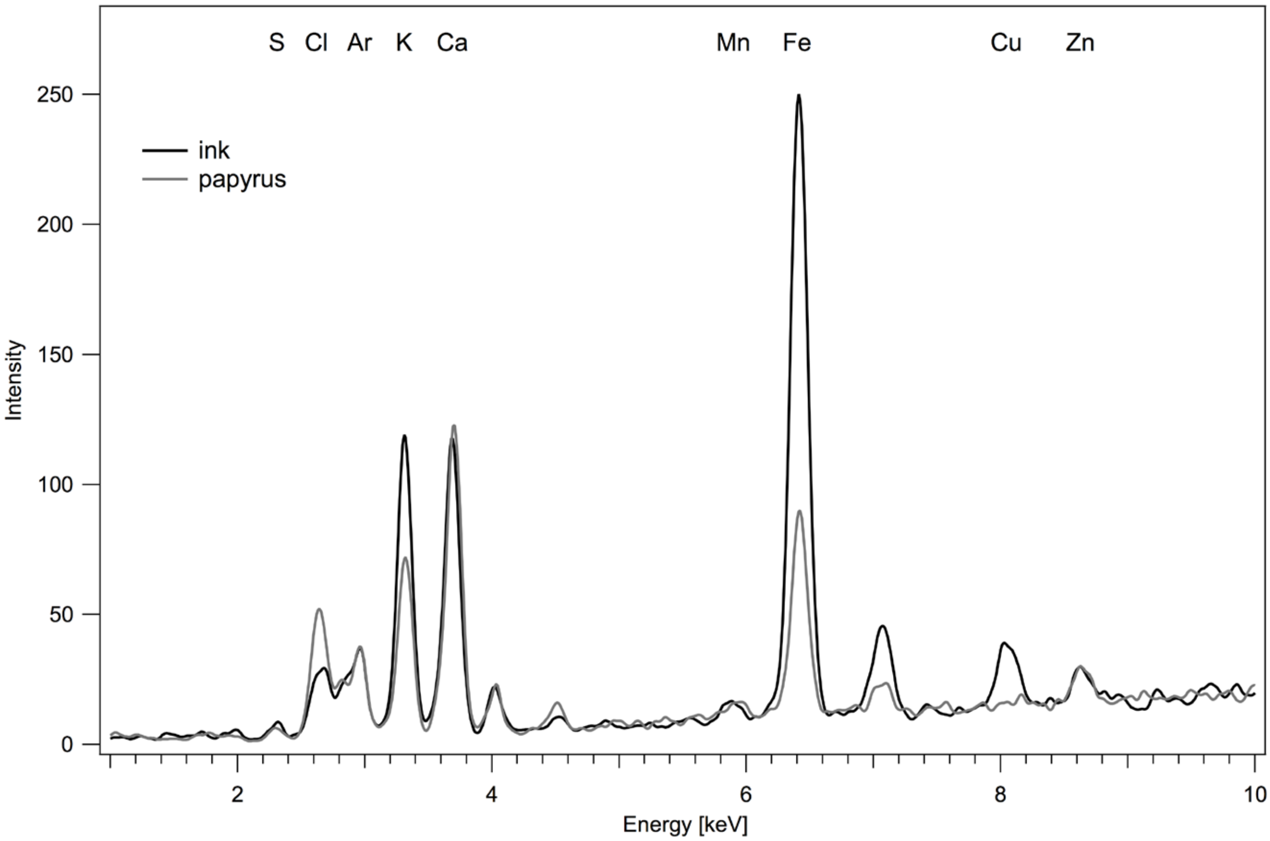

Fig. 3c: XRF spectra of the papyrus and the ink (grey and black curves, respectively).

Fig. 4a: VIS images of a black ink from Codex II preserved at the Egyptian Museum in Turin.

Fig. 4b: NIR images of a black ink from Codex II preserved at the Egyptian Museum in Turin.

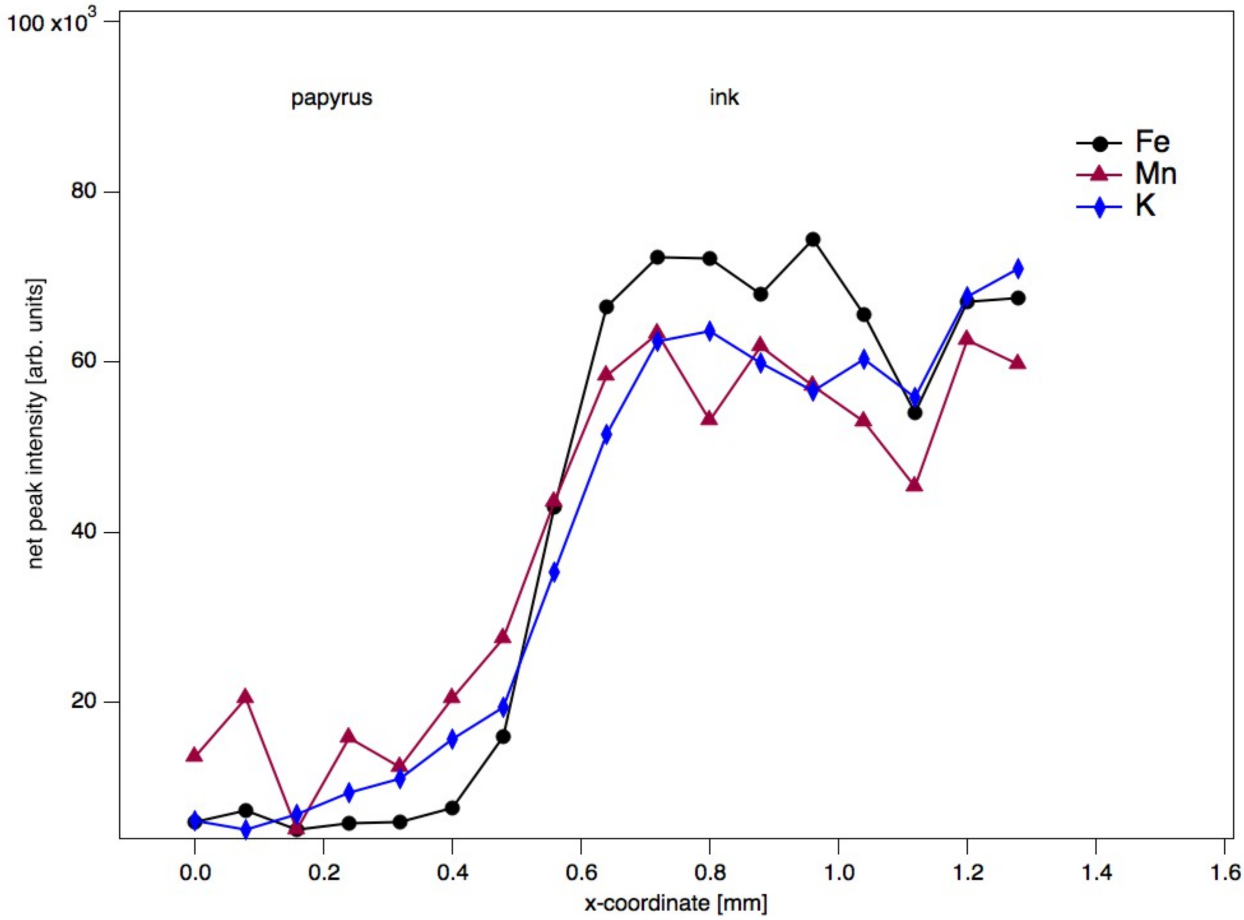

Fig. 4c: Intensity profiles of the characteristic ink from Codex II preserved at the Egyptian Museum in Turin.

Our next surprising finding was that a deep black colour of the ink from the Thi(ni)s fragments corresponded to iron-gall rather than carbon ink, as we instinctively believed. As in the previous case, the change in opacity observed in reflectographic analysis indicated the iron-gall nature of the ink. The composition study by means of XRF analysis confirmed a considerable growth of the iron signal in the ink. Figure 4b shows the intensity profiles of the elements iron, potassium, and manganese extracted from the measurements taken along the line connecting non-inked and inked areas, called the line scan. From the similarity of the profiles, we conclude that all three elements belong to the ink composition. Potassium is usually present in plant inks, but its increased abundance most probably indicates that gum arabic was used here as a binder in accordance with many recipes for iron-gall inks. The element manganese could be an indication of the use of a specific form of vitriol that lacked copper and zinc. On the other hand, it could be an indication that the ink was produced using a source of iron other than vitriolic salts. We plan to address this question in our future experiments.

Our third preliminary result that we would like to mention here is connected with the Michaelides collection preserved at the Cambridge University Library. Here we find carbon and iron-gall ink in different fragments that allegedly originated in the same region and within a relatively short time span, thus confirming the coexistence of different kinds of ink in Coptic Egypt.

Conclusion

The number and reputation of the institutions involved indicate that the study attracts the attention not only of the community of scholars working on Coptic manuscript tradition, but also of all professionals dealing directly or indirectly with the history of inks and writing materials. In fact, this pioneering study aims not only at a better understanding of the complex Coptic multicultural and plurilingual society, but also and mainly at clarifying the links among the Coptic and other societies in the ancient and medieval eras. Finally, it will cast light on the history of the technological development of inks in the Eastern world, from Antiquity to the Middle Ages.

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We would like to acknowledge the help of the personnel of the museums, archives and libraries who permitted our access and supported our work. Our special thanks go to the staff of Fondazione Museo delle Antichitá Egizie di Torino, in particular to Susanne Töpfer, Thomas Christiansen, and Sara Aicardi, who allowed and supported every step of our analytical campaign. Warm thanks are also due to the staff of the Staatsbibliothek zu Berlin, especially to Christoph Rauch, Melitta Multani, and Nicole Fürtig.

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TEA GHIGO, IRA RABIN

ARCHAEOMETRIC STUDY OF INKS FROM COPTIC MANUSCRIPTS IN THE COLLECTION OF THE APOSTOLIC VATICAN LIBRARY*

The frame of the project on Coptic inks

While studying the socio-geographic history of inks, the division 4.5 of the BAM (Bundesanstalt für Materialforschung und Prüfung),[1] dedicated to the study of cultural material, together with the Centre for the Study of Manuscript Cultures in Hamburg[2] concluded that the continuous production of Coptic manuscripts from late Antiquity to the Middle Ages offers a unique opportunity for the historical study of the ink in a large geographic area. Thanks to the collaboration with the ERC project "PATHs" (www.paths.uniroma1.it), based at the Sapienza University of Rome, and within the activities of a joint PhD project between the University of Hamburg and the Sapienza University of Rome, we therefore created a new branch of our project focused entirely on the analysis of Coptic inks, pigments, and dyes.[3] This pioneering systematic study of writing materials coming from a specific area and time frame (4th-12th century) aims not only at a better understanding of the complex Christian Egyptian multicultural and plurilingual society, but also and mainly at clarifying the links among the Coptic and other manuscript cultures between the ancient and medieval eras. Finally, it will cast light on the history of the technological development of inks in the eastern world, from Antiquity to the Middle ages.

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* The research presented in this article was carried out at the SFB 950 "Manuskriptkulturen in Asien, Afrika un Europa", funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) and within the scope of the Centre for the Study of Manuscript Cultures (CSMC), in collaboration with the ERC Advanced Grant Project "PAThs" – "Tracking Papyrus and Parchment Paths: An Archaeological Atlas of Coptic Literature. Literary Texts in their Geographical Context: Production, Copying, Usage, Dissemination and Storage" (project no. 687567) of "Sapienza" University of Rome. Our special thanks go to the staff of the Apostolic Vatican Library who permitted our access and supported our work.

[1] [www.bam.de].

[2] [https://www.manuscript-cultures.uni-hamburg.de/index_e.html].

[3] T. Ghigo – O. Bonnerot – P. Buzi – M. Krutzsch – O. Hahn – I. Rabin, *An attempt at a systematic study of inks from Coptic manuscripts*, in *Manuscripts Cultures* 11 (2018), pp. 157-164.

The analytical protocol

Our protocol for ink analysis consists of a primary screening to determine the type of the ink and a subsequent in-depth analysis using several spectroscopic techniques.

The primary screening is carried out by means of near-infrared reflectography. This technique allows distinguishing between carbon ink, which stays black even at longer wavelengths (above 1200 nm), iron-gall ink that becomes transparent above 1200 nm and plant ink which becomes transparent at ca. 750 nm. To perform this analysis, we use Dino-Lite, a small USB microscope equipped with three different lights: NIR (940 nm), UV (390 nm) and an external white light source. Working at 940 nm we can determine the ink typology observing the changes in its opacity. At this wavelength carbon-based inks show no change in their opacity, while the opacity of iron-gall inks changes considerably, and plant inks become totally transparent. The in-depth analysis is carried out mainly using micro X-ray fluorescence. This technique detects any chemical element heavier than sodium contained in the inks. In the case of carbon and plant inks it allows the identification of any contaminant or any other element added to the pure ink. In the case of iron-gall inks micro X-ray fluorescence (XRF) is used to establish their fingerprints, meaning the relative composition of the metal salts used to produce the ink.[4] Finally, in specific cases that may require more insight and further investigation, Raman and Fourier Transformed Infrared spectroscopies (FTIR) are performed to collect information on the chemical composition of the inks and binders, while Fibre Optic Reflectance Spectroscopy (FORS) is applied to identify colorants and coloured pigments.

Results

Thanks to the support and permission from the Apostolic Vatican Library, we examined 31 parchment leaves now bounded in 5 different modern volumes. We also examined 4 papyrus leaves from *Pap. vat. copt.* 9. Given to time and logistical reasons not all the analytical techniques mentioned in the previous paragraph were applied to all the examined leaves. The table below describes the analysis performed on each leaf.

[4] O. HAHN – W. MALZER – B. KANNGIESSER – B. BECKOFF, *Characterization of iron-gall inks in historical manuscripts and music compositions using x-ray fluorescence spectrometry*, in *X-ray Spectrometry* 33 (2004), pp. 234-239.

Shelfmark	Leaves	Micro-NIR reflectography	XRF	FORS
Vat. copt. 1	1r	X	X	
Vat. copt. 1	31v	X	X	
Vat. copt. 1	65v	X	X	
Vat. copt. 1	66r		X	X
Vat. copt. 1	97v		X	X
Vat. copt. 1	157r	X	X	
Vat. copt. 1	166r	X	X	
Vat. copt. 1	225r	X	X	
Vat. copt. 1	225v	X	X	
Vat. copt. 57	1r	X	X	X
Vat. copt. 57	16r	X	X	
Vat. copt. 57	74r	X	X	
Vat. copt. 57	179r	X	X	X
Vat. copt. 57	184r	X	X	
Vat. copt. 57	230v	X	X	
Vat. copt. 57	256v	X	X	
Vat. copt. 58	10r		X	X
Vat. copt. 58	123r	X	X	X
Vat. copt. 58	132r	X	X	
Vat. copt. 58	138v	X	X	
Vat. copt. 58	150v	X	X	
Vat. copt. 68	5r	X	X	
Vat. copt. 68	15v	X	X	
Vat. copt. 68	16r		X	X
Vat. copt. 68	30r		X	X
Vat. copt. 68	33r		X	X
Borg. copt. 109, fasc. 141	9r	X	X	
Pap. vat. copt. 9	Glass 39	X		
Pap.vat.copt. 9	Glass 45	X		

Of the 31 examined leaves, 26 were produced in the Monastery of St. Macarius in the region of Wādī al-Naṭrūn. All the leaves coming from this monastery showed a quite homogeneous original nucleus, written using an iron-gall ink. This ink appears to be very similar in all the leaves examined since it contained mainly iron and only some traces of other metals such as copper and zinc. Considering that the amount of copper and zinc in an iron-gall ink can sometimes be very consistent depending on the composition of the salts employed in the ink making process (we found cases of iron gall ink containing 25% copper or 10% zinc), we can say that the original nucleus of the examined leaves was written with an ink manufactured using vitriol salt that contained only small amounts of metals other than iron (around 1-2%).

Iron-gall ink is, however, not the only type of ink that we found on these leaves. Evidence of later marginal notes and retracing made with carbon ink and mixed ink was found on *Vat. copt. 57*, f. 256v, *Vat. copt.* 58, f. 123r, *Vat. copt.* 1, ff. 65v and 157r. Mixed ink is a peculiar type of ink known to us through the ink recipes from the islamicate world that has often attracted little scholarly attention. A recent article casted new light on this type of ink stressing the need for an analytical procedure for unequivocal identification of it.[5] Unfortunately, the protocol we generally employ for the ink characterization isn't always sufficient in the case of inks containing both carbon and plant ink with or without the addition of metallic elements such as iron. Considering that for the time being the only written evidence we have on mixed inks comes from the islamicate world, the presence of mixed inks on Coptic manuscripts is a topic that deserves further attention. Mixed inks may offer a good opportunity to study the cultural interactions between the Egyptian and Arabic written traditions.

Another remarkable finding during the study of the collection from the Apostolic Vatican Library regards the 4 papyrus leaves that were examined (shelfmark: *Pap. copt.* 9). The analysis revealed that the ink used for writing was once an iron-gall ink. Considering the early dating of these leaves (5th century CE) this finding confirms the existence of iron-gall ink way before the appearance of the first recipe for its production we have so far (Theophilus Presbiter, 12th century CE). Although relevant, this is not a surprising result, since the first analytical evidence we have on iron-gall ink is on a Book of Proverbs preserved at the Staatsbibliothek of Berlin and dating to the 4-5th century CE (*Ms. or. oct.* 987).

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[5] C. Colini – O. Hahn – O. Bonnerot – S. Steger – Z. Cohen – T. Ghigo – T. Christiansen – M. Bicchieri – P. Biocca – M. Krutzsch – I. Rabin, *The quest for the mixed inks,* in *Manuscripts Cultures* 11 (2018), pp. 41-46.

Among the leaves from the Monastery of St. Macarius, the case of those preserved under the shelfmark *Vat. copt.* 1 was remarkable, they were all part of the same codicological unit which presents various levels of stratification: an original nucleus palaeographically dated around the 10^{th} century, some later leaves added whose script suggest a 13^{th}-14^{th} century dating, a marginal Arabic translation added on all the leaves of the codex whose palaeographical dating is not possible and some illuminations covering the whole early text on some of the leaves. The analysis of inks detected a difference in the composition of the metallic salts used to produce the ink of the main text of the original leaves, which contains mainly iron, and the ink on the main text of the added leaves, which contains iron and copper. This is a proof of the fact that the leaves come from a different writing phase. In an attempt to understand in which writing phase the Arabic translation was added, we compared its ink with the ink of the main text of original leaves and added leaves. Our results show that the ink used to write the Arabic translation contains both iron and copper and the ratio of latter to the former is in average higher than in the ink used to write the main text on the added leaves. This suggests that the Arabic translation belongs to a third writing place, which unfortunately cannot be placed in time. However, given the complexity of the structure of this codex, to confirm this outcome a thorough archaeometrical codicological study (i.e., based on the results from a greater number of analytical measurements) should be performed.

FORS and XRF were applied to identify pigments and colorants from the leaves of: *Vat. copt.* 1, *Vat. copt.* 57, *Vat. copt.* 58 and *Vat. copt.* 68. The identification was difficult since the pigments were often mixed together or overlapping. We identified different types of red pigments: red ochre, minium and cinnabar. Yellows were always identified as orpiment, and greens as malachite. Unfortunately, it was not possible to identify the organic blue pigment used to paint the mantle of the Virgin on *Vat. copt.* 1, f. 66r. All the pigments identified are coherent with the dating of the examined leaves, and they represent the typical medieval palette.

Archaeometric analysis on the Vat. copt. *57*

Our team has already many years of experience in handling unique and fragile samples for the purposes of instrumental analysis. In the specific case of *Vat. copt.* 57, during micro-NIR reflectography a piece of a Japanese paper was placed between the manuscripts and the USB microscope, to ensure no direct contact between the instrument and the page under investigation. This procedure limits the exposure of the fragile layers of pigments and ink to physical stress. For XRF analysis the fragment must be mounted in such a way that the surface under investigation is as flat as possible. Given the large dimension of this codex, we first used foam pillows to secure it and keep it in place. Then we used small cardboard frames padded with disposable Japanese paper to delimit the spots of analysis. The frames were kept in place by light ceramic weights designed for this purpose. The exposed section was generally two-three centimeters wide.

We analyzed a total of 7 different leaves from *Vat. copt.* 57. We chose 6 spots per folio, 3 recto and 3 verso, making sure to have a good representation not only of the ink used to write the main text, but also of the inks used for the titles, the decorations, the colophon and the two different types of corrections that were possible to distinguish with the bare eye: corrections made with what now appears to be a brownish ink (visible on f. 16r) and corrections made with what appears now to be a much darker ink (f. 1r, Fig. 1).

Results showed that the original nucleus of the manuscript (the main text, the titles, the decorations, the colophons and the brownish corrections found on f. 16r) was written with iron-gall inks that display the same fingerprint, suggesting that this all belongs to a single writing phase. Given the difference in colour between these inks and the one used to write the corrections on f. 1r, one may think that a different kind of ink was used to make these corrections. However, archaeometric analysis didn't show any difference between the composition of the metallic salt of this much darker ink and of other inks used. This suggests that the ink used for the corrections on f. 1r belongs to a different writing phase, but it was written probably in the same place of production of the rest of the Codex. A difference can be seen in the content of potassium, being in the darker ink about three times higher than in the other inks. Potassium was contained in high percentage in the binder that were used to prepare the inks, as well as in the gallnuts. In this case it is likely that this ink was prepared using a different proportion of binders and gallnut water mixed with the same kind of vitriol. The present study, however, does not aim at a thorough understanding of the different writing phases of the examined leaves. To do so, a statistically sound study, i.e. investigation of a larger number of leaves is needed,[6] as it was performed in the case of the Codex Germanicus 6.[7] The study of the pigments revealed that the red used for the titles and part of

[6] I. Rabin – O. Hahn – M. Geissbühler, *Combining Codicology and X-Ray Spectrometry to unveil the history of production of Codex Germanicus 6 (Staats- und Universitätsbibliothek Hamburg)*, in *Manuscripts Cultures* 7 (2014), pp. 126-131.

[7] M. Geissbühler – I. Rabin – O. Hahn, *Advanced codicological studies of Cod. germ. 6: part 2*, in *Manuscripts Cultures* 11 (2018), pp. 133-139.

the text was in some parts retraced using a different pigment (it is clear on f. 1r). The original red used is an ochre, while the retrace is made with cinnabar, a mercury based red pigment. The yellow pigment was identified as orpiment, and the green as malachite. A final remark needs to be done on two marginal notes found on ff. 179r (in Arabic, Fig. 13), 74r (Fig. 5) and 256v (in Coptic, Fig. 17). The Coptic note on f. 256v was written using a carbon ink and it is different from the others. The notes on ff. 179r, 230v and 74r were instead written using iron-gall ink. However, while the ink of the Coptic note on f. 74r contains mostly iron and it is similar to the ink used to write the main text, the inks of the Arabic notes contain both iron and copper, suggesting that they were written in a different phase. Unfortunately, on the reason why different notes were written on the same codex with different inks we can only speculate. The results achieved so far with our project on Coptic inks do not allow to place in space and time an inscription based on the kind of ink it was written with. However, this may be possible in the future, once enough analytical data will be collected to trace a map of the technological evolution of writing inks.

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ORIGINAL PAPER

Black Egyptian inks in Late Antiquity: new insights on their manufacture and use

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Abstract
We present here our methodological approach applied to the study of Egyptian inks in Late Antiquity. It is based on an interdisciplinary strategy, bringing together a variety of disciplines from humanities and natural sciences, and it aims at systematically collecting a statistically relevant amount of data regarding the composition of the inks. The application of a well-established, non-invasive protocol that includes near-infrared imaging and X-ray fluorescence spectroscopy for in situ measurements enables the identification and characterisation of inks dating from the end of Late Antiquity onwards. However, sometimes this method limits our understanding when characterising more ancient inks. Trying to overcome these limitations, the potential of a new device for the characterisation of organic compounds is here explored by conducting preliminary tests on mock samples. In this work, we present the results from 77 codicological units that include some of the earliest manuscripts of our corpus that presently lists 159 units.

Keywords Ink · Manuscript · Multi-instrumental analysis · Papyrus · Interdisciplinary approach

Introduction

To date, most of the scientific studies focusing on black writing media deal with iron-gall inks and their corrosion patterns (Rouchon-Quillet et al., 2004; Kolar and Strlic 2006; Rouchon and Bernard 2015), while only a minor part of the ongoing research aims at the characterisation of the materials used in the making of historical inks. Among the latter studies, many deal with the characterisation of inks on manuscripts from the Middle Ages onwards (Hahn et al. 2004; Rabin et al. 2014; Aceto and Calà 2017; Díaz Hidalgo et al. 2018). Similarly, it is well documented that in Antiquity mostly carbon ink was used as a writing material (Lucas 1922; Nicholson and Shaw 2000, pp. 238–239). In contrast, we have very scarce data regarding the manufacturing of inks from the Hellenistic period to the Middle Ages.[1]

Published in 1983, the study on the history of inks by Monique Zerdoun Bat-Yehuda (Zerdoun Bat-Yehuda 1983) is until today the only investigation systematically addressing the technological evolution of inks from Late Antiquity to early Renaissance, in a geographical frame extending from the Mediterranean world to Asia. In her survey, Zerdoun collects the written recipes available in literature, making an effort to identify all their ingredients, despite the terminological difficulties posed by different languages and historical

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[1] It should be stressed that the definition of different historic periods is a non-trivial issue. Given the different schools of thought regarding the division into periods that exist for ancient history, it is difficult to generalise, and every generalisation leads inevitably to a simplification of the reality. Intending to use such simplification for mere classification purposes, the authors would like to clarify how they interpret the subdivision of historical periods. The time span from the death of Alexander the Great (323 BCE) to the battle of Actium (31 BCE) is referred to as Hellenistic period. It follows the Roman period which ran until the fourth century CE, when the Late Antiquity started. The Middle Ages began in the seventh century CE when the Arabs conquered Egypt.

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periods. A parallel systematic approach covering the passage between the Hellenistic period and Middle Ages has never been attempted in the material characterisation of writing inks. The difficulties in getting access to cultural heritage collections, together with the challenges in dealing with manuscripts securely dated, have often discouraged scientists.

This does not mean, however, that no information is available. Scientific literature provides us with some results on the composition of inks from this transition period. The use of pure carbon ink seems to have changed from the Hellenistic period onwards, according to a few analyses that uncovered the presence of metals in carbon-based inks of this period. In the Middle East, we have evidence of copper containing carbon inks in the Genesis Apocryphon scroll from the Dead Sea Scrolls collection (Jerusalem, Shrine of the Book, 1*QGenAp*) (Nir-El and Broshi 1996), in two fragments of private letters from Pathyris, the nowadays Gebelein, and in two others from the Tebtunis temple library (Copenhagen, Carlsberg collection) (Christiansen et al. 2017). All of them are dating from a period between the last centuries before the Common Era and the first centuries after. Similarly, lead was recently found as an additive in carbon inks on a charred fragment from Herculaneum (Paris, Institut de France) (Brun et al. 2016). Unfortunately, we do not know in what chemical species these metals were added to the ink, given that their presence was detected using X-ray-based techniques. Carbon ink with or without the addition of metals was not the only writing medium in use during the Hellenistic period in Egypt. In a group of bilingual documents preserved at the Louvre and dating between the third and the first centuries BCE (Paris, Musée du Louvre, *N* 2433, *N* 2416, *N* 2410, *N* 2422), all Demotic texts were written in carbon ink, while Greek texts were penned in a copper-based ink. Although never empirically verified, the presence of tannins in these copper-based inks was tacitly assumed based on their brownish colour (Delange et al. 1990). Finally, among the earliest evidence of iron-gall inks, we can list the Book of Proverbs in Akhmimic preserved at the Staatsbibliothek in Berlin (Berlin, *Ms.or.oct* 987) dated to the third–fourth centuries CE (Ghigo et al. 2018), the Vercelli Gospel (*Codex Eusebii Evangeliorum*) at the Museo del Tesoro del Duomo in Vercelli dating probably to the fourth century CE (Aceto et al. 2008), and the Vienna Dioskurides (Vienna, *Codex Vindobonensis Med. gr.* 1) from the sixth century CE (Aceto et al. 2012).

In an effort to collect more data and fill the gaps of this fragmented scenario, the BAM (Bundesanstalt für Materialforschung und – prüfung) together with the CSMC (Centre for the Study of Manuscripts Cultures, University of Hamburg) created a new project in the framework of their ongoing research on the socio-geographic history of inks. This work is carried out in a close cooperation with the ERC Advanced Grant 'PAThs'[2] dedicated to the study of Coptic literature.[3] Coptic manuscripts were initially chosen as a focus for our investigation because of their continuous production between the Late Antiquity and the Middle Ages. In this context, the project 'PAThs' helps in placing the data obtained from archaeometric analysis in the historical context to which they belong. Based on an interdisciplinary approach involving philology, codicology, archaeology and digital humanities, the 'PAThs' project joins efforts to investigate the processes of production, dissemination and storage of Coptic literary works in relation to their geographical contexts. Its aim is to provide a range of digital tools where the scattered pieces of relevant information available are studied, collected and geo-chronologically organised to make them accessible to the professionals working in manuscripts cultures (Buzi 2017). Unfortunately, however, Coptic literary manuscripts rarely contain clear information regarding their chronology or geography. Therefore, dating and locating are only possible through a complex analysis that cross-links data regarding the text, the palaeographical and codicological features and the archaeological context of the finding. Given the necessity of collecting data from securely dated and localised manuscripts, we decided to extend our investigation to documentary texts. These are more likely to display a clear indication of the place and date of issuing and can be written in Latin, Greek or Coptic since Egypt was characterised by a multilingual society during Late Antiquity (Bausi 2018; Buzi 2018a). Despite the linguistic bias, the documents investigated were produced in the same areas and similar time span as the Coptic literary texts and represent interesting terms of comparison.

Types of ink and ingredients

Generally speaking, an ink is a writing medium obtained by mixing a binding agent such as gum Arabic or animal glue with a pigment or a dye. Carbon ink is based on a dispersion of carbon particles in the form of charcoal or soot in the water-soluble binding agent. Plant ink is a solution of tannins derived from tree bark, gallnuts or other vegetal matter containing tannins. Iron-gall ink presents a specific case since the insoluble pigment results from a chemical reaction. The black complex, on which this type of ink is based, is uniquely produced by mixing Fe^{2+} (obtained, for example from green

[2] This article is a scientific outcome of the ERC Advanced Grant (2015) 'PAThs—Tracking Papyrus and Parchment Paths: An Archaeological Atlas of Coptic Literature. Literary Texts in their Geographical Context. Production, Copying, Usage, Dissemination and Storage', directed by Paola Buzi and hosted by Sapienza University of Rome (grant no. 687567) [http://paths.uniroma1.it/].

[3] The results of Egyptian literary production from the third century CE onwards.

vitriol—$FeSO_4 \cdot 7H_2O$) with gallic acid contained in tannins, which becomes insoluble upon oxidation in air. In contrast to the recipes just described, containing only the basic ingredients required to prepare an ink, written historical sources usually mention a broader variety of constituents, some of which are still not univocally identified. This is the case for *chalcanthon* (*χάλκανθον*), a copper-based substance (in Greek *chalcos* = copper) whose exact chemical formula in Antiquity evades identification (Bailey 1932, p. 175), though from the Middle Ages onwards, it is clearly identified as copper sulphate (blue vitriol). The term *chalcanthon* appears in the treatise written in the third century BCE by Philo of Byzantium who uses it to make re-appear invisible text written on leather using gallnut extract (Garlan 1974, p. 324). Around the first century CE, Dioscorides adds this substance to pure carbon ink, mentioning its good antiseptic properties (Dioscorides Pedanius et al. 2000, book V: 114, 183). The same *chalcanthon* appears in the Papyrus V of Leiden dating to the third century CE (Preisendanz 1931, p. 83), where it is mixed with gum, gallnut extract, myrrh and *misy* (allegedly, a metallic salt whose composition has never been clarified) to prepare a magical ink (was it iron-gall?). Pliny wrongly equates this substance with *atramentum sutorium* (Rabin 2017) and aware of his mistake recent literature often refers to it as a mixture of copper, iron and other sulphates, commonly called vitriol (Zerdoun Bat-Yehuda 1983; Karpenko and Norris 2002). To date, there is no evidence that allows to disambiguate the chemical composition of this substance before the Middle Ages.

Corpus of investigation and institutions involved

For the time being, our investigation includes 159 different codicological units (i.e. one or more fragments preserved in a certain place and belonging to the same original manuscript). They include manuscripts on papyrus, parchment, paper and ostraca which were distributed across a very broad time span (third century BCE–eleventh century CE) and which were produced in different areas of Egypt. The fragments are nowadays preserved in the collections of eigth different institutions: the Museo Egizio in Turin, the Biblioteca Apostolica Vaticana in Rome, the Staatsbibliothek and the Ägyptisches Museum und Papyrussammlung in Berlin, the Cambridge University Library, the Chester Beatty Library in Dublin, the Fundació de San Lucas Evangelista in Barcelona and the Monasterio de Santa Maria in Montserrat. The fragments studied were chosen based upon several criteria. The conservation state is of course a limiting factor when handling fragile materials, and therefore the first criterion in discriminating the selection. Despite this limitation, we strived to choose manuscripts coming from renowned scriptoria or archaeological findings, giving priority to those whose dating and production place were more securely assessed.

In this work, we present the results obtained on some of the earliest manuscripts we studied, dated to the period between the second and eighth centuries CE. They are divided into three clusters according to their date, provenance and text genre. Here, we discuss the correspondence between these variables and the type of ink. Although only a limited number of leaves are illustrated in this article as being representative of a cluster, the contribution of this work lies in the attempt at examining a relevant number of manuscripts to draw conclusions on the distribution of the ink typology throughout space and time. Table 1 lists the shelf marks of the manuscripts presented, the details regarding their dating, language and provenance and the cluster to which each manuscript belongs, along with the total number of units forming part of such cluster.

The first cluster of manuscripts forms part of the collection from the Cathedral of Thi(ni)s, nowadays Ǧirǧā, and is preserved at the Museo Egizio in Turin. The library of Thi(ni)s is indeed a crucial and transitional instance in the history of Coptic manuscripts, which saw on the one hand the creation of new codicological and palaeographical features and on the other hand the progressive emergence of multiple-text codices (Buzi 2017; Buzi 2018b). Additionally, the fact that the manuscripts in question have very likely been manufactured in a limited span of time and have been penned by a limited number of copyists, placed the study of the library of Thi(ni)s as a first choice in our corpus.

The manuscripts of the second cluster have in common the dating, palaeographically established around the fourth century CE. Of these 3 codicological units, the Apostolic Vatican Library, *Pap. copt.* 9 and the Montserrat, Roca Puig, *Inv.* 145 are probably part of the so-called Bodmer Library, one of the most famous collections of papyri from Late Antique Egypt (Fournet 2015). It owes its name to a rich collector from Switzerland, Martin Bodmer, who in the 1950s exported an important batch of manuscripts from Egypt. The collection acquired by Bodmer was then dismembered in the following years, often by Bodmer himself, as it is the case of the leaves he donated to Pope Paul VI, now preserved in the Apostolic Vatican Library. From 1960 onwards, Bodmer stopped the importation of papyri, but Ramón Roca Puig still acquired some leaves, probably coming from the same findings, that are nowadays preserved in the Monasterio de Santa María in Montserrat (Schubert 2015). The exact composition, dating and provenance of this collection are still debated. One of the hypotheses indicates that the manuscripts were produced around the fourth century CE in the Pachomian Monastery of Pbou, close to the area of Panopolis, where they were probably found (Fournet 2015; Lundhaug and Jenott 2015).

The third codicological unit belonging to this cluster is known as Athanasius' roll (Montserrat, Roca Puig collection, *Inv.* 14) and is not considered to be part of the Bodmer

Table 1 Description of the clusters of manuscripts analysed, with details regarding the shelf marks of those presented in this work and the assigned cluster

Shelf mark	Dating	Provenance[1]	Language	Cluster (assigned)	Total number of codicological units of the cluster
Turin, Egyptian Museum, *Codex* IX Provv. 8592	Seventh/eighth centuries CE	Thi(ni)s (31° 50′ 30.81″, 26° 20′ 29.35″)	Coptic	1: Literary manuscripts from the library of the Cathedral of Thi(ni)s produced around the seventh–eighth centuries CE	4 codicological units: Turin, Museo Egizio, Codex II Turin, Museo Egizio, Codex IX Turin, Museo Egizio, Codex XIII Turin, Museo Egizio, Codex XV
Apostolic Vatican Library, *Pap. copt.* 9_ *glass*39_93-70	Fourth century CE	Area of Panopolis? (31° 44′ 42.63″, 26° 33′ 53.6″)	Coptic	2: Literary manuscripts produced around the fourth century CE	3 codicological units: Rome, Biblioteca Apostolica Vaticana, *Pap. copt.* 9 Montserrat, *Roca Puig collection, Inv.* 126–178, 292, 238 Montserrat, Roca Puig collection, *Inv.* 14
Montserrat Abbey, Collection Roca Puig, *Inv.* 145	Fourth century CE	Area of Panopolis? (31° 44′ 42.63″, 26° 33′ 53.6″)	Greek		
Montserrat Abbey, Collection Roca Puig, *Inv.* 308	491 CE	Oxyrhynchus (30° 39′ 6.19″, 28° 32′ 33.27″)	Greek	3: Documentary texts produced in various areas of Egypt between the second and eighth centuries CE	70 codicological units including texts in Latin, Greek and Coptic
Montserrat Abbey, Collection Roca Puig, *Inv.* 715	Eighth century CE	Bawit (30° 42′ 30.04″, 27° 33′ 4.08″)	Coptic		

[1] The DMS coordinates provided refer to the archaeological sites and have been extracted from the PAThs Atlas [http://paths.uniroma1.it/atlas/places]

collection. The dialect used in the roll indicates that it was produced in the area around Panopolis (Torallas Tovar 2018). This means that if the hypothesis regarding the Bodmer collection is accepted, all the manuscripts from cluster 2 have in common not only the dating but also the provenance. Finally, the results obtained on the literary manuscripts from these two clusters will be compared with those obtained on the third cluster, formed by documentary texts produced in various areas of Egypt between the second and eighth centuries CE.

Experimental

Our standard protocol for ink analysis consists of a primary screening to determine the type of ink and a subsequent in-depth analysis using several spectroscopic techniques: XRF and, only occasionally, FTIR and Raman (Rabin et al. 2012).

The primary screening is carried out by means of near-infrared reflectography. Strictly speaking, optical differences between carbon, plant and iron-gall inks are best recognised when comparing their response to the infrared light: carbon ink has a deep black colour, iron-gall ink becomes transparent above 1400 nm and plant ink disappears at ca. 750 nm (Mrusek et al. 1995).[4] The in-depth investigation includes XRF analysis to obtain the contribution of the inorganic components of the ink. In the case of iron-gall inks, we establish the fingerprints, i.e. the characteristic ratios of the metallic components of the ink (Hahn et al. 2004; Rabin et al. 2012).

This non-invasive and portable analytical protocol has proved to be very effective in characterising inks based on late Medieval European recipes, offering great support to the codicological analysis (Hahn et al. 2007; Rabin et al. 2014; Geissbühler et al. 2018; Hahn et al. 2018). However, it does not contain a routine identification of the organic components, and therefore, it does not offer full elucidation and becomes problematic when unknown media such as Late Antique inks are under scrutiny. In a previous work, we extensively pointed out the difficulty in characterising mixed inks using our current protocol (Colini et al. 2018). Given the inability of detecting tannins, we cannot distinguish carbon inks containing metals from mixtures of carbon and iron-gall inks. For the same reason, we cannot identify mixtures of carbon and plant ink. In order to achieve a more accurate characterisation, we decided to test the potential of mass spectrometry, thanks to a new portable sample holder that allows to collect a negligible amount of sample. If successful, this technique would allow to gain insights into the nature of binders and tannins employed in the making of the ink. Although extensively mentioned in

[4] In their study, Mrusek et al. indicate that iron-gall ink becomes transparent at 1200 nm. However, our recent tests using an IR camera showed that fresh iron-gall ink becomes completely transparent at longer wavelengths.

medieval recipes, gallnuts are not the only source of tannins historically used in the ink making. Theophilus, for example mentions the use of the bark from a bush (Theophilus 1979, p. 49), and analytical evidence coming from some Yemenite fragments dating between the seventh and eighth centuries CE suggests the use of other ingredients than gallnuts (Bicchieri et al. 2013). Therefore, the discrimination between different families of tannins, namely hydrolysable (highly concentrated in gallnuts) and condensed (present in mangrove), may offer a valuable parameter for the classification of inks. In this work, we present for the first time the results obtained from a laboratory study on a set of mock samples.

DinoLite USB microscope, AD413T-I2V

This small USB microscope measures only 10 cm and it is equipped with three different lights sources: near-infrared (940 nm), UV (395 nm) and a white LED light (external). Comparing the VIS micrograph with the corresponding near-infrared, we determine the ink typology by observing the changes in the opacity of the ink. At 940 nm, carbon-based inks show no change in their opacity, while the opacity of iron-gall inks changes considerably, and plant inks become transparent.

Elio Bruker Nano GmbH (formerly XG Lab)

This X-ray spectrometer features a 4-W low-power rhodium tube, adjustable excitation parameters and a 17-mm^2 SDD detector with energy resolution < 140 eV for Mn Kα. It was used to collect measurement on single spots and has a beam size of ca. 1 mm. All measurements were performed at 40 kV and 80 μA, with an acquisition time of 2 min. Peak fitting and semi-quantitative data evaluation were conducted using Bruker's SPEKTRA software.

ArtTAX 800 Bruker Nano GmbH

ArtTAX is an X-ray spectrometer well known in the field of cultural heritage and belongs to the standard equipment in the majority of large museums. It features a low-power, air-cooled molybdenum X-ray tube, polycapillary optics resulting in a beam spot of about 100-μm diameter, a CCD camera for sample positioning and an electrothermally cooled Xflash detector (SDD, area 10 mm^2) with an energy resolution of < 150 eV for Mn Kα at 10 kcps. The movable probe is operated by XYZ motors that enable spot measurements to be performed as well as line and small area scans. The mobile XRF probe moves over the object at ca. 5-mm distance and stops for the duration of a single measurement. All measurements were made along a line containing between 10 and 30 spots for analysis, operating at 50 kV and 600 μA, with an acquisition time of 30 s per spot (live time). Peak fitting and semi-quantitative data evaluation were conducted using Bruker's SPEKTRA software.

ASAP Xevo G2-XS QTOF Waters

This is a useful tool for the analysis of volatile and semi-volatile solid and liquid samples using atmospheric pressure ionisation (API). This technique utilises a heated nitrogen de-solvation gas to vaporise the sample and a corona discharge for sample ionisation. Complex mixtures can be analysed without the need of any sample preparation. The sample is simply collected by rubbing the glass sampler on solid analytes or by immersing it in liquid analytes. Then, it is inserted in the instrument for examination. The analysis was performed using negative-ion pattern, with de-solvation temperature of 650 °C and corona current of 10 μA. The mass range considered was between 50 and 1200 Da with a scan time of 1 s.

Results and discussion

When investigating iron-gall inks, the fingerprint model has been suggested in the past as a possible approach to perform qualitative and quantitative studies of ink traces on paper writing surfaces (Hahn et al. 2004). We often successfully apply a simplified version of this model that considers only an approximation of the contribution from the support and yet gives an indication of the different writing phases involved in the production of a manuscript. The model involves at first the subtraction of the net peak intensity of all the elements in the support from the values of the corresponding elements in the inked areas. This is a necessary step given that the X-rays are penetrating and measuring the contribution from the support and ink together. The values thus obtained for each element are then normalised to iron, under the assumption that a coherent writing phase is characterised by the same ratio of the satellite elements to iron, the main component of the vitriol used to make iron-gall inks in medieval recipes. However, iron is contained in different proportions in the most common writing supports as well. Therefore, for this method to provide reproducible results, the content of iron in the support must show a certain homogeneity and its median value should be considerably lower than the median value of iron intensity detected in the inked areas. This is generally the case of medieval manuscripts written on parchment or European paper. For instance, the simplified version of the fingerprint model could be successfully used in advanced codicological studies on Hamburg, Staats- und Universitätsbibliothek, *Cod. germ.* 6 (Rabin et al. 2014; Geissbühler et al. 2018). Unfortunately, in the case of ancient papyri, the writing support is hardly ever homogeneous. To begin with, the structure of the plant itself is rather heterogeneous, made of contiguous capillary fibres of

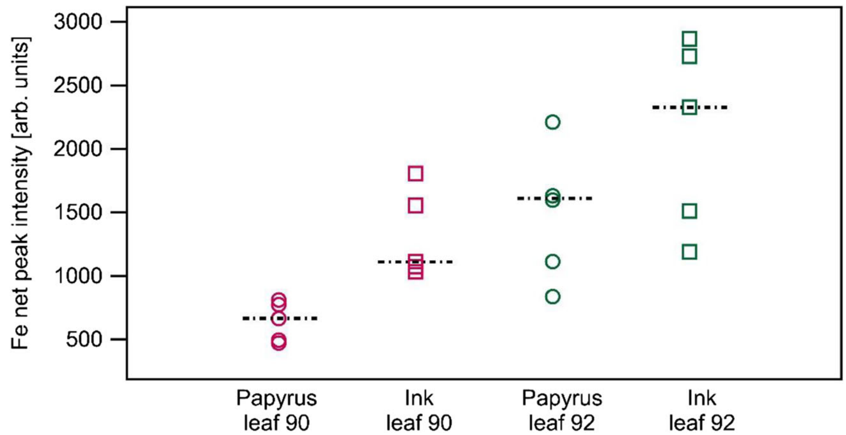

Fig. 1 Individual values plot for iron. Each dot represents the value of net peak intensity obtained through XRF measurement on a spot of ink or support on two leaves of Rome, Biblioteca Apostolica Vaticana, *Pap. copt.* 9. The horizontal dashed line represents the median value per each set of measurements performed using Elio spectrometer

different thickness. Despite the pressure applied during the manufacturing process of the papyrus leaves, the fibrous structure is still recognizable even to the bare eye. In addition, processes of deterioration acting over centuries generally increase the heterogeneity of the leaves, physically affecting each fibre differently. Finally, archaeological material is usually contaminated by different elements depending on the diagenetic surrounding. Unfortunately, iron belongs to the primary pollutant agents, especially in sandy environments. All these processes result in a writing support that is characterised by a widely heterogeneous iron content. Figure 1 shows the distribution of the values for iron measured in the papyrus and in the ink on two different leaves of Apostolic, Vatican Library, *Pap. copt.* 9. First of all, we see that the iron intensity is far from constant with a larger spread corresponding to the ink. This is not surprising since the thickness of the ink is not necessarily constant throughout the inscribed portions subjected to analysis. Deterioration processes such as flaking or abrasion certainly also contribute to the heterogeneity of the ink thickness. Figure 1 illustrates that exceptional heterogeneity of iron in both papyrus and inks makes quantitative and semi-quantitative evaluation rather difficult. Note that the gap between the maximum intensity value in the support and the minimum one in the ink is very small in the case of leaf 90, and non-existent on leaf 92, where the two intervals largely overlap. Under these circumstances, even when it is possible to conduct the XRF measurements for the ink and the support in great proximity, we use the fingerprint model rather cautiously.

However, even in cases in which the semi-quantification of the elements contained in the ink is not possible, we found that the qualitative information collected using our analytical protocol was often enough to discriminate among different clusters of manuscripts when performing a study on a large geographical area and a broad time span. In the following paragraphs, the differences in the elemental composition of the inks examined will be highlighted and discussed.

The literary manuscripts: clusters 1 and 2

Figure 2 shows the results on Turin, Museo Egizio, *Codex* IX, classified as cluster 1. Observing the visible and near-infrared micrograph, we notice a significative change in opacity, indicating that the manuscript investigated had been written with iron-gall ink. Looking at the XRF spectra, we observe that the net peak intensity of the Kα line of iron at 6.4 keV is substantially higher in the inked area as compared with that of the support, confirming this result. The content in potassium may

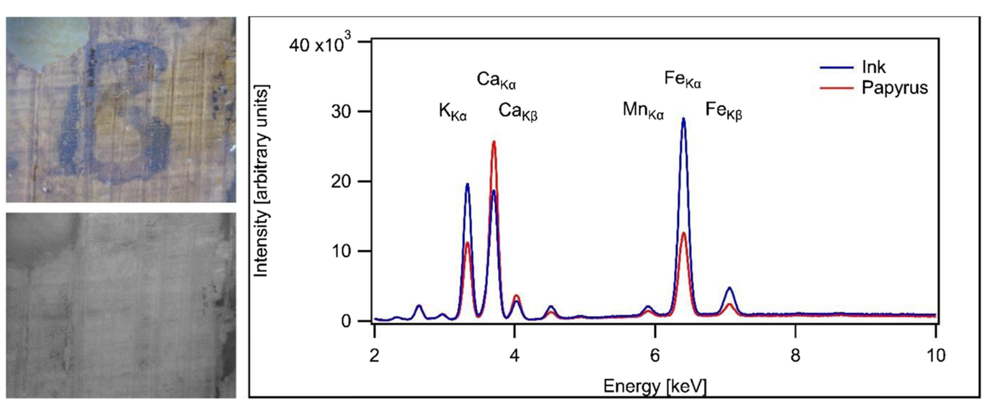

Fig. 2 Visible and near-infrared micrographs (left top and bottom, respectively) and XRF spectra (right) of an inked and non-inked spot (blue and red, respectively) in Turin, Museo Egizio, *Codex* IX- *Provv.* 8592. The XRF measurements were performed using ArtTax spectrometer

be attributed to the binder and the tannins, while it is surprising that satellite elements like copper and zinc, usually found in vitriol (and largely attested in Medieval European manuscripts and recipes) are absent (Aceto et al. 2017; Geissbühler et al. 2018). During the sixteenth century, the addition of metallic iron to a solution of vitriol became a common procedure to cause the copper to precipitate, leaving a solution rich in iron sulphate (Karpenko and Norris 2002). It seems unlikely that such a technology could have been applied eight centuries before. We believe this might be an indication that common iron filings were used instead of vitriol to prepare this type of iron-gall ink. We have record of the use of this ingredient in Arabic recipes from the Middle Ages onwards.[5] For this reason, we designate the inks containing only iron as 'non-vitriolic iron-gall inks'. The collection from the library of the Cathedral of Thi(ni)s showed a great homogeneity in the ink composition, given that a similar result was obtained on all the other leaves from cluster 1, after collecting 30 measurement spots on inks from 6 leaves belonging to 4 different codicological units.

A different type of ink was identified on the leaves of the literary fragments from cluster 2, originally produced around the fourth century CE, presumably in the area of Panopolis. Figure 3 shows the net intensity profile of the elements iron, potassium, copper and manganese (often associated with iron) extracted from the XRF measurements on Montserrat Abbey, Roca Puig collection, *Inv.* 145, along the line connecting the papyrus and an inked area, a so-called line scan. We observe that these elements show a similar profile, increasing in intensity when moving from the support to the inked area, attesting that they are all present in the ink. Iron, copper and manganese could be attributed to the metallic salt(s) used to make an iron-gall ink, while the potassium could be present as a sulphate salt or attributed to the binder or the tannins. However, the interpretation of near-infrared reflectography challenges the possibility that iron-gall ink was indeed used in this case, posing some interesting questions. The ink appears quite pale under near-infrared light, but the comparison between visible and near-infrared micrographs shows only a slight change in opacity, which is in contrast with the one observed on the inks of cluster 1, or with those we generally observe on medieval iron-gall inks. This makes the typological characterisation of this ink rather uncertain, casting doubts on its nature. Are we looking, instead, at a mixed ink containing both iron-gall ink and carbon? As far as we know, this type of ink was not necessarily produced intentionally. We have records of some Arabic recipes in which the ingredients were roasted, (e.g. Grohmann 1967, p. 129). If this procedure was ever applied to iron-gall inks, carbon would have formed, entering the blend as a by-product. Alternatively, it is plausible that at the very beginning of the existence of iron-gall inks, the scarce knowledge regarding their chemical structure resulted in darkish inks rather than black ones, thus carbon may have been used to blacken the mixture. A recent study seems to corroborate this idea, demonstrating that, in contrary to what Robert Fuchs asserts in his definition of 'imperfect inks' (Fuchs 2003), not only gallic acid but also other polyphenols commonly contained in tannins can form darkish complexes with Fe^{2+}, but the complex iron gallate remains the blackest (Díaz Hidalgo et al. 2018). This raises another question: could it be that the ink on Montserrat, Roca Puig, *Inv.* 145, rather than being a mixed ink, is simply evidence of an undocumented type of ink, prepared using metallic salt(s) and a vegetal ingredient containing mainly other polyphenols than gallic acid? May this be a rough attempt at producing iron-gall ink, obtaining a sort of precursor? In this case, the metal-polyphenol complex(es) formed may be characterised by its own behaviour at 940 nm.

The results obtained on Montserrat, Roca Puig *Inv.* 145 are coherent within all the 5 leaves examined from the same manuscript and similar to those found on the other codicological units from cluster 2, namely Apostolic Vatican Library, *Pap. copt.* 9 (Fig. 4) and Montserrat, Roca Puig, *Inv.* 14. Clearly, the portable equipment we normally employ is not sufficient to fully elucidate the nature of these inks. To unequivocally establish the presence of carbon, the method of choice seems to be IR reflectography performed at longer wavelengths, at which only carbon remains visible. Unfortunately, the dimensions of the equipment partially limit its portability. Another possibility is the application of Raman spectroscopy. However, given the limitation of portable Raman instruments, this analysis often requires bench equipment or the collection of samples. Even in such a case, poor conservation state of the ink often renders the examination fruitless.

Even if possible, the identification of carbon would not provide a complete understanding of the nature of these inks. As discussed, recent experiments proved that the complexity of the inks containing vegetal matter and metallic salts can hardly be described using the term iron-gall ink in a 'traditional' way, i.e. considering only the complex iron-gallic acid as responsible for the ink's properties (Díaz Hidalgo et al. 2018). In addition, the recipes collected in the works of Colini[6] and Zerdoun show the variety of organic ingredients employed in the manufacturing of the inks (Zerdoun Bat-Yehuda 1983). Against this background, the characterisation of the organic compounds becomes crucial to enable an accurate classification of the typologies of ink. We believe that mass spectrometry performed in atmospheric solid analysis probe (ASAP) mode

[5] Colini C (forthcoming) 'I tried it and it is really good' Replicating recipes of Arabic black inks. Traces of ink: Experiences of Philology and Replication.

[6] Colini C (forthcoming) from recipes to material analysis the Arabic tradition of black inks and paper coatings (ninth–twentieth century). Universität Hamburg. Pp: 149–277.

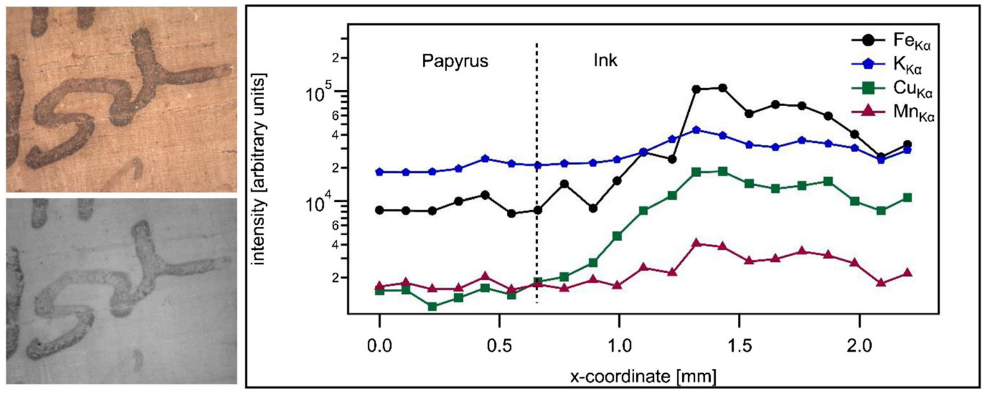

Fig. 3 Visible and near-infrared micrographs (left top and bottom, respectively) and XRF neat peak intensities collected along the line connecting inked and non-inked areas (right) of an ink on Montserrat, Roca Puig collection, *Inv.* 145. The XRF measurement was performed using ArtTax spectrometer

could well serve this purpose. Because of its high sensitivity, this technique may lead to satisfactory and reliable results even on degraded materials and, compared with current mass spectrometry, it has the advantage of being quasi-non-invasive. Including this method in our standard protocol would lead to new insights and a greater level of accuracy in the characterisation of many inks from Late Antiquity that are so far still poorly understood. Some tests on mock samples performed with this technique are presented at the end of this article.

The presence of both copper and iron in the inks attributed to cluster 2 may suggest that vitriol (a mixture of sulphates including iron and copper) was used in their preparation. However, sulphur is a light element; therefore, XRF analysis is sometimes not sensitive enough to detect its presence in the inks examined. Even when it is possible to detect it, it does not deliver an unequivocal proof that its presence must be related to sulphates. Though unlikely, we cannot exclude the possibility that iron and copper entered the ink preparation in a form other than vitriol. In addition, we must consider the possibility that more than one ingredient, each containing different metallic component(s), was employed in the preparation of these inks. The textual examination of the existing recipes does not cast light on this matter, given that the exact composition of many of the ingredients mentioned is still rather unclear, as discussed before. However, although just as a speculation, it is interesting to point out the possible parallel between the inks identified on the manuscripts from cluster 2 and the recipe written in the Papyrus V of Leiden, which dates at the third century CE and was found in a tomb in Thebes, not far from the area around Panopolis, where the papyri from this cluster may have been produced. The fair amount of copper contained in the inks seems to provide evidence of the use of *chalcanthon* (a copper-based substance) mentioned in the recipe. If we assume that this compound did not contain any other metallic element besides copper, we could suppose that some iron-based substance may have been added in an attempt to obtain a black complex more suitable for writing. Interestingly, the recipe mentions also *misy*, a metallic salt of unknown composition that could have provided the content of iron necessary to form the black iron-gallate complex.

The documentary texts: cluster 3

The results obtained on the documentary texts examined were very different from those obtained on clusters 1 and 2. Figures 5 and 6 show the near-infrared reflectography performed on inked areas of Montserrat, Roca Puig, *Inv.* 308 and *Inv.* 715, respectively. We observe no change in opacity between visible and near-infrared light, thus indicating that both fragments were written using a carbon-based ink. Also, the XRF analysis performed on both documents confirmed

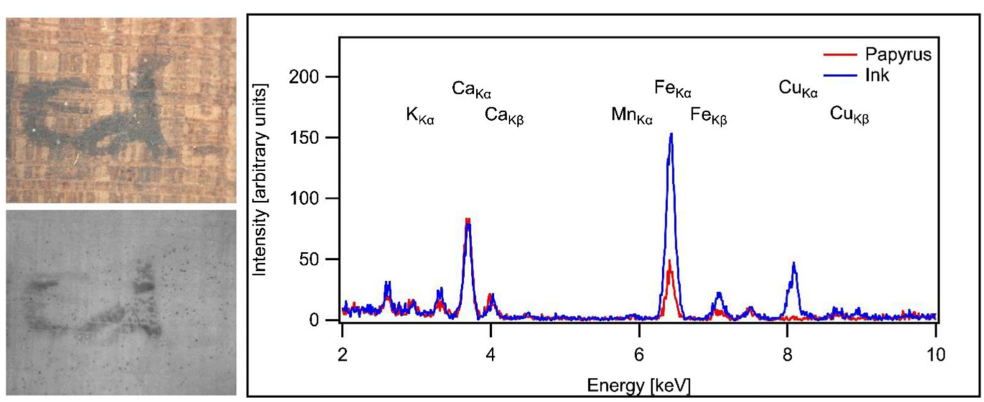

Fig. 4 Visible and near-infrared micrographs (left top and bottom, respectively) and XRF spectra (right) of an inked and non-inked spot (blue and red, respectively) in Rome, Biblioteca Apostolica Vaticana, *Pap. copt.* 9. The XRF measurements were performed using Elio spectrometer

Fig. 5 Montserrat, Roca Puig collection, *Inv.* 308 (© Montserrat Abbey). On the right, the micrographs under visible (top) and near-infrared (bottom) light

this result since it did not detect any consistent presence of metallic elements.

This is an interesting result considering that these manuscripts are respectively dated at the fifth century CE and eighth century CE. By this time, iron-gall ink (or at least an ink showing a very different behaviours than carbon under near-infrared light and containing a fair amount of iron and other metals, maybe a precursor?), was already in use, as demonstrated by the results obtained on the cluster 2. This poses an interesting question: is it possible that the type of ink used was correlated to the type of manuscript produced, when considering the literary and documentary genres? The results obtained on the full corpus of manuscripts examined so far highlighted the predominant presence of two types of ink that clearly show different features, although an accurate characterisation was not possible due to the limitation of our current analytical protocol. On the one hand, we have a group of inks showing a black colour in the near-infrared region (940 nm) and no change in opacity when comparing near-infrared and visible images, revealing the presence of a significative amount of carbon black. In some cases, XRF analysis on this group of inks revealed the presence of metals such as iron,

Fig. 6 Montserrat, Roca Puig collection, *Inv.* 715 (© Montserrat Abbey). On the right, the micrographs under visible (top) and near-infrared (bottom) light

Table 2 Chronological distribution of the manuscripts analysed

Century	Documentary manuscripts			Literary manuscripts		
	Number of units	Units in carbon-based ink	Units in other inks*	Number of units	Units in iron-gall ink or similar	Units in carbon ink
2nd	9	9	-	3	-	3
3rd	2	2	-	-	-	-
4th	4	4	-	5	5	-
5th	3	2	1	11	11	-
5th–6th	1	1	-	3	3	-
6th	6	6	-	1	1	-
6th–7th	-	-	-	5	5	-
6th–8th	1	1	-	-	-	-
7th	5	5	-	1	1	-
7th–8th	6	5	1	4	4	-
8th	33	25	8	1	1	-
Total	70	60	10	34	31	3

*Here, 'Other inks' include iron-gall ink, mixed ink and coloured inks

copper and in some rare cases, lead. On the other hand, we have inks showing a pale colour in the near-infrared region (940 nm), at least a slight change in opacity when comparing visible and near-infrared micrographs and containing a significant and consistent amount of metals. In some cases, they are clearly identified as iron-gall inks, while in others, the characterisation is more problematic, but given the consistent presence of iron and other metals, they may be defined as 'similar to iron-gall ink'. These inks occasionally presented signs of corrosion. It is very interesting to discuss the distribution of these two groups of inks along the corpus. Carbon-based ink has been found on 60 out of 70 documentary texts, representing more than 80% of cases in a time span between second and eighth centuries CE. For the sake of clarity, Table 2 shows the chronological distribution of the units analysed, along with the typology of ink found on their leaves. In contrast, iron-gall ink or similar has been found on 31 out of 34 literary texts, representing more than the 90% of cases in the same time span. The use of this type of ink in literary manuscripts continues between the ninth and eleventh centuries CE, when it was found on all the 30 units analysed. Similarly, it was found on all the 13 literary manuscripts from the Michaelides collection[7] that were analysed at the Cambridge University Library. Although this collection has been poorly studied and a date for every single manuscript has still not been established, its leaves can be placed in a time span between the sixth and tenth centuries CE.

The results obtained suggest that the transition between carbon ink, used everywhere in antiquity, and iron-gall ink, very popular in Medieval Europe, did not happen as a result of the mere function of time. Other factors, like the environment of production of a manuscript (given that documentary and literary texts were most likely produced in different environments), influenced the type of ink used. No other correlation of this dimension was observed between type of ink and support, as it was previously suggested (Lucas 1922; Macarthur 1995), neither was it found between ink and language, as demonstrated in Table 3, where the results obtained are sorted according to the language of each unit examined.

The choice of certain materials for the manufacturing of manuscripts must have been the result of economic factors. Poorer environments of production probably used cheaper ingredients to prepare the inks. It is possible that less expensive ingredients were mixed together with more pricey ones to function as diluents, and this may have conducted to the production of mixed inks. Unfortunately, to date we have no records stating the cost of one or another type of ink, nor of its ingredients. It may seem logical to think that carbon ink has always been cheaper, given that charcoal or soot can be easily produced by combustion of a variety of common materials, such as pine logs as described by Pliny. However, Pliny mentions also the soot obtained from the combustion of ivory (precious and therefore more expensive) and the importation of carbon ink from India, suggesting that different qualities of carbon ink were circulating at that time, given that these last ones must have been finer and more expensive. At this point, it is difficult to say whether iron-gall ink was higher-priced than ivory soot or Indian carbon ink, making it impossible to draw any conclusion on this matter until further analytical and historical information is made available. On top of the

[7] This collection includes papyrus, parchment and paper fragments and originally belonged to the Greek collector George Michaelides. We have no secure information on the provenance of these manuscripts. In an article from 1952, Michaelides vaguely refers to a native from Egypt bringing him Coptic and Greek manuscripts from Fayuum (Michailides 1952, p. 45).

Table 3 Distribution of the languages in the documentary manuscripts between the second and eighth centuries CE. The bilingual units appear twice in the table

Language	Documentary manuscripts			Literary manuscripts		
	Number of units	Units in carbon ink	Units in other inks*	Number of units	Units in iron-gall ink	Units in carbon ink
Coptic	43	35	8	23	23	-
Greek	27	25	2	11	8	3
Latin	1	1	-	1	1	-
Total	70	60	10	34	31	3

*Here, 'Other inks' include iron-gall ink, mixed ink and coloured inks

economic factors, there is a possibility that the choice behind the type of ink used was linked to the physical properties of carbon and iron-gall ink. The former simply sits on top of the support, adhering to it thanks to the binder, but it can be easily scraped off, even accidentally, and it is therefore more suitable in the case of ephemeral manuscripts, as in the case of receipts or private messages. In this regard, we have record of an epigraph by Martial dating from the first century CE who describes the process of removal of an ink using a 'Punic sponge'. This proves that the practice of erasing an ink from the support once the text has lost its relevance was in use at that time (Martial 2015, pp. 67–69). In contrast, iron-gall ink penetrates the support deeply and it can be erased only in critical acidic conditions that can be achieved, for instance, by intentionally treating the ink with weak acids. Its durability makes this type of ink the best choice when writing a manuscript with the specific intention to make it last in time, as it is the case with literary texts, especially of literary codices produced as part of the library of a religious institution (it must be stressed that these represent most cases existing in the corpus examined). The manuscripts from the library of the Cathedral of Thi(ni)is, presented in this work as the cluster of manuscripts number 1, may well serve as an example. Clearly, the scenario described so far is only a partial interpretation of a much more complex phenomenon that still requires further investigation, especially focusing on those documentary texts that may have been produced with the intention to last in time, such as testaments. As a final remark, it must be stressed that the data collected so far is representative mainly of the areas of Bawit, Oxyrhynchus, Thi(ni)s and the area around Panopolis. There is a big portion of Egyptian geography that could not so far be covered, despite the logistical efforts. In addition, until now, it was not possible to compare directly a significative number of literary and documentary texts coming from the same area and dating to the same time. Therefore, the results presented in this work provide far from a homogeneous representation of the whole Egyptian reality in the time span considered. We must acknowledge that the general situation may have been very different from the one represented by the analytical data collected.

Tests with ASAP Xevo G2-XS QTOF waters

Given the difficulties previously described in characterising the inks of some of the manuscript in our corpus, the goal of this experiment was to prove the effectiveness of the method in the identification of organic compounds, this time centring our attention on hydrolysable tannins. These can be found in high amounts in gallnuts. The latter have been already studied using mass spectrometry in conjunction with chromatography (Arpino et al. 1977; Mämmelä et al. 2000). The main purpose of those studies was the identification of different tannins or tannin mixtures rather than the mere verification of their presence. We propose to use gallic acid and ellagic acid, with molar masses of 170.12 and 302.2 respectively, that can be found in high amounts in gallnuts, as well as pyrogallol (molar mass 126.11) detected as a daughter ion of gallic acid in the mass spectra obtained with different ionisation techniques (Wyrepkowski et al. 2014), as indicators of the presence of tannins in the mixture. Previous studies on the tanned parchment of Dead Sea Scrolls proved that it was possible to identify at least gallic acid even on heavily deteriorated materials (Reed and Poole 1964). For the purpose

Table 4 Description of the samples analysed and their results

Sample	Description	Pyrogallol	Gallic acid	Ellagic acid
A	Gallnut extract	√	√	√
B	Iron-gall ink prepared mixing gallnut extract and iron sulphate	√	√	√
C	Mixed ink obtained mixing iron gall as in B and carbon	√	√	-
D	Copper ink prepared mixing gallnut extract and copper sulphate	√	√	√

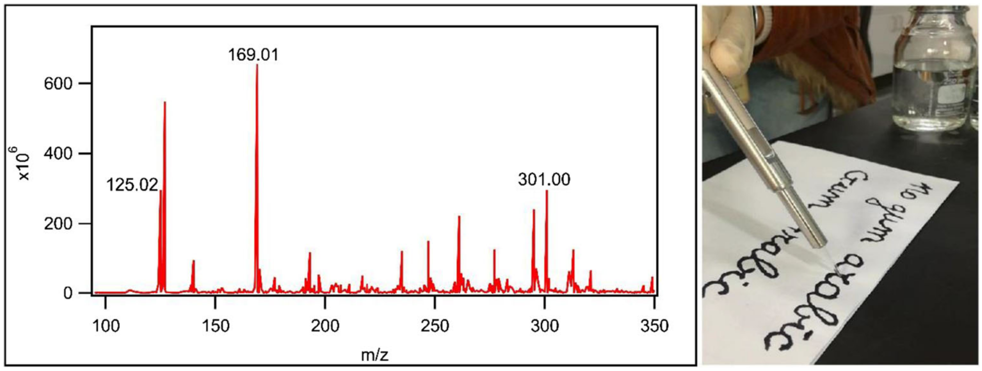

Fig. 7 Mass spectrum of the sample B. The ions of pyrogallol, gallic and ellagic acid are found respectively at 125.02, 169.01 and 301.00 m/z. The signal at 126.90 m/z is due to calibration of the machine using iodide ion

of this study, four mock samples of different typologies of ink were prepared using gallnut extract and analysed both liquid and dry, to make sure that their physical state would not influence the final result. The microsampling was performed by either rubbing a glass wire onto the dry sample or immersing it into the liquid. In both cases, the amount of sample collected was invisible to the naked eye. No further sample preparation was needed; the glass holder was inserted directly in the machine for examination. Since the analysis was performed using negative-ion pattern, the precursor ions of pyrogallol, gallic and ellagic acid are found respectively at around 125, 169 and 301 m/z. Table 4 lists the description of the samples and the results obtained.

We find it encouraging that all the samples investigated showed prominent peaks corresponding to at least two out of three characteristic components of the family of hydrolysable tannins and consider it to be a demonstration of the effectiveness of the technique in the identification of these components. In this preliminary study, we neither studied the effects of the ionisation conditions on the resulting spectra nor used a collision cell for controlling the fragmentation processes. Despite this fact, gallic acid and its fragment pyrogallol seem to be easily detectable whereas a lower amount of ellagic acid might pose a problem. Figure 7 shows the sampling technique as well as the mass spectrum of sample B, on which the peaks corresponding to deprotonated pyrogallol, gallic acid and ellagic acid have been highlighted.

Conclusion

The first results of this study show that the use of a rather simple analytical protocol leading to only partial characterisation of inks used in Egypt during Late Antiquity could be sufficient to cluster the inks according to their types. This observation suggests that such a typological diversity in the composition of the inks can be potentially exploited to collocate an unknown manuscript in space and time, once a proper geochronological map based on a statistically relevant amount of data is assembled. However, to refine the classification of the inks, other techniques for a routine identification of organic components must be added to our protocol. The present study indicates that ASAP-MS might be the technique of our choice, because of its high sensitivity coupled with a quasi-non-invasive and versatile sampling method.

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Authors' contributions Tea Ghigo performed the analytical campaigns, evaluated the data collected and prepared the manuscript. Ira Rabin provided feedback during the data evaluation and revised the manuscript. Paola Buzi revised the historical and codicological part of the manuscript.

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Between Literary and Documentary Practices: The Montserrat *Codex Miscellaneus* (*Inv. Nos.* 126-178, 292, 338) and the Material Investigation of Its Inks*

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Abstract
The Montserrat *Codex Miscellaneus* (TM 59453/LDAB 552) has been the subject of numerous studies since the publication of its first text by its owner, father Ramon Roca-Puig. Scholars have dealt with the content of its texts, as well as interrogated its origin and materiality. It is a fourth-century papyrus single quire codex, which contains texts in both Latin and Greek. It has been argued that it belonged to the Bodmer library, connected to a Pachomian library in the Thebaid. In this paper we want to contribute to the material study of the codex by presenting the first results of an archaeometric analysis performed upon the inks. The analysis was carried out within the framework of the 'PAThs' project based at Sapienza University of Rome, and executed with the close cooperation of DVCTVS, a team of scholars who curate the Roca-Puig collection. The results obtained have not only cast light on the history of production of the codex, but also, and perhaps most importantly, point out that a meaningful interpretation of the analytical data is only possible through an interdisciplinary collaboration between the humanities and the natural sciences.

Keywords
Codex Miscellaneus, book production, palaeography, archaeometry, ink analysis, interdisciplinary approach.

1. *The Montserrat* Codex Miscellaneus

The Montserrat *Codex Miscellaneus* (TM 59453/LDAB 552) was acquired by father Ramon Roca-Puig in 1955. He produced several editions of the texts contained in the codex.[1] It has been ever since the subject of much attention, and multiple studies have dealt with the content of its texts in addition to its origins and materiality.[2] It is a fourth-century papyrus single quire codex, containing texts in both Latin and Greek. It has been argued that it belonged to the Bodmer library, allegedly connected to a Pachomian library.[3]

* Tea Ghigo contributed to this work performing the archaeometric analysis on the *Codex Miscellaneus* and writing paragraphs 2 and 3. Sofía Torallas Tovar contributed by performing the palaeographic analysis and writing paragraph 1. Paragraphs 4 and 5 were written in collaboration between the two authors. The archaeometric analysis performed on the *Codex Miscellaneus* has been supported by the Cluster of Excellence 'Understanding Written Artefacts' funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG), and within the scope of the Centre for the Study of Manuscript Cultures (CSMC) at the University of Hamburg and by the ERC Advanced Grant project *Tracking Papyrus and Parchment Paths: An Archaeological Atlas of Coptic Literature. Literary Texts in their Geographical Context: Production, Copying, Usage, Dissemination and Storage*, project no. 687567, P.I. Paola Buzi (Sapienza University of Rome), http://paths.uniroma1.it/. This paper is the first collaboration of the DVCTVS team (PGC2018-096572-B-C21), curators of the Roca-Puig papyrological collection at the Abbey of Montserrat, and the Bundesanstalt für Materialforschung und -prüfung enterprise to study systematically inks in ancient manuscripts and documents. We are very grateful to the Benedictine community at the Abbey of Montserrat, especially fathers Pius Tragan and Gabriel Soler, responsible of the papyrus collection, for allowing us to work at the Abbey and perform all the analysis necessary for this paper. Our warm thanks go to our colleagues Ira Rabin, Oliver Hahn, Olivier Bonnerot, Simon Steger and Zina Cohen from the BAM, for their constant support. Also special thanks to Serena Ammirati for her useful suggestions and Lucas Binion for polishing the English expression.

1 On Ramon Roca-Puig and his papyrus acquisitions, see Tragán 2015, 20-29; Ortega Monasterio 2011, 59-76; Ortega Monasterio 2015, 43-52. On the first editions of the codex, see Roca-Puig 1965 and Roca-Puig 1977.

2 E.g. Torallas Tovar - Worp 2006, 11-24; Gil - Torallas Tovar 2010, 17-31; Nocchi Macedo 2013, Nocchi Macedo 2014, 26-48; Ammirati 2015a, 57-58.

3 The *Codex Miscellaneus* was claimed to belong to the Bodmer Library by James M. Robinson already in (1990-1991) 26-40, esp. 34. See also Brashear *et al.* 1990, 3-32. Lowe had observed the palaeographical resemblance between the Montserrat codex and Chester Beatty AC1499: see Lowe 1971, no. 1782. Other formal similarities include page set up and codex typology. Camplani 2015, 124-125, also observed the coherence in the Christian contents of the *Codex Miscellaneus* and some of the Bodmer books; see also some critical remarks on the last hypothesis in Mihálykó 2019.

It may seem out of context that a project like 'PAThs', dedicated to the study of Coptic Egypt, invested its resources into the archaeometric analysis of a codex written in Greek and Latin. However, it cannot be forgotten that Egypt was characterised as having a multilingual society at that time.[4] The results obtained from the analysis of Egyptian manuscripts written in languages other than Coptic represent valid terms of comparison, thus establishing a diversity of sources crucial to maintaining a broad perspective on codices produced during the time period.

In addition, as already said, the *Codex Miscellaneus* is generally recognised as being part of one of the most important collections of manuscripts from the Late Antiquity: the so-called Bodmer Library.[5] Given the intricate and delicate situation of this reconstructed 'library', whose dating and provenance are still debated, an archaeometric approach to the study of the inks and writing supports could help future understanding of the manuscripts' history, from their production to their arrival in the institutions where they are nowadays preserved.

1.1 Description

This papyrus codex consists of a single quire,[6] of which twenty-six out of at least twenty-eight original bifolia are preserved. Eighteen bifolia are virtually complete. It is a multiple-text codex, composed of several production units, since it has been written in different moments.

The codex bears the inventory numbers 128-178, 292 and 338 in the Roca-Puig papyrus collection at Montserrat (called *P.Monts.Roca*).

The size of each folium is ca H. 12.3 x W. 11.4 cm.[7] The pages have a rather trapezoidal shape, since their height diminishes slightly from the centre of the bifolia towards the outer edge of each folium. The bifolia, originally folded vertically in the centre, were sewn together with two double stitches. Some remnants of the string are preserved, as well as pieces of parchment, which had been inserted between the papyrus leaves and the string for purposes of reinforcement. The vertical fibres appear on the outer side of the first preserved folium, the horizontal fibres appearing in the inner side of the folium. This order continues until the centre of the codex, inv. no. 153-154, where one finds two pages, 56-57, showing both horizontal fibres. After that the order of fibres changes to horizontal alternating with vertical fibres.[8]

The general content of the codex is as follows:

A: Inv. no. 128↓–149↓, pp. 5-47 of the codex (Latin): Cicero, *Catilinarian Orations*, 1-2.[9]

B: Inv. no. 149→ –153→, pp. 48-56 of the codex (Latin): *Hymn to the Virgin Mary*.[10]

C: Inv. no. 154→, p. 57, of the codex: Drawing of a mythological episode.[11]

D: Inv. no. 154↓– 157↓, pp. 58-64 of the codex (Greek): Anaphora.[12]

E: Inv. no. 158→ –161→ (the other ↓ side of Inv. no. 161 is blank), pp. 65-71 [72] of the codex (Latin): *Alcestis* in Latin hexameters.[13]

F: Inv. no. 162→ –165↓, pp. 73-80 of the codex (Latin): Tale about the Emperor Hadrian.[14]

G: Inv. no. 166→ –178↓, pp. 81-106 of the codex (Greek): Alphabetised stenographical *Commentarium*.[15]

4 Rochette 1996, 153-168; Rochette 1998, 177-196; Oréal 1999, 289-306; Fewster 2002, 220-245; Thompson 2009, 395-417; Fournet 2009, 418-451; Torallas Tovar 2010a, 17-43; Torallas Tovar 2010b, 253-266; Buzi 2018, 15-67.

5 Fournet 2015, 8-37; Schubert 2015, 41-46.

6 This practice is the common procedure in early codices. See Kenyon 1933, I, 10-11. Ibscher 1937 claims that all papyrus codices up to the third century are single-quire codices, and it was from the fourth century on that they started to be composed in more than one quire. However, the Bodmer codices are dated to the fourth century. It is taken also as a sign of the fact that the codex comes from a school environment, cf. Kasser - Cavallo - van Haelst in Carlini 1991, 108, n. 10. For a full survey on the subject, see Robinson 1978; and also Turner 1977, 51-55, 61.

7 This is Turner's group 10; see Turner 1977, 22.

8 This is perfectly typical in single-quire codices; cf. Turner 1977, 58-60 and 65.

9 Roca-Puig 1977; Willis 1963.

10 Roca-Puig 1965.

11 Roca-Puig 1989, 139-169, text no. 4; Musso 1990, 30-32; Horak 1992, 230 (ViP 48); Nocchi Macedo 2010, 91-117.

12 Roca-Puig 1994.

13 Roca-Puig 1982; Marcovich 1988; Lebek 1983, 1-29; Parsons - Nisbet - Hutchinson 1983, 31-36; Tandoi 1984, 3-11; Nosarti 1992; Liberman 1998; Nocchi Macedo 2014.

14 Gil - Torallas Tovar 2010; Berg 2018; Ammannati 2018, 221-240.

15 Torallas Tovar - Worp 2006, 11-24; Luiselli 2017, 36-40.

At least two folia are missing from the beginning of the codex, and one more after the first preserved page. At the end of the codex, given the average length of the six individual word lists in the last section, G, we calculate that one more folium is missing with the page containing the last entries of the sixth sub-list.[16]

The binding features dimensions of H. 12.3 x W. 11.7 cm. The outside material is low quality parchment, which is at present in very brittle condition. Its hair side is on the outer side of the binding, while the inside material of the binding consists of various layers of papyrus used for padding the parchment of the binding. This papyrus-padding material still shows traces of writing and has been affected by worms.

Furthermore, four stripes of leather knotted on the inner side of one cover of the binding have been preserved, while the other cover has only two such knots preserved; there are two more holes in the parchment of this cover which might have been made for holding two more knots, establishing a symmetry between the two covers of the binding. These knots are drawn through the parchment and the padding inside, and were probably meant to keep the padding material in place.

1.2 Palaeography of the codex

While studying the history of the production of a certain manuscript, its palaeography is a crucial element that needs to be established as accurately as possible, and should be prioritised as much as any merely textual element. The fact that one or more scribes might be at work, for example, can be palaeographically established, and then successively confirmed by observing the composition of the inks as revealed by archaeometric analysis.

The successive sections of the codex (A-G) feature a different page layout.[17] The main difference is between the first six sections, which present running text, and the last, Section G (Inv. no. 166→ –178↓, pp. 81-106 of the codex), which presents three columns of, on average, thirty-two lines/entries. These sections, moreover, feature texts both in Latin and Greek. The handwriting across all texts is inscribed in a regular cursive, featuring an “informal round” for the Greek, and a minuscule with some ligatures for the Latin, both of which datable to the second half of the fourth century. Despite variations in the size of the writing and in the page layout from one text to another, the corroboration of many colleagues has helped us conclude that one single hand is responsible for both the Greek and Latin texts.[18]

The Greek hand of the codex can be described as a small, quickly written cursive, roughly bilinear (the vertical strokes of β, ϰ, ι, ρ, υ often reach below the lower line), and sloping slightly to the right. There are often ligatures of ει, αυ, αι, γε, επ, ελ, θω, λλ, etc. Last letters of the words sometimes project into the intercolumnar space, but not systematically. Accents and breathings have not been written. Occasionally, there is diaeresis on ι and υ.

The Latin hand is not calligraphic either. The Latin hand in the portion containing Cicero’s *Catilinarian Orations* is probably the same hand, though it is written slightly smaller, as the one in the Hadrian section of the codex. It can be described as an upright mixed writing, featuring uncial and cursive elements. Lowe[19] calls it ‘early half uncial’. He already pointed to the resemblance of the Montserrat codex (in Lowe, Suppl. 1782) with Chester Beatty AC 1499, though he dated this one to the end of the fifth century and preferred to date the Montserrat text to the end of the fourth century.[20] Orsini also indicates that the hand of our codex might be the same as one of the hands of the Menander codex, also from the Bodmer library.[21]

1.3 Acquisition

In 1955, Dr Ramón Roca-Puig (1906-2001) purchased a number of papyrus fragments in Cairo which turned out to belong to our codex. Two documents from Roca-Puig’s personal papers may give a clue to the co-

16 For further calculations on this, see Torallas Tovar - Worp 2006, 19-20.

17 Described with line numbers and measurements in Gil - Torallas Tovar 2010, 19-21.

18 Wouters 1988, 18, n. 49, notes that almost all editors of Graeco-Latin papyri have pointed out the resemblance between both hands. There are however cases when differences are so striking that two scribes are considered to have been at work. Most recently on the hands of the codex, Ammirati 2015a, 59 and Ammirati 2015b, 16-18.

19 Lowe 1971, no. 1683.

20 With different dates in CLA 1650 and 1785, cf. Orsini 2015, 65.

21 Orsini 2015, 65.

dex's original source. Both are handwritten by father Sylvestre Chauleur, Director of the *Institut Copte* in Cairo at that time.[22] Both were completed by the summer of 1955, when, apparently, father Chauleur visited the city of Barcelona and delivered the papyri to Roca-Puig personally. In 1973, through an exchange with the *Bodmer Foundation*, Roca-Puig acquired additional fragments also belonging to this codex; these are now inv. nos. 134-135.[23] Later on, an additional fragment from the same codex showed up in the collection of Duke University (inv. no. 798), and was edited by W.H. Willis (1963); this papyrus was subsequently given an imaginary inventory number 129 in Roca-Puig's files.

1.4 Origin

The origin of the codex is not completely clear. Unfortunately, the cover of the codex does not contain any indication of its owner nor scribe. Neither is there much information to be found within the codex itself, as the only reference to an owner appears in the colophons of two of the sections.

As mentioned above, it has been claimed that the codex belongs to the Bodmer library,[24] whose manuscripts were probably produced in the Thebaid. The fact that Chauleur's letter to Roca-Puig mentions the Pachomian monasteries could be used to reinforce the thesis presented by Robinson,[25] but we have to consider the possibility that the introduction of this idea was just a marketing strategy deployed back in the 1950s, so we will not force a conclusion on this matter.[26] There are, however, some material aspects that can help us reconstruct and understand the Bodmer library, and thus find a connection between the pieces in the hypothetical corpus. The reconstruction of this 'library' is mostly the work of James M. Robinson, who lists almost 60 items that, according to him, belonged to the same collection. This is what Fournet calls the 'maximalist inventory'.[27] In assembling this list, Robinson overlooked some acquisition information[28] and often based his hypothesis on unreliable informants,[29] but there still remains some consensus on the coherence of some of the material characteristics and even the textual contents of some of the codices.

A different matter altogether is that of the origin of the codex.[30] Some, including Robinson, claim that this was the library of the Pachomian monastery of Pbow. Others prefer to think that these books belonged to a centre of high education, perhaps in Panopolis.[31] There is also the issue of the geographical proximity of the supposed origin of the Bodmer library and the Nag Hammadi find, which, together with codicological and palaeographical criteria, has been an argument for associating both libraries and proposing a Pachomian origin to both of them.[32] All arguments are based on hypotheses and analogies that cannot be proven in a definite way. Turner[33] already advanced the possibility of a Panopolitan origin, seeing as some of the Bodmer rolls were copied on Panopolitan administrative documents.[34] Gilliam suggests a

22 Both edited in Gil - Torallas Tovar 2010, 25-27.

23 For the exchange affair with Kasser and Braun, see Roca-Puig 1977: xii-xiii.

24 The most recent approach is the monographic section of *Adamantius* 21 (2015) and Nongbri 2018, with an extensive study on the acquisition of this hoard(s) and material features of these books.

25 See n. 5, and Robinson 1990-1991 and Robinson 2011. Kasser 2000, xxi-xxxvii.

26 In spite of the connection of some texts with Pachomian content, the association of the Bodmer Library with the Pachomian communities is at least an open question, if not, as many think, very dubious. Fournet 2015, 12, 16-17. Camplani 2015, 127.

27 Fournet 2015, 8.

28 Kasser 2000, xxiv, n. 5.

29 Kasser 1988, collects two contradictory testimonies: the antique dealer who negotiated its sale to Mr. Bodmer said on his deathbed that they came from Ed-Debba, 5 km. from Nag Hammadi; Mr Bodmer's secretary, on the contrary, claimed that they came from Mina or Minia, in the outskirts of Assiut and that the provenance cited by the antique dealer applied only to *P.Bodm.* 17, from a different lot. Too much speculation, indeed.

30 On the proposals, Fournet 2015, 17-19.

31 Contra Robinson, see Blanchard 1991; Cribiore 2001, 200, and n. 74, both say that this hoard must have belonged to a Christian school of advanced learning. See also Fournet 1992, 253-266. Kasser 1988, 191-194. Kasser 1995, 28, n. 37. But see recently: Pietersma - Turner Comstock 2011.

32 Also led mainly by Robinson 2014, 1118-1135. Recently reopened by Lundhaug - Jenott 2015. For a debate on this see Wipszycka - Piwowarczyk 2017.

33 Turner 1968, 51-53.

34 The rolls of the *Iliad* in *P.Bodm.* 1 (third-fourth century) are copied on the verso of a Panopolitan land register (dated to 208/9). See Geens 2014, 80; Miguélez Cavero 2008, 221-222. See the codicological argument advanced by Fournet 2015, 14.

Panopolitan origin as well, but in his opinion the use of Latin in some pieces of the library contradicts the possibility of the library ever having belonged to a monastery.[35] Fournet and Gascou propose new evidence to link the Bodmer library to Dendera, in the Panopolitan nome but very close to Dishna, based on the evidence provided by documents (and the onomastics in these documents) found in the bindings of some of the codices.[36]

Since all evidence for a safe identification both of the geographical spot and the nature of the 'library' is circumstantial, we will never really know to which hoard the *Codex Miscellaneus* belonged. More than one hoard, however, may have been in circulation and up for sale in those years,[37] and the fact that books with different content and different dates could have belonged to the same library in Antiquity has to be considered as a possibility as well. What is pertinent for our inquiry, however, is the connections between different books presenting similar material features or even textual contents regardless of the library to which they eventually belonged, connections which can instead point to the *scriptorium* from which they might have emanated. A future intervention regarding the ink of codices allegedly belonging to the same 'library' could confirm or dismantle some of these hypothetical reconstructions. May this paper be a first step in embarking upon this worthy project.

2. *Experimental protocol and handling of the fragments*

The archaeometric analysis was performed using portable and non-invasive instrumentation. This way, it was possible to work directly *in-situ* and collecting samples from the leaves analysed was unnecessary. The experimental protocol we applied for the analysis of inks on this codex consisted of a primary screening using NIR reflectography to determine the typology of ink, followed by an elemental analysis using XRF spectroscopy.[38]

Given the peculiar structure of this codex, divided in 7 different textual sections, we decided to analyse one papyrus leaf per section, in order to compare the ink(s) used across the manuscript. Table 1 gives the shelfmarks of the leaves analysed.

Shelfmark	**Section**
Inv. 145	A – Cicero, *Catilinarian Orations*
Inv. 150	B – *Hymn to the Virgin Mary*
Inv. 154	C – Drawing of a mythological episode
Inv. 157	D – *Anaphora*
Inv. 161	E – *Alcestis* in Latin hexameters
Inv. 163	F – Tale about the Emperor Hadrian
Inv. 172	G – Alphabetised stenographical *Commentarium*

Table. 1. Shelfmarks of the leaves analysed and correspondent textual sections.

The leaves of this codex were preserved in glass frames sealed with paper tape. The near-infrared reflectography was performed without removing the glass frame, holding the USB microscope in direct contact with the top glass. This procedure prevented the papyrus leaves from exposure to even the most miniscule amounts of physical stress due to the contact between the writing support and the external surface of the microscope. Unfortunately, it is not possible to perform XRF analysis without removing the glass frames, given that the X-ray beam must be focused directly on the surface of the manuscript. However, during this second step we decided to remove only the top glass, leaving the papyrus leaves positioned

35 Gilliam, 1978, 128-131: while both Menander and Homer are not out of place in a monastery, Latin is however unexpected. Cf. Evelyn White 1926, 320-321, for inscriptions on walls of cells with lines of the Iliad and Menander's *sententiae*. See also Stramaglia 1996, 131-135. Other hypotheses propose a Christian secondary school rather than monastic library.

36 Fournet 2015, 18.

37 As Fournet 2015, 12 also claims.

38 Rabin *et al.* 2012. For further information, see the section "Analytical protocol" contained in the paper "Gaining perspective the materiality of manuscripts: the contribution of archaeometry to the study of the inks of the White Monastery codices" in this same volume.

Fig. 1. Montserrat Abbey, Roca Puig collection, Inv. 150. On the right the micrographs under visible (top) and near-infrared (bottom) light.

on the bottom half of the glass frame. This way it was not necessary to handle the papyri directly, since the bottom glass was used as a support to move the leaves while positioning them under the X-ray beam. We followed this procedure for every leaf examined after verifying that the chemical elements present in the glass were not interfering with the analysis of the ink and papyrus. When possible, we collected at least 4 measurement spots on the inks per leaf in an attempt to portray an accurate representation of the whole surface of the text. Because X-ray penetrates the whole cross-section of the papyrus, to perform XRF it is necessary to have a blank surface on the other side of the leaf that corresponds with the spot of ink chosen for analysis. This often represented a challenge, given both that the text was very densely distributed on the two sides of each folio, and that the spots closer to the border of the paragraph, where generally it is easier to find the condition described, were often too deteriorated to obtain a satisfactory outcome.

3. *Results and discussion: the* Codex Miscellaneus

Fig. 1 shows the results of NIR reflectography on *P.Monts.Roca* inv. 150. Comparing the visible and near-infrared images we observe a slight change in the opacity of the ink. This feature is generally typical of iron-gall inks, although in this case the change in opacity is not everywhere as evident as it is normally observed in medieval iron-gall inks. A closer look at the visible and near-infrared images shows the first letter on the left changes its opacity less than the other letters. Similar observations were made on *P.Monts.Roca* inv. 145, inv. 154, inv. 157, inv. 161, and inv. 163, although the change in opacity between visible and near-infrared micrographs was in some cases more prominent than in others. In a previous work we extensively discussed the limitation of our current analytical protocol to characterise mixed inks obtained through blending carbon with either iron-gall or plant ink.[39] Since it is impossible to predict the behaviour of such inks in the near-infrared region, we tend to be cautious in the interpretation of the results from NIR reflectography when identifying the typology of ink (namely: carbon, iron-gall or plant). In the case of the inks observed on leaves belonging to sections A to F of this codex, we cannot exclude that in some cases small amounts of carbon were added to the mixture.

39 Colini *et al.* 2018.

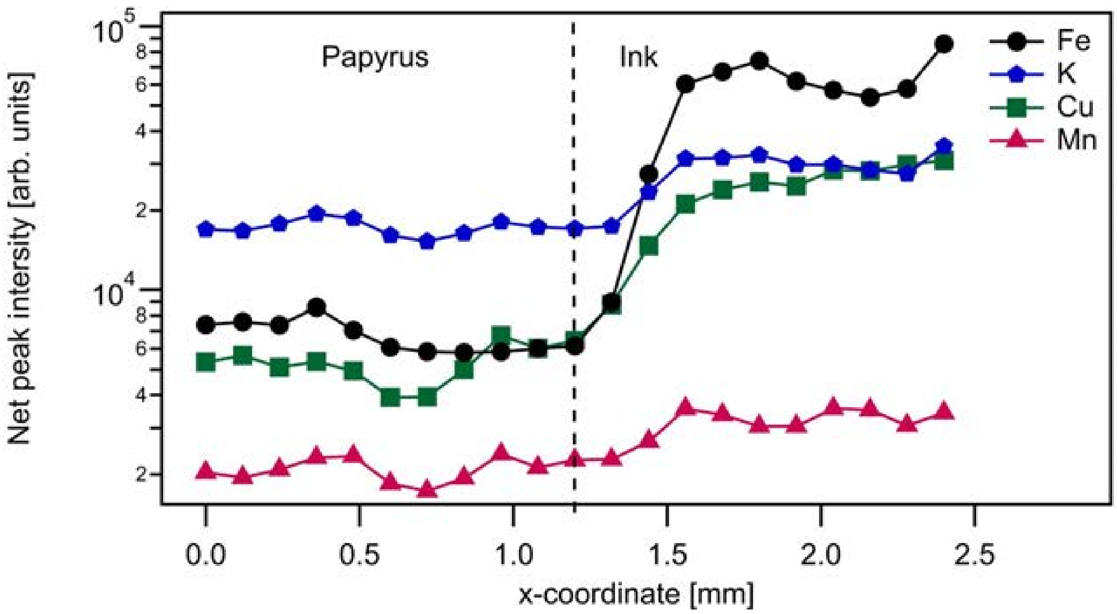

Fig. 2. XRF intensity profiles of different elements collected at the interface between papyrus and ink on Inv. 150.

XRF analysis on these same leaves detected consistent amounts of iron, copper, and potassium, along with small amounts of manganese in all the inks examined. As an example, Fig. 2 shows the intensity profiles of the elements iron, copper, potassium and manganese extracted from the XRF measurements taken along the line connecting the support and an inked area on *P.Monts.Roca* inv. 150 (i.e. the so-called line scan). The similarity of the profiles indicates that all these elements are contained in the ink. Calcium was sometimes found in large amounts, but its presence was at least partly the result of contamination, perhaps originating from papyri contained in the mummy cartonnage that was preserved in the same collection, forming a group of documents probably kept and sold together in the same lot by the papyrus trader in Cairo. This result, together with the slight change in opacity observed in the near-infrared micrographs, indicates that the main component of the writing media used on these leaves is iron-gall ink.[40] The content of potassium may generally be attributed to the binder or to the tannins, while iron, copper and manganese were probably contained in the metallic salt(s) used to prepare the inks.

It is interesting to notice that the ratio of these other elements to iron (i.e. the so-called fingerprint) is heterogeneous along the various sections of the codex, as shown in Fig. 3. Here we observe that the difference between the fingerprints from different spots of ink on *P.Monts.Roca* inv. 145, inv. 154, inv. 157, inv. 161, and inv. 163 is often of such a magnitude as to suggest that this codex was written in more than one phase, a fact that could explain many of its variations in size and page set-up.

In fact, we assume that a coherent writing phase is characterised by the same ratio of other elements to iron, the main component of iron-gall ink. Such ratio can be affected by different factors of impact. The most obvious is the preparation of a new batch of ink once the previous has been used up. In this case, depending on the ingredients (especially the metallic salts) used in the manufacturing of the new ink, the fingerprint can be either completely different in its elemental composition, or simply display a different ratio of elements to iron. In any case, it is very unlikely that the new ink prepared would display the exact same fingerprint as the old one. Differences in the preparation process might also lead to changes in the ink. Another factor influencing the fingerprint is the potential for a new binder to have been added to the ink at some point in order to prevent the particles of pigment from depositing on the bottom of the inkwell. In this case, given the characteristically high concentration of potassium in Egypt's most common binder, gum Arabic, the effect on the fingerprint would most likely be an increase in the ratio of potas-

40 To obtain iron-gall ink a source of iron (generally metallic salts) is mixed with hydrolysable tannins. These are rich in gallic acid which complexes iron to form a black pigment called iron-gallate.

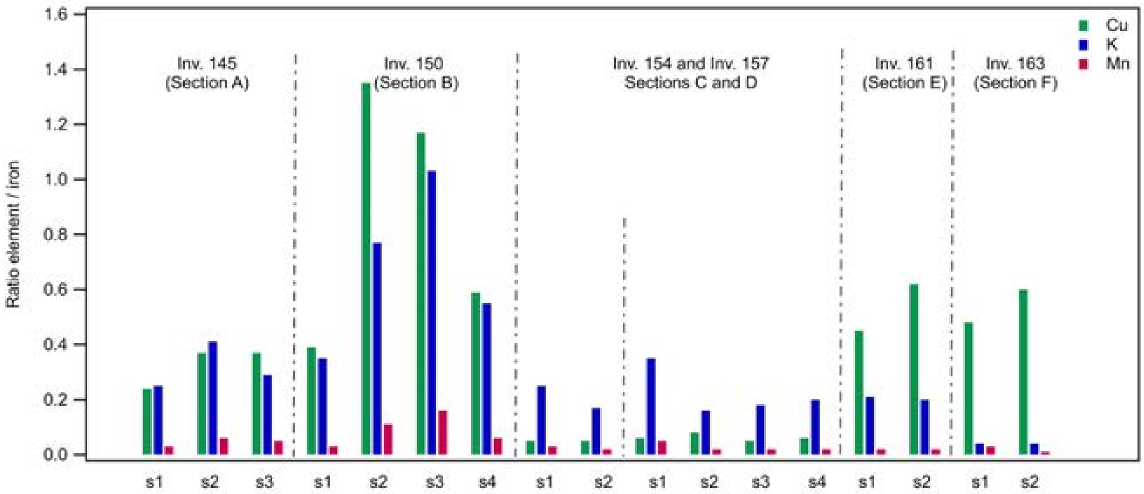

Fig. 3. Fingerprint of different spots of ink (s1, s2, s3…) on the leaves from sections A to F of the *Codex Miscellaneus*.

sium to iron. Finally, the fingerprint can change as a mere effect of time because of deposition and drying processes affecting the ink. Furthermore, experimental studies performed on iron-gall inks preserved in sealed bronze containers showed that the metallic vessel can leak into the ink with the passing of time, thus increasing the concentration of one or another element.[41] It must be stressed, though, that the use of metallic ink well during Late Antiquity has not been largely attested so far. One of the few examples we have comes from Hamuli and is probably dated between the ninth and tenth century CE.[42] Because it registers the factors of change discussed so far, the fingerprint model was applied in the past to complement codicological studies, and it successfully led to the characterisation of each writing phase when applied to texts written on rather homogeneous supports, such as parchment or European paper.[43]

Unfortunately, the situation is by far more complicated in the case of papyrus manuscripts because the heterogeneous structure of the writing support largely hampers an accurate determination of the inks' fingerprints.[44] Consequently, comparisons between the fingerprints of inks from different leaves of the *Codex Miscellaneus* must be treated with extreme caution. In any case, the analytical data presented in this work do not aim at providing an exact determination and characterisation of the various writing phases. Even if we were dealing with a more homogeneous support, this task could certainly not be accomplished analysing only a few spots of ink on 6 of the over 50 leaves that compose sections A to F of the codex. It is possible, though, to obtain a general indication regarding the different stages of writing by observing the data from Fig. 3. Here we can distinguish 5 groups of fingerprints that show significant variations in the ratios of other elements to iron:

- section A (folio 145) displaying similar ratios of copper and potassium and a lower ratio of manganese;
- section B (folio 150) where the ratio of all these three elements tends to be higher;
- section C and D (folios 154 and 157) showing ratios of potassium higher than ratios of copper and manganese;
- sections E (folio 161) displaying a ratio of copper that is almost doubling the ratio of potassium;
- section F (folio 163) showing a fair ratio of copper and very small ratios of potassium and manganese.

Obviously, the one presented here is just a rough discrimination, as can be inferred by observing the ink spot 1 analysed on section B. Its fingerprint much more closely resembles those in section A than those which immediately follow in section B. This suggests the possibility that the writing phases of the codex

41 Nehring 2019.

42 Depuydt 1993, 601, pls 465-467.

43 Hahn *et al.* 2007; Rabin - Hahn - Geissbühler 2014; Geissbühler *et al.* 2018; Hahn - Heiles - Rabin 2018.

44 Ghigo - Rabin - Buzi 2020.

Fig. 4. Montserrat Abbey, Roca Puig collection, Inv. 172. On the right the micrographs under visible (top) and near-infrared (bottom) light.

did not always coincide with the limits of a textual section. It is plausible that the scribe took breaks from writing or prepared new ink while working at the same section.

The last section of the codex (section G) is peculiar compared to the others. Unlike the previous sections it does not contain strictly a literary text, but a list of words related to the practice of stenography.[45] It is interesting to notice how the results obtained on *P.Monts.Roca* inv. 172 suggest that such peculiarity extends as well to the typology of ink used. Fig. 4 shows the corresponding visible and near-infrared micrographs. Here, no change in the opacity of the ink is observed, leaving no doubts that the text was written using a carbon-based ink. Furthermore, XRF analysis did not detect any inorganic element consistently present in the ink, confirming that this leaf was written using a pure carbon ink.

During our archaeometric studies of inks from late antique Egypt, we sometimes found carbon inks (or mixed inks containing consistent amounts of carbon) used in *marginalia* on the medieval parchment codices from the library of the White Monastery and of Saint Macarius monastery. However, the *Codex Miscellaneus* is the only case we have recorded so far of a manuscript displaying a significant discrepancy in the typology of ink used to write the main text of different parts of the codex. Carbon and iron-gall ink are very different both in the ingredients used for preparation and in the manufacturing procedure. This made us wonder about the reason of such discrepancy within the same codex. Since the practice of stenography was confined in antiquity to the sphere of the administration and justice, we decided to compare the results obtained on section G with those obtained on *P.Monts.Roca* IV 70, a documentary papyrus written in the same period.

4. *Results and discussion:* P.Monts.Roca *IV 70*

P.Monts. Roca IV 70 (inv. nos. 194 + 193 + 192 + 113 + 1204; TM 219245) contains the remains of a legal dossier, with accounts and a report of legal proceedings. In all likelihood, its provenance is Alexandria, since it contains the text of the proceedings of a trial before the Prefect of the Annona of Alexandria, Fl(avius) Cratinus. It has an internal date, 378/9 CE. It has been written in a skilled fourth-century cursive hand, performed with a very thin calamus, leaving very sharp strokes and elegantly executed letters. This fact

45 On the text, see Torallas Tovar - Worp 2006, 25-35. Stenography (or tachygraphy) is connected to notarial practice in Antiquity. On shorthand manuals and papyri, see Boge 1974; Boge 1976; Irigoin 1989; Menci 1992; Lewis 2003; Torallas Tovar - Worp 2006; Kaltsas 2007.

Fig. 5. Montserrat Abbey, Roca Puig collection, Inv. 113+192+193+194+1204. On the right the micrographs under visible (top) and near-infrared (bottom) light.

places our text in the context of a professional scribe linked to administration. Interestingly, the situation is similar for the last section of the *Codex Miscellaneous*, where one can clearly notice that a thinner calamus has been used.

The similarity between these two manuscripts extends to the type of ink used as well. Fig. 5 shows the results of the NIR reflectography on this document. The comparison between visible and near-infrared micrographs reveals that it was written using a carbon-based ink, exactly like the last section of the *Codex Miscellaneus*. In addition, XRF elemental analysis did not detect the presence of any inorganic element.

It could be argued that the comparison between the *Codex Miscellaneus* and *P.Monts. Roca* IV 70 is not appropriate, given that the area of provenance of the two manuscripts is indeed very different. In this regard, it must be mentioned that a recent study over a more significant number of documentary and literary texts, pointed out that carbon-based inks were found in most cases when analysing documentary papyri from various areas of Egypt, while iron-gall ink (or inks showing similarities to iron-gall) were used mostly in literary texts.[46] Against this background, if we accept that documentary and literary texts were produced in separate environments, we must acknowledge that both the textual contents and the archaeometric results coincide in suggesting that section G and sections A to F were composed in different environments, or in any case, using a different set of tools and materials.

5. *Conclusions*

The comprehensive analysis presented in this work cross-links textual, palaeographical, codicological, and archaeometric information, and casts light on the process of production of the *Codex Miscellaneus*. Previous palaeographic analysis identified only one hand as responsible for the composition of the codex, both in its Greek and Latin texts. The variation in language, page set-up and contents suggested that the book was not conceived as a single product, but was probably produced in successive phases according to the needs of the scribe. Now, elemental analysis on some of the leaves has revealed and confirmed that it was written in consecutive phases. We observed that there was a difference in the composition of the inks from the several sections, and in some cases, even within the same section, thus further indicating that the production did not happen in one instance, but rather the scribe stopped, maybe produced or procured new ink, and then continued writing at a later moment. In addition, both archaeometric and textual analysis suggest that the last section, the list of Greek words connected to stenography, was written in a different environment than the other sections. Further research on samples of papyrus and parchment manuscripts has pointed out the split that remained for a few centuries in the literary and documentary

46 Ghigo - Rabin - Buzi 2020.

use in some areas of Egypt: iron-gall inks used mostly for the former vs. carbon inks extensively used for the latter. We imagine that such traditions and customs weighed heavily in the production of ink in the *scriptoria* or offices where documents were produced.

In conclusion, we can assume that this small codex belonged to one single person who composed it in different moments. This only confirms the hypothesis already formulated in the past about this and similar miscellaneous codices.[47] It was most likely that the small dimensions of these types of codices made it easy to use them as 'notebooks' and thus to carry them around, a practice which likely left traces of different typologies of ink used across in different environments. The owner of the codex used iron-gall ink in the composition of the literary texts, but when he copied the words list (section G) – the only text in the codex which is not literary –, he used a different kind of ink, perhaps because he was at that point working in a *scriptorium* or office devoted to the production of documents.

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47 Radiciotti 1997, 132-134; Crisci 2004, 129-132; Ammirati 2015a, 57-58: uses the denomination 'codice biblioteca'.

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Gaining Perspective into the Materiality of Manuscripts: The Contribution of Archaeometry to the Study of the Inks of the White Monastery Codices

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Abstract
An interdisciplinary approach to the study of manuscript traditions is here applied to the analysis of the leaves from the White Monastery, one of the greatest centres of literary production in Late Antique Egypt. In the framework of the 'PAThs' project, archaeometric analyses complement the information pieced together by a range of disciplines in the field of humanities. The use of different complementary analytical techniques provides information on the type of ink used and its elemental composition, unveiling interesting details regarding the materials and methodology of manufacturing of writing media. Moreover, this contribution takes a step forward and discusses the possible existence of a regional arrangement in the elemental composition revealed in the inks studied.

Keywords
archaeometry, ink analysis, interdisciplinary approach, Coptic studies, manuscript making.

1. *Introduction*

In November 2017 the CSMC (Centre for the Study of Manuscript Cultures, University of Hamburg), the BAM (Bundesanstalt für Materialforschung und -prüfung, Berlin), and the ERC Advanced grant project 'PAThs', based at Sapienza University of Rome, started an interdisciplinary project aimed at bringing new insights into the material study of manuscripts.[1] This collaboration is based on a dedicated PhD project, that addresses primarily the archaeometric analysis of writing materials in Coptic Egypt. The main purpose is to collect data on a statistically relevant number of manuscripts, trying to reconstruct the technological evolution of black inks and coloured pigments, while giving support to palaeography and codicology.[2] It is in this frame-

* Tea Ghigo performed the analytical campaigns, evaluated the data collected and prepared the manuscript. Ira Rabin provided feedback during the data evaluation and revised the manuscript. The research presented in this article has been funded by the European Research Council, Horizon 2020 Programme, with an ERC Advanced Grant 2015 destined to support the project "Tracking Papyrus and Parchment Paths: An Archaeological Atlas of Coptic Literature. Literary Texts in their Geographical Context: Production, Copying, Usage, Dissemination and Storage", project no. 687567, P.I. Paola Buzi, http://paths.uniroma1.it. This work was carried out in cooperation with the SFB 950 "Manuskriptkulturen in Asien, Afrika und Europa" funded by the German Research Foundation (DFG) and within the scope of the Centre for the study of manuscript Cultures (CSMC). We would like to acknowledge the help of the personnel of the libraries who permitted our access and supported our work. Our special thanks go to the staff of the Staatsbibliothek in Berlin, in particular to Christoph Rauch, Melitta Multani and Nicole Fürtig. Warm thanks are also due to Paolo Vian, Delio Vania Proverbio, Irma Schuler, Angela Nuñez and the staff of the conservation laboratory at the Apostolic Vatican Library. Special thanks also to the staff of the Cambridge University Library, in particular to Ben Outhwaite, Anna Johnson, Maciej Pawlikowski and our Olivier Bonnerot, for dedicating his time to perform the analysis on *Or.* 1699 ff. M1-M2 in this collection. We are deeply indebted to our colleagues Oliver Hahn, Zina Cohen and Simon Steger from the BAM, and especially thankful to Francesco Valerio and Paola Buzi, who supported this work from the very beginning, providing crucial information and fostering new interdisciplinary dialogue.

1 Ghigo *et al.* 2018.

2 The corpus of manuscripts to examine is in constant development in accordance with the results obtained during the work. So far, we have analysed texts from six different collections. Among the papyrus collections, we examined some fragments from the 'Bodmer Library' and some codices from the library of the cathedral of Thi(ni)s (Ghigo - Rabin - Buzi 2020; Ghigo - Torallas in this volume). Among the parchment collections, we examined the codices from the Monastery of Apa Jeremiah, the heterogeneous Michaelides collection preserved at the Cambridge University Library, the parchment codices from the Monastery of Saint Macarius (Ghigo - Rabin 2019), and those from the library of the White Monastery presented in this work.

work that the material analysis of the inks used on the leaves from the library of the White Monastery has been developed.

The White Monastery, or better the confederation of monasteries that it coordinated, became one of the most relevant focal points of Coptic literary production under the strenuous guidance of Shenoute (ca. 350-465/66 CE), who himself became the most prolific Coptic writer.[3] What remains of the library, however, dates back for the most part to a much later period, between the ninth-eleventh centuries CE, although a nucleus of earlier papyrus and parchment manuscripts might have survived.[4] The codices from this ancient collection were often divided up while circulating the antiquity market. For this reason, their leaves are nowadays to be found in several European and non-European collections. [5]

The parchment leaves examined within the research described here date back to the tenth-eleventh centuries, and most of them are preserved at the Staatsbibliothek zu Berlin Preußischer Kulturbesitz, as part of a set of fragments bought in 1887. This purchase included 69 leaves, which, once at the Staatsbibliothek, were bound in eleven modern volumes.[6] At the Staatsbibliothek we examined 25 parchment leaves originally belonging to 17 different codicological units. In addition, we also analysed 5 parchment leaves originally divided in 3 codicological units forming part of the Borgian collection at the Apostolic Vatican Library. These were brought to Europe on the initiative of Cardinal Stefano Borgia, who acquired them in 1778.[7] Finally, we examined 2 leaves from a single codicological unit now preserved at the Cambridge University Library which, according to Catherine Louis, belong to a codex from the White Monastery.[8]

Table 1 lists the shelfmarks, number of folio and modern collection for each codicological unit examined. For sake of clarity, we added the CMCL sigla[9] and the 'PAThs' IDs (CLM numbers, in the latter case)[10] as a univocal way of determining a specific codicological unit, as it appears in the *Archaeological Atlas of Coptic Literature*.

It is fundamental to remark that the codices that formed part of this library were not produced exclusively in the scriptorium of the White Monastery. Some of their colophons reveal that, as a gesture to save their souls, some donors commissioned manuscripts to a *scriptorium* in Touton,[11] in the Fayyūm, far away from the White Monastery in Sūhāǧ (Sohag). This seems to have been a professional *scriptorium* that spent part of the time producing codices to be donated to the White Monastery. Table 1 reports, where possible, the information available regarding the place of production of the leaves examined.

2. *Analytical protocol*

The analytical protocol applied on the leaves from the White Monastery consists of a primary screening to determine the type of the ink and a subsequent in-depth analysis using several spectroscopic techniques: X-ray Flourescence (XRF), Fourier Transformed Infrared Spectroscopy (FTIR), and Raman spectroscopy.[12] The primary screening is carried out by means of near-infrared reflectography. Strictly speaking, optical differences between carbon, plant and iron-gall inks are best recognized when comparing their response to the infrared light: carbon ink has a deep black colour, iron-gall ink becomes transparent above 1200 nm and plant ink disappears at ca. 750 nm.[13] We performed the analysis using a small USB microscope equipped with a NIR light at 940 nm, an UV light at 390 nm and an external white light source. Working at 940 nm we determined the ink typology, observing the changes in the opacity of the ink. Here, car-

3 Orlandi 2002; Buzi 2016.

4 Buzi 2014, 64.

5 On Shenoute's and the manuscripts of the White Monastery, see above all Emmel 2004.

6 Buzi 2014, 61-63.

7 Buzi 2009, 7-8; Louis forthcoming, 7.

8 Louis forthcoming, 365 (n. 919).

9 Corpus dei Manoscritti Copti Letterari (CMCL): www.cmcl.it.

10 'PAThs' – Archaeological Atlas of Coptic Literature: https://atlas.paths-erc.eu. The *siglum* CLM stand for Coptic Literary Manuscripts.

11 Nakano 2006.

12 Rabin *et al.* 2012.

13 Mrusek - Fuchs - Oltrogge 1995.

Preservation place	Shelfmark	Folio(a)	CMCL	CLM	Production place
Berlin, Staatsbibliothek	*Ms.or.fol.* 1348	ff. 1-3	MONB.LN	502	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1350	f. 1	MONB.AB	264	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1350	f. 3	MONB.OO	576	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1605	f. 1	MONB.IB	427	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1605	f. 2	MONB.IE	430	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1605	f. 3	MONB.NL	547	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1605	f. 6	MONB.KH	476	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1606	f. 3	MONB.NT	555	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1607	ff. 1-2	MONB.DN	343	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1607	ff. 9-10	MONB.GC	400	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1608	f. 3	MONB.EZ	375	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1609	ff. 1-2	MONB.VG	3350	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1609	f. 3	MONB.AW	283	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1609	f. 4		1572	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1611	f. 1		1710	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1612	ff. 1-3	MONB.AR	278	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1613	f. 1	MONB.DQ	346	Unknown
Berlin, Staatsbibliothek	*Ms.or.fol.* 1614	f. 1	MONB.CR	325	Unknown
Apostolic Vatican Library	*Borg.copt.* 109 *cass.* 16, f. 57	f. 2	MONB.KM	480	Fayyūm (?)
Apostolic Vatican Library	*Borg.copt.* 109 *cass.* 26, f. 131	ff. 2-3	MONB.CE	314	Touton - Fayyūm
Apostolic Vatican Library	*Borg.copt.* 109 *cass.* 29, f. 166	ff. 1-2	MONB.NC	538	Fayyūm
Cambridge University Library	*Or.*1699	ff. M1-M2	MONB.LY	511	Touton – Fayyūm

Table 1. List of the leaves analysed. The information on the production place was extracted from the section 'Manuscripts' of the *Archaeological Atlas of Coptic Literature*: https://atlas.paths-erc.eu/manuscripts (last accessed 13.02.2019). Further details are discussed in the following paragraphs.

bon-based inks show no change in their opacity, while the opacity of iron-gall inks changes considerably, and plant inks become transparent. The in-depth investigation includes micro-XRF analysis to detect the elemental composition of the ink. In the case of iron-gall inks we sometimes establish the so-called fingerprints, i.e. the characteristic ratios of the metallic elements contained in the ink.[14]

3. *Preliminary results*

We focused our analysis on both the black inks and the coloured pigments displayed in the leaves of the codices.

The XRF analysis of red, green and yellow pigments found on some of the leaves of this collection led to their identification, showing a palette composed of minium (Pb_3O_4) for the red-orange tones, orpiment (As_2S_3) or realgar (As_4S_4) for the yellow hues, and copper-based greens whose mineralogical composition was not possible to investigate further. These results were not surprising as these pigments occur in nature and are widely distributed. Furthermore, the use of arsenic-based pigments is documented in Egypt since Pharaonic times[15] while evidence of minium is recorded from the Greco-Roman period onwards.[16]

In contrast, interesting results were obtained while investigating the black inks. The examination using NIR reflectography revealed that the main body of the text, the titles and the colophons of all the leaves analysed were written using iron-gall ink. Furthermore, XRF analysis revealed a difference in their elemental composition. After comparing the data obtained from all the codicological units studied, we observed two different clusters: inks containing only iron (Fig. 1), and inks also containing copper and, in some cases, a little zinc (Fig. 2), as reported in Table 2.

14 Rabin *et al.* 2012.

15 Lee - Quirke 2000; Daniels - Leach 2004; Di Stefano - Fuchs 2011.

16 Ahmed Afifi 2011.

Preservation place	Shelfmark and folia	Elements detected		
		Fe	Cu	Zn
Berlin, Staatsbibliothek	*Ms.or.fol.* 1348	*	*	*
Berlin, Staatsbibliothek	*Ms.or.fol.* 1350, f. 1	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1350, f. 3	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 160, f. 1	*	*	
Berlin, Staatsbibliothek	*Ms.or.fol.* 1605, f. 2	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1605, f. 3	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1605, f. 6	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1606, f. 3	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1607, ff. 1-2	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1607, ff. 9-10	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1608, f. 3	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1609, ff. 1-2	*	*	*
Berlin, Staatsbibliothek	*Ms.or.fol.* 1609, f. 3	*	*	
Berlin, Staatsbibliothek	*Ms.or.fol.* 1609, f. 4	*	*	
Berlin, Staatsbibliothek	*Ms.or.fol.* 1611, f. 1	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1612, ff. 1-3	*		
Berlin, Staatsbibliothek	*Ms.or.fol.* 1613, f. 1	*	*	*
Berlin, Staatsbibliothek	*Ms.or.fol.* 1614, f. 1	*	*	
Apostolic Vatican Library	*Borg.copt.* 109 *cass.*16.57, f. 2	*		
Apostolic Vatican Library	*Borg.copt.* 109 *cass.*26.131, ff.2-3	*		
Apostolic Vatican Library	*Borg.copt.* 109 *cass.*29.166, ff.1-2	*		
Cambridge University Library	*Or.*1699 ff. M1-M2	*		

Table 2. Elemental composition of the black inks from the codicological units studied.

A variety of mediaeval recipes mention the use of vitriol in the manufacturing of iron-gall inks. The term itself referring to a mixture of sulphates appeared during the late Middle Ages.[17] Vitriol has been commonly equated to the Greek term *chalcanton*, a copper-based substance often mentioned in ancient treatises.[18] According to Pliny, *chalcanton* could be obtained during Antiquity from crystallization of drain waters proceeding from mines containing sulphates,[19] and we can suppose that throughout history it could have been directly extracted from those mines as well. Either way, the resulting salt will most likely contain a mixture of different sulphates, typically iron, copper and zinc, as has been supported by the analysis of the inks of mediaeval European manuscripts.

The absence of a variety of metallic elements in the inks of some of the manuscripts from the White Monastery collection might be an indication that other materials, such as common iron nails or iron filings, were used instead of vitriol to prepare this type of iron-gall ink. Arabic recipes from the Middle Ages onwards corroborate this possibility.[20] Alternatively, vitriol may have been purified before being used in the preparation of the ink: the addition of solid iron to the vitriol solution to obtain pure iron sulphate is reported in literature.[21] In any case the two groups of inks revealed through elemental analysis reflect differences in the materials and methodology of manufacture of the inks.

Generally, we tend to assume that manuscripts belonging to the same collection show a certain degree of homogeneity in the materials used for the preparation of the ink. However, this is not the case for

17 KARPENKO - NORRIS 2002.

18 We must recognise, though, that to date we have no direct proof of the correspondence between *chalcanton* and vitriol before the early Middle Ages.

19 Pliny, 34.32.

20 COLINI forthcoming.

21 KARPENKO - NORRIS 2002

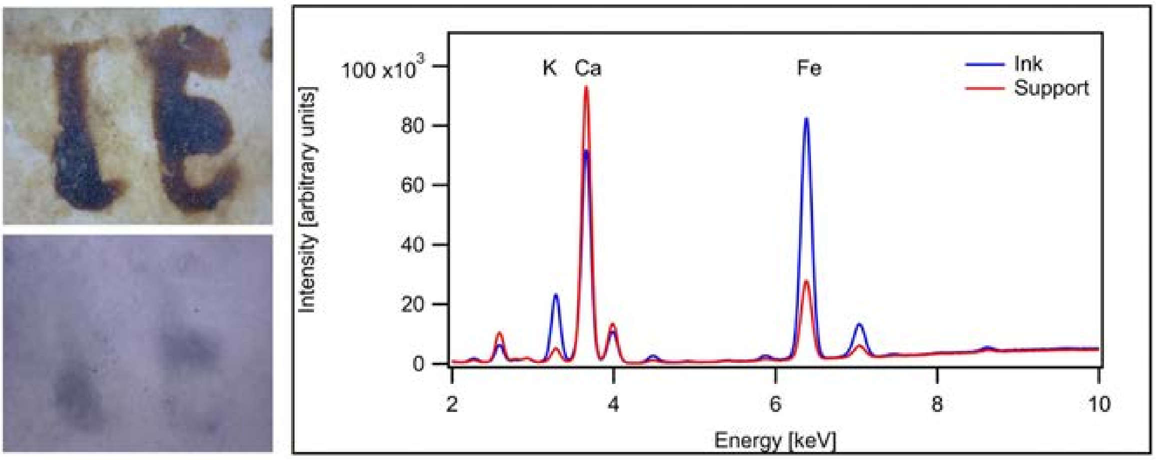

Fig. 1. Visible and near-infrared micrographs (left top and bottom, respectively) and XRF spectra (right) of the inked (blue) and non-inked (red) area on Berlin, Staatsbibliothek, *Ms.or.fol.* 1350, f. 1.

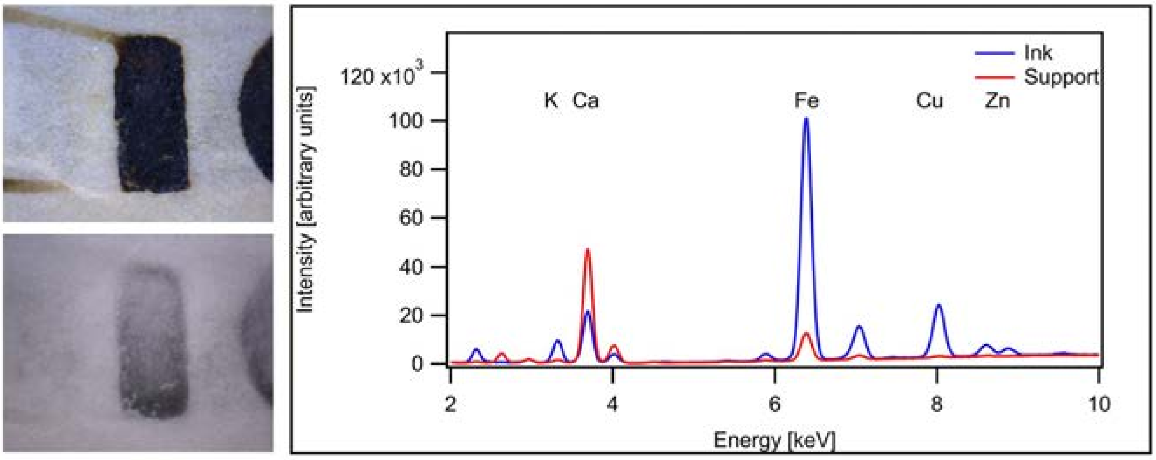

Fig. 2. Visible and near-infrared micrographs (left top and bottom, respectively) and XRF spectra (right) of the inked (blue) and non-inked (red) area on Berlin, Staatsbibliothek, *Ms.or.fol.* 1609, f. 1.

the manuscripts from the White Monastery. We should not forget though, that the codices forming part of this collection were most probably produced in at least two different places: the Touton *scriptorium*, in the Fayyūm region, and the White Monastery itself. Trying to gain further insight, we focused our attention on the few codices available that were attributed to Touton or more generally to the area of the Fayyūm, and therefore produced in the north of Egypt rather than in the area of Sūhāǧ, where the White Monastery was located. According to palaeographical and codicological studies, the leaves at the Cambridge University Library, *Or.* 1699 and those preserved at the Apostolic Vatican Library, *Borg.copt.* 109 *cass.* 26, f. 131 were originally part of codices produced in Touton (respectively MONB.CE = CLM 314 and MONB.LY = CLM 511). In fact, as it has been pointed out by Francesco Valerio,[22] both are decorated in the so-called 'Touton Style', which was identified and defined by Petersen[23]. Moreover, Apostolic Vatican Library, *Borg.copt.* 109.*cass.* 29, f. 166 (MONB.NC = CLM 538) can be generically attributed to the area of the Fayyūm according to some dialectal forms typical of this region,[24] while *Borg.copt.* 109 *cass.* 16, f. 57 (MONB.KM = CLM 480) may have

22 Personal communication (26th June 2019).

23 Petersen 1954.

24 Louis forthcoming, 373-375.

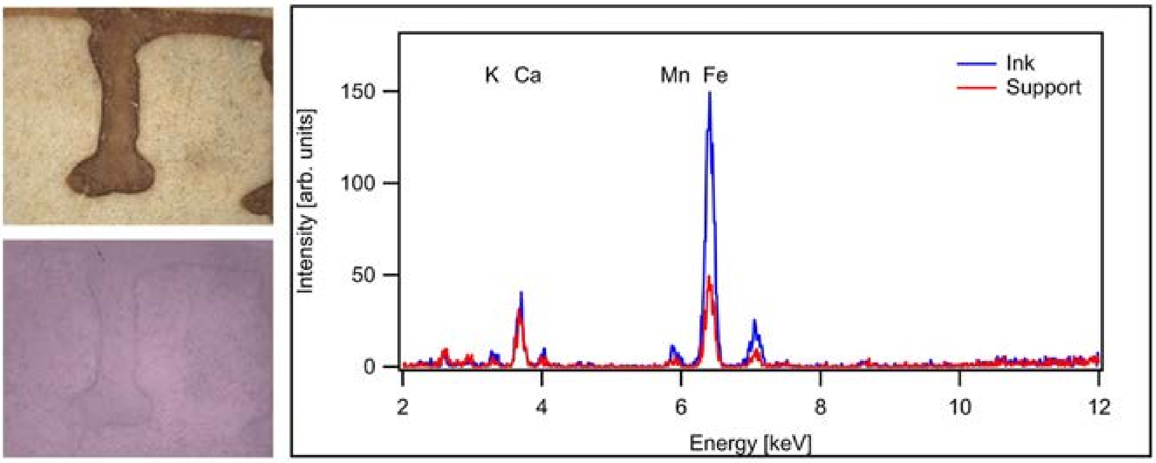

Fig. 3. Visible and near-infrared micrographs (left top and bottom, respectively) and XRF spectra (right) of the inked (blue) and non-inked (red) area on Apostolic Vatican Library, Borg.copt. 109 cass. 26, f. 131.

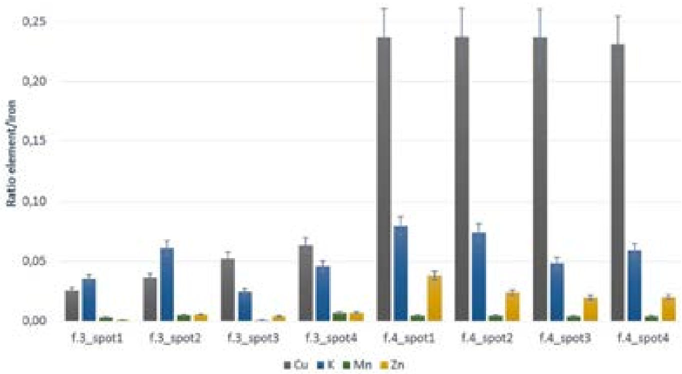

Fig. 4. XRF elemental analysis on four spots of ink from f. 3 and four spots of ink from f. 4 of Berlin, Staatsbibliothek, Ms.or.fol. 1609. The results are reported as ratio of each element to iron (i.e.: fingerprint).

been produced in the same region according to the typology of superline strokes used.[25]

It was interesting to note that the inks found on all these four different codicological units contained exclusively iron, with no trace of copper or zinc (see for instance the results obtained on *Borg.copt.* 109 *cass.* 26, f. 131 in Fig. 3). Despite the fact that the number of manuscripts from Touton and the Fayyūm that have been investigated is far from being statistically meaningful, the consistency in the result obtained seems to suggest there may be a trend in the composition of the inks used in northern Egypt. This hypothesis was corroborated by the analysis of four codices from the Monastery of Saint Macarius in Wādī al-Naṭrūn that revealed the use of iron-gall inks containing exclusively iron, but of course it will be necessary to make more tests before reaching trustable conclusions.[26] This analytical evidence, together with the textual information demonstrating that the manuscripts from the White Monastery were produced in different places, poses some interesting questions: is it possible that the inks produced in the north of Egypt in a period between the ninth and eleventh centuries all contained exclusively iron? Could this have been a peculiar trait characteristic only of the inks produced in that area? And if so, what implication would this have for the analytical results obtained on the collection from the White Monastery? Is it possible that the manuscripts whose inks contain only iron were produced in the north of Egypt, while those whose inks contain other elements were produced elsewhere, for instance inside the same monastery? These matters are of great importance. If further analysis could confirm that a consequential number of manuscripts produced in northern Egypt were penned with inks containing only iron, while a significant number of manuscripts produced inside the monastery were written with inks containing also copper and zinc, that would indicate the existence of local differences in the materials and methods used in the manufacturing of writing

25 Louis forthcoming, 145-147. Archaeometric studies often rely on few pieces, given the limited access that it is possible to obtain to the collections when it comes to perform scientific analysis. Therefore, every piece of information that is possible to obtain matters, even in case of manuscripts whose historical context is still unclear. For sake of clarity, it is pointed out that the attribution to a specific geographic location is, in this case, dubious.

26 Ghigo - Rabin 2019.

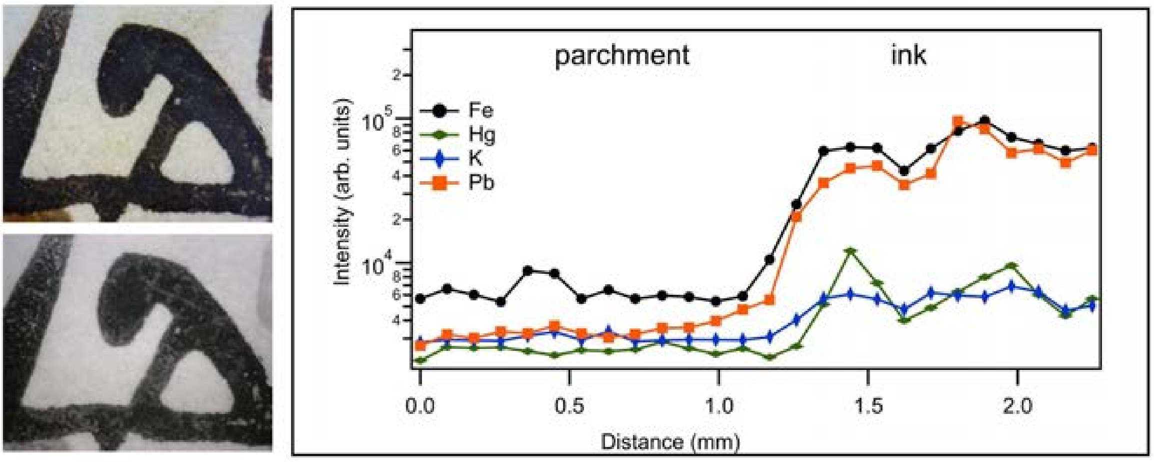

Fig. 5. Visible and near-infrared micrographs (left top and bottom, respectively) and XRF intensity profiles (right) of different elements extracted from a line-scan connecting non-inked and inked areas on Berlin, Staatsbibliothek, Ms.or.fol. 1605, f. 6.

media. Most importantly, this typological diversity could be exploited to establish the place of production of a certain codex.

Archaeometric analysis, at least in some cases, can support palaeographical and codicological studies, providing them with additional tools to gain insight on the production of manuscripts in a certain scriptorium. It is the case of Berlin, Staatsbibliothek, *Ms.or.fol.* 1609, ff. 3 and 4 (CLM 283 and 1572). In her catalogue of the Coptic manuscripts at the Staatsbibliothek,[27] Buzi suggests that these two leaves may come from the same codicological unit, since the hand is very similar, if not the same. After performing XRF analysis, we calculated the fingerprint (i.e.: the ratio of each element to iron) of the ink used on both these leaves. In Fig. 4 the result of this calculation is displayed. Here we observe a diversity in the ratio of copper to iron in folio 3, where is around 5%, and in folio 4, where is around 25%. Although on this basis we cannot claim that these two leaves belong to different codicological units or were written by different persons, we can certainly assess that they come from different writing phases. In fact, even when the same ink is used for a certain period, and it is left to rest in the inkwell or in any other storage place for some time, it might change its fingerprint due to deposition and drying processes. Alternatively, every new batch of ink displays a slightly different fingerprint. Such differences in the fingerprint have been successfully used in the past to discriminate between several writing phases on a certain codex.[28] The case study on Berlin, Staatsbibliothek, *Ms.or.fol* 1609, ff. 3 and 4 was presented at the University of Hamburg during the summer school dedicated to Coptic literature that took place in September 2018,[29] in the presence of scholars who had directly studied these leaves. According to Diliana Atanassova, despite the similarity in the handwriting, the two leaves were written indeed by two persons. Alin Suciu added that these two hands very likely belong to a teacher and a pupil who worked closely in the same *scriptorium*, thus explaining the similarity in the handwriting.

Lastly, we will discuss the case of the peculiar type of ink found on f. 6 of Berlin, Staatsbibliothek, *Ms.or.fol.* 1605 (MONB.KH = CLM 476). Right in the middle of this leaf there is evidence of a marginal note added later, that corresponds to the numbering of chapters of biblical works according to the Greek system.[30] Fig. 5 reports the results on this spot. Near-infrared reflectography shows that there is no change in opacity when the ink is illuminated using 940 nm light. This clearly indicates that it contains carbon. However, XRF analysis detected the presence of iron, lead and mercury together with potassium, that could be attributed to the binder. The intensity profiles of each element detected along a line that connects non-inked and inked areas reveal that iron and lead intensities increase significantly moving from the support to the inked area, indicating that we are probably dealing with one of the

27 Buzi 2014.

28 For instance Hahn - Heiles - Rabin 2018.

29 See https://www.manuscript-cultures.uni-hamburg.de/register_coptic2018.html.

30 Schüssler 2007, 81.

rare examples of mixed inks recorded so far. Moreover, potassium and mercury are present in lesser amounts. The pattern of the intensity profiles is very similar in the case of potassium, iron and lead, and suggests that they were all contained in the ingredients employed, together with carbon, in the ink manufacturing. The high iron content may suggest that carbon was mixed with iron-gall ink, although the presence of tannins that need to react with iron to produce this type of ink could not be identified using the current analytical protocol. While potassium can normally be attributed to the binder, lead is generally not contained in vitriol or iron filings used to prepare iron-gall inks, and therefore could have a different origin. There exists the possibility that this ink was prepared by mixing carbon, iron-gall and red lead (minium), to give a warmer hue to the black colour. Or, simply, that lead was introduced from contaminated water. Finally, the line profile of mercury, appears slightly different from the one characterising the other elements. This suggests that the trace of ink was contaminated by something containing mercury, for example the same pen was first used to apply a mercury-based red ink (cinnabar) and then used to write this marginal note.

At present, the evidence we have on mixed ink produced by blending carbon and iron-gall ink consists of different recipes contained in Arabic treatises from the ninth century onwards describing its preparation, and a Syriac manuscript from the fourteenth century where a mixture of iron-gall and carbon ink was unequivocally identified.[31] Unfortunately, we do not have any information on the period in which this marginal note was added. It was definitely after the tenth-eleventh centuries CE, when this codex was first produced, and surely before its dismemberment. In fact, Francesco Valerio pointed out that such chapter numbers, all written by the same hand, are detectable in all the extant leaves belonging to this codicological unit.[32] According to him, as a lower chronological term for the addition of such numbers, a reasonable date is the thirteenth-fourteenth century CE, when Coptic 'monolingual' manuscripts ceased to be produced and used, having been replaced by the bilingual Copto-Arabic ones.[33]

5. *Conclusion*

The results obtained on the leaves from the White Monastery seem to suggest that there may exist local trends involving different materials and methods used in the manufacture of black inks in Egypt between the ninth and eleventh centuries, encouraging further investigation in this direction. If such trends could be systematically demonstrated, the chemical composition of the inks may serve to complement palaeographical and codicological information on the place of production of certain codices. Moreover, the archaeometric analysis of inks on Berlin, Staatsbibliothek, *Ms.or.fol.* 1609, ff. 3 and 4 revealed interesting details regarding the production of the manuscript, offering new insights on the different phases involved in the writing process. Finally, this study unveiled one of the first experimental proof of the existence of a mixed ink probably obtained by adding carbon to iron-gall ink, although further investigation is needed to support this conclusion.

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31 COLINI 2018; COLINI *et al.* 2018.

32 See the table dressed by SCHÜSSLER 2007, 81.

33 Personal communication with Francesco Valerio, 27 June 2019.

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