Select Papyri from Danish Collections
Christiansen, Thomas

Publication date: 2016

Document version
Other version

Document license: CC BY-NC-ND

Citation for published version (APA):
Select Papyri from Danish Collections: Philological and Archaeometric Studies

Thomas Christiansen
In memoriam
Allan Christiansen (1949-2016)
Select Papyri from Danish Collections: Philological and Archaeometric Studies
Thomas Christiansen

Front cover: European Radiation Synchrotron Facility (ESRF), Grenoble, France.
List of contributions

Introduction

Thomas Christiansen

First part: philological studies

The Carlsberg Papyri 13: Catalogue of Egyptian Funerary Papyri in Danish Collection

Thomas Christiansen, Kim Ryholt

P. Carlsberg 326 – A Letter from the Late New Kingdom

Thomas Christiansen, Dora Olsen

Interlude

Review of the textual sources pertaining to the manufacture of black ink in the ancient Mediterranean

Thomas Christiansen

Second part: archaeometric studies

Chemical characterization of black and red inks inscribed on ancient Egyptian papyri: the Tebtunis temple library

Thomas Christiansen, David Buti, Anna Vila, (Kim Dalby), Poul Erik Lindelof, Kim Ryholt

Copper-containing carbon inks from ancient Egypt: a μXRF and μXANES study

Thomas Christiansen, (Marine Cotte), (René Loredo Portales), Sine Larsen, Poul Erik Lindelof, Kell Mortensen, Kim Ryholt

Postlude

Experimental report and experimental method: Study of the composition of various types of black and red ink – determination of provenance

Thomas Christiansen, Sine Larsen, Poul Erik Lindelof, Kell Mortensen, Kim Ryholt

English and Danish résumé
As hinted by the title, *Select Papyri from Danish Collections: Philological and Archaeometric Studies*, my Ph.D. thesis consists of a number of contributions: one book and four papers. It ends with a report on an experiment performed at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, and a proposal for a new experiment at the same facility. Each contribution can be read independently, but certain themes also tie them together, like: the invention and evolution of ink and the archaeological context and acquisition history of Egyptian manuscripts.

Five of the contributions are co-authored. This format has not been used as a frame for a Ph.D. thesis in Egyptology at the University of Copenhagen in the past. In order to understand why it was deemed necessary to present my doctoral research in this format, some background information on the nature and the history of my stipend is needed.

My research was funded by the University of Copenhagen Programme of Excellence (UCPH 2016) project CoNeXT (Copenhagen Neutron and X-ray Technologies).¹ CoNeXT is an interfaculty project that was initiated by the new neutron and X-ray research infrastructures that are operational or under construction in Lund, Sweden, and Hamburg, Germany: ESS, MAX IV, Petra III and the European XFEL. The aim of the project is to ensure that the University of Copenhagen will be able to use the full potential of the new neutron and X-ray sources and to unite scientists who are experienced users of such large facilities with less experienced researchers that see the great potential in them.

My advisor, prof. in Egyptology and Co-PI of CoNeXT, Kim Ryholt, falls in the latter category. He formulated the basic tenures of my research project, namely that it should consist of two separate parts: a micro-historic study based on papyri from the Papyrus Carlsberg Collection and an investigation of the perspectives that large infrastructure X-ray sources hold for papyrology. It was originally envisioned that the first part should comprise a socio-economic study of the Adler papyri, an ancient Egyptian private archive from the late second and early first centuries BCE, which had recently become part of the collection through a generous grant by the Augustinus Foundation and the Carlsberg Foundation (2012).² The second part should address one of the central challenges facing the papyrologist: the fact that the majority of ancient Egyptian (and Mediterranean) papyri lack a recorded archaeological context. It was expected that X-ray analysis of select papyri from the Papyrus Carlsberg Collection would deliver chemical and structural fingerprints, which could be used to map characteristic elemental traits of the ink and thereby enable the sorting of manuscripts along a geographical axis.

As is most often the case in research, asking basic questions is tantamount to opening a ‘Pandora’s Box’. It was early on realized that non-invasive chemical studies of ancient ink and papyri presented a new field of research, which required complicated experimental setups and multifarious analytical strategies. At the point of writing this introduction, the interpretation of the results obtained from X-ray analysis of select papyri from the Papyrus Carlsberg Collection involves a dozen scientists in the fields of Egyptology, Chemistry, Physics, Geology and Material

¹ http://conext.ku.dk/
² T. Christiansen, ‘Horos arkivet’ [the Horos archive], *Papyrus* 33 (1), 4-9
Science. Further, it entailed that I was “schooled” in the basics of chemistry and physics – fields of research that I, being an Egyptologist by trade, had no prior training in whatsoever.

Consequently, it was decided that I instead of providing the mentioned socio-economic study should focus on providing text-editions of twenty-three unpublished Egyptian manuscripts that I was working on at the time (2013). The editions should emphasize the acquisition histories and materiality of the manuscripts, whereas the second part should present micro-historic chemical studies on ancient ink as a technology.

As evidenced by the list of contributions, the thesis is divided into two main parts: Philological Studies and Archaeometric Studies. The first part consists of the abovementioned book, The Carlsberg Papyri 13: Catalogue of Egyptian Funerary Papyri in Danish Collections, co-authored with Kim Ryholt; and an article published in the Journal of Egyptian Archaeology 101, ‘P. Carlsberg 326 – A Letter from the Late New Kingdom’, written together with Dora Olsen.

The book presents an exhaustive catalogue of twenty-two Egyptian funerary manuscripts in Danish collections. It includes sixteen papyrus manuscripts, two of which are preserved intact, and smaller pieces of inscribed linen from six mummies. The material spans a period of more than a millennium, ranging from c. 1200 BCE to 100 CE. Most of the manuscripts are guides to the afterlife; eighteen of them contain texts and vignettes from the Book of the Dead, while a minor fragment preserves an illustration from the Book of Amduat. The three remaining manuscripts are funerary passes. The article presents an edition of a letter from the late New Kingdom in the Papyrus Carlsberg Collection (inv. 326). The final text editions appeared in print in 2016. The authors are equal contributors and their names are listed in alphabetical order in the publications.

The second half of the thesis, Archaeometric Studies, also consists of two contributions: ‘Chemical characterization of black and red inks inscribed on ancient Egyptian papyri: the Tebtunis temple library’ and ‘Copper-containing carbon inks from ancient Egypt: a μXRF and μXANES study’. Both papers present chemical studies of selected papyrus fragments from the Papyrus Carlsberg Collection performed respectively at the Centre for Art Technological Studies and Conservation (CATS), the National Gallery, Copenhagen, Denmark; and at the microscopy beamline ID21, the European Radiation Synchrotron Facility (ESRF), Grenoble, France. All the analyzed papyri derive from two primary archaeological contexts in Egypt, private archives found at the military camp Pathyris (modern: Gebelein), dating to late second and early first centuries BCE; and manuscripts, which once formed parts of the temple library in Tebtunis (modern: Umm el Breigât), dating to the first and second centuries CE.

These two contributions were written in close collaboration with scholars from CoNeXT, Sine Larsen (PI, Chemistry), Poul Erik Lindelof (Physics), Kell Mortensen (Physics), Kim Ryholt (Egyptology) and external collaborators, David Buti (CATS), Marine Cotte (ESRF), Kim Dalby (Nano-Science Center, UCPH), René Loredo Portales (Department of Pharmacy, University of Guanajuato, Mexico) and Anna Vila (CATS). The role these scientists played in the experiments and interpretation of the data is described and acknowledged in the individual contributions.

---

3 http://www.cats-cons.dk/
4 http://www.esrf.eu/UsersAndScience/Experiments/XNP/ID21
In both instances, I am the principal author and have been responsible for the final editing. Co-authorship has been assigned according to the Vancouver-protocol. These publications have not seen print before, primarily because further analysis is needed. They are written and submitted as finished papers, but with arguments that take into account that more work is necessary, before they can be submitted to a final review. The scholars, whose names have been placed in parentheses in list of contributions and in the articles, all played a central part in acquiring and interpreting the data, but were not able to assist in writing up of the contributions to this thesis. Their comments and corrections will be included in the prospective publications of the results of the experiments.

It should be noted, that the two parts are written for different audiences. The first part mainly addresses the specialized Egyptologist – although everybody should be able to enjoy the plates accompanying the book. The second part is written for researchers interested in the application of science for the study of cultural heritage. This being said, there are undoubtedly passages that will be hard to follow for the historian without a basic grasp of chemistry and physics. However, I hope that the conclusions reached and the perspectives drawn will be of some interest to a wider audience, since the non-invasive X-ray techniques described in the second part can be applied to practically any archaeological object. The two contributions of the second part can with advantage be read sequentially, since the experiments described in the first paper are the logical precursors of the ones presented in the second article.

The contribution ‘Review of the manufacture of black ink in the ancient Mediterranean’ can be read as an introduction to the second part. In this article the scantily preserved textual evidence that describe the manufacture of black ink in Antiquity is collected for the first time and compared to the previous analytical record. This contribution, of which I am the sole author, was submitted for review to the Bulletin of the American Society of Papyrologists during the summer of 2016.

The thesis ends with reproducing an experimental report on the results obtained during 48 hours of beamtime at the ESRF and an application for further experiments at the same facility. They can be read as brief communications and status report on the current status of the human science project in CoNeXT: ‘Ancient Ink as a Technology’. They further succinctly provide new information on one of the aspects of the archaeometric studies, which is in need of further analysis, namely the composition of some of the red inks used in the Tebtunis temple library. Finally, they provide the general reader with an impression of the procedures involved in acquiring and applying for beamtime at a large facility. They were submitted to the ESRF on the ninth of September, 2016. In both cases, I was the principal author and responsible for finalizing the manuscripts.

All contributions are written adhering to different style sheets. Therefore, spelling (English/American), layout and reference system are not uniform throughout the thesis. For this reason the contributions have been paginated separately and follow the unnumbered sequence outlined in the list of contributions (p. iii). The thesis (the book aside) is not supplied with a bibliography, but with extensive references.

* To iterate the methodologies, arguments and conclusions put forward in each contribution would be both an arduous and meaningless task, since they were written autonomous, but a few general

---

6 http://conext.ku.dk/research/large-facilities/
observations are warranted. It can be argued rightfully that my thesis is disiecta membra. Besides being an apt description of the format of my thesis, this Latin phrase encapsulates the contents of a large papyrus collection. A case in point is the Papyrus Carlsberg Collection that houses hundreds of incomplete manuscripts, which have been put together from thousands of disjointed fragments. Further, adjoining pieces of these manuscripts – spanning millennia of history, covering all societal aspects and written in a multitude of scripts and languages – are spread throughout the modern world.

It is evident that these scattered manuscripts and fragments can only be collected, studied and made available for both scholars and public alike, through a joint effort, involving researchers from a variety of disciplines. As such, these philological and archaeometric studies are my reflections of different ways of approaching a papyrus collection using both methods that are well-established and unconventional within the fields of Egyptology and Papyrology.

* These studies would not have been possible without the support of numerous people. First I would like to acknowledge the efforts of my co-authors. Of these I have to single out Poul Erik Lindelof, who has not only been instrumental in teaching me the basics of Physics and Chemistry, but in the process have become a dear friend. I hope that we will continue to “go a roving late into the night.” Special thanks is also due to Kim Ryholt, who introduced me to the Papyrus Carlsberg Collection many years ago and later entrusted me with the keys to the kingdom; Sine Larsen, who believed in me and walked more than an extra mile to ensure the best possible outcome of my project; and Marine Cotte for being so patient with me, when I had a hard time grasping the import of our studies at the ESRF. I have enjoyed our collaboration with David Buti and Anna Vila at CATS immensely and they have saved me from making many unfounded claims.

Further, I would like to acknowledge Ira Rabin for putting me on the right track, when I lost my way. I would never have embarked upon the study of the materiality of ancient Egyptian papyri, had it not been for Leyla Lau-Lamb, who many years ago introduced me to the art of papyrus conservation. I still think back on our time together as some of the brightest days during dark times. I am deeply indebted to Lena Tambs, who spent many a day and night proof-reading and commenting upon the thesis. I hope to be able to pay you back at a future date.

Finally, I should thank some close friends, who during the years have listened to many a rant from me and faked interest: Paul Flemming Hartvigson, Jakob Moesgaard, Dora Olsen and Jacob Schmidt-Madsen. These studies are dedicated to the memory of my father, Allan Christiansen. I sorely miss you.
First part: philological studies


Das Motiv ist damit an zwei Stellen literarisch verwendet worden, die rund 500 Jahre auseinander liegen. Die Vorstellung muss demnach trotz des großen Zeitabstandes in der religiösen Gemeinschaft lebendig geblieben sein. Der Autor hält jedenfalls die Wahrscheinlichkeit für gering, dass sie zweimal auf völlig jungfräulichem Boden gewachsen ist.

Stefan Bojowald

P. Carlsberg 326: a letter from the late New Kingdom*

Edidio princeps of a letter from the late New Kingdom (inv. P. Carlsberg 326) that mentions a prophet of Sobek by the name of Peuhrai. The authors argue that the letter is of Theban provenance and that it belongs to the corpus collected by Jaroslav Černy under the heading ‘Late Ramesside Letters’. The article is supplemented by a hieroglyphic transcription, a facsimile (fig. 1) and a scan (fig. 2).

The authors would like to thank Fredrik Hagen and Kim Ryholt for their comments and valuable advice. They would further like to acknowledge the skillful conservation of the papyrus performed by Leyla Laulamb in 2010.

* The authors would like to thank Fredrik Hagen and Kim Ryholt for their comments and valuable advice. They would further like to acknowledge the skillful conservation of the papyrus performed by Leyla Laulamb in 2010.
Introduction

The letter from the Ramesside Period published in this article belongs to the Papyrus Carlsberg Collection. There are only two other texts from the New Kingdom in the Collection: P. Carlsberg 6, a copy of the teachings of Merikare, and P. Carlsberg 8, a medical treatise dealing with obstetrics. Publications of these appeared over half a century ago by the hands of Erik Iversen and Aksel Volten.¹

The papyrus is in a poor state of preservation and does not shed much light on the actors or their situation, but it is worthwhile to study, as it may have belonged to a dossier or an archive from the period,² and could conceivably become an essential part of a larger puzzle at some point. If nothing else, it provides the student of late New Kingdom hieratic with another sample of formal letter writing.³

Acquisition and Provenance

It is not known when P. Carlsberg 326 was bought and when it entered the collection. It does not seem to be one of the manuscripts that H. O. Lange acquired on his travels in Egypt (1899–1900, 1929–30). More likely, it was part of the assemblages of papyri the Carlsberg Foundation bought on the antiquities market in Cairo at his instigation during the years 1931–38, or later, in 1954, at Aksel Volten’s.⁴ The bulk of these stems from a temple library and archive in Tebtunis and date to the Ptolemaic and Roman Periods. The provenance of the associated material and the mention of a prophet of Sobek might therefore indicate the region of the Fayum as place of origin of the letter, though some arguments—outlined in the discussion below—speak in favour of a Theban provenance.

In this context, it is noteworthy that the first acquisitions by the Carlsberg Foundation are roughly contemporary with that of Alan Gardiner in 1933 of some fragments of a letter from Deir el-Medina.⁵ These came to the antiquities market as a result of theft or clandestine digging by the inhabitants of Gurna in the wake of the expedition of the same year by the French Institute at Cairo.⁶ This is the latest documented acquisition of a Late Ramesside Letter and it seems reasonable to speculate that P. Carlsberg 326 reached Cairo around this time from similar sources and that there it became mixed up with the recently unearthed Tebtunis material.⁷

Physical Description

P. Carlsberg 326 is of a dark brown colour.⁸ The full height of the sheet (19.6 cm) is preserved. Both the right and left sides of the document are broken off and it is therefore difficult to ascertain the original width. In its present state it measures 12.5 cm. The total loss is probably around 9 cm, since the standard horizontal measure of a letter in this period is 21–22 cm;⁹ a spatium of blank space follows the last line of the recto, where the letter comes to an end, and

¹ The editiones princeps are E. Iversen, Papyrus Carlsberg No. VIII. With Some Remarks on the Egyptian Origin of Some Popular Birth Prognoses (Copenhagen, 1939)—on the verso of the manuscript there is an unpublished medical text dealing with eye diseases—and A. Volten, Zwei altägyptische politische Schriften (Copenhagen, 1945).
³ I.e. a letter ‘proper’ and not a communication. For the distinction, cf. J. J. Janssen, Late Ramesside Letters and Communications in the British Museum (Hieratic Papyri in the British Museum VI (Dorchester, 1991), 8.
⁴ The two abovementioned New Kingdom papyri were acquired independently of this material. For H. O. Lange and the antiquities trade, cf. F. Hagen and K. Ryholt, Antiquities Trade in Egypt 1880s–1930s: The H. O. Lange Papers (in press).
⁵ The present location of the fragments are not known, cf. Janssen, Late Ramesside Letters and Communications, XX.
⁶ J. Černy, Late Ramesside Letters (Bibliotheca Aegyptica IX; Bruxelles, 1939), XVII.
⁷ Papyri from other regions, e.g. Thebes, Hermopolis, Soknopaiou Nesos, were mixed up with the Tebtunis material; these, however, all stem from the Late Period.
⁸ For a clearer impression, we have reproduced both a scan and a facsimile of the papyrus
⁹ Černy, Late Ramesside Letters, XVIII; but cf. the comments made by Janssen, Late Ramesside Letters and Communications, 48–9.
the right side therefore seems to have incurred most of the damage.\(^{10}\) The breaks along the sides are even—offering some hope that further fragments might come to light in the storage room of some other collection.

There are ten incomplete lines of text on the recto and a single stroke on the bottom of the verso (probably a remnant of the address). Both the recto and verso of the papyrus show the document to be a palimpsest—the only clear trace of earlier writing on the recto, however, is the light grey colouring found between the lines and in the area around the ‘\(\dot{s}i\)-sign in line 3; on the verso, several unintelligible lines are visible.\(^{11}\) The letter has been folded from the top of the verso outwards. Seven folds can be observed, increasing in height from the bottom of the recto to the top.

\(^{10}\) Disregarding the square breaks on the left side of the sheet in lines 4–6.

\(^{11}\) The washed-off text is written in a hand that is tiny compared to the one of the present letter.
Fig. 2. Scan of P. Carlsberg 326 (courtesy of the Papyrus Carlsberg Collection)
Transcription

(Top Margin)

(Bottom Margin)

Transliteration and translation

(1) …] n hm-ntr n Sbk Pyw-hry [...] to the prophet of Sobek, Peuhrai [in life, prosperity, health and in the favour of

(2) …] nsw ngy: w tw=i hr dd n ‘Imn-Rˁ nsw ngy: w [...] Amun-Re] King of the Gods. I speak to Amun-Re, King of the Gods [...

(3) …] iwt. ˁ3 hsw.t knw ˁ3i [...] a great old age and very many favours [...

(4) …] hnr dd wnn tày= l k [spr r=k [...] and further: When my letter [reaches you...

(5) … Hri=nh] p3 ływ jw=k [...] Horiankh], this guardian, and you [...

(6) …] dl= w sw n=f p ływ=f ir? [...] it was given to him his .? [...

(7) …] it ływ=j tm dl.t= w n[f] [...] barley, but I did not to give it to him [...

(8) … Hrj=nh] p3 ływ dl= i ływ=f [...] Horiankh], this guardian. I will let him come [...

(9) …] ptr hsb iri n=k mtrj [...] Look, (I) have send (this) to serve you as a testimony [...

(10) …] Hri=nh p3 ływ [...] Horiankh, this guardian.


Discussion

The letter is addressed by an unknown person to a prophet of Sobek named Peuhrai. What little can be gleaned from the content of the letter indicates that it concerns a dispute, in which a guardian called Horiankh plays a prominent role, over an economic transaction involving barley.

The bold and unsightly handwriting demonstrates that it should be dated to the late New Kingdom and there are a few, although in no way definitive, arguments for more specifically ascribing the papyrus to the correspondence collected under the heading ‘Late Ramesside Letters’: the mention of a ‘prophet of Sobek’ in P. Turin 1979, the dearth of ‘formal’ letters from this period from other archeological provenances and the preserved parts of ‘the complimentary preamble’ (lines 2–3) that closely mirror the phrasing found in that corpus.

In P. Turin 1979 ‘the scribe of the treasury’ Painefernerefer asks the scribe Tjaroi to revoke an action (imprisonment?) taken against a certain Kassu, until the prophet of Sobek returns to the city and states his claim in the matter. It is clear from the phrasing that the prophet is a person of influence and importance in the community:

With relation to this, it is important to note that the cult of Sobek is well-documented in the Theban nome during this period. More specifically, he was numbered among the popular gods in Deir el-Medina and this veneration was expressed through diverse objects found there, including stelae, house-shrines, as well as the personal names found in the Late Ramesside Letters, e.g. Nessobek, Sobeksankh.

Thomas Christiansen and Dora Olsen

Zu zwei Versen aus Die Menge vorlassen: ‘Orthographie’ in einem spätmittelägyptischen Ritualtext

Discussion of two brief passages from the ritual text *Introducing the Multitude on the Last Day of Tekhi* on the basis of all available versions. In both cases, new readings can be proposed, the stable transmission of seemingly unusual writings providing the main argument.

енарك للبركيس

دراسة لتجهيز نص طبيعي متأخر تقديم الحشود، متفق على جدران دهليزين

دراسة لمقطعين قصيرين من نص طبيعي يقدم الحشود في اليوم الأخير لـ *Tekhi* (يتخي) استندًا إلى كل النصوص المتاحة، حيث يمكن في كلا الحالتين اقتراح قراءة جديدة فالانتقال السلمي لما يبدو كتابات غير معادية يقدم برهان هام.

13 H. Ranke, *Die ägyptischen Personennamen* (Glückstadt, 1935), 128 n. 22.
16 He also seems to be an object of some concern in the ‘Nubian letters’, P. BM EA 1026, P. Turin 1971, P. Turin 2026, where his name is written Kas or Kasy, cf. E. F. Wente, *Late Ramesside Letters* (SAOC 33; Chicago, 1967), 9.
18 PM, 867.
19 For these and a few other examples, cf. the index in Černy, *Late Ramesside Letters*, 75–81.

* Mark Smith bin ich für die Durchsicht einer früheren Fassung des Manuskripts sehr dankbar.
Interlude
Review of the textual sources pertaining to the manufacture of black ink in the ancient Mediterranean

Thomas Christiansen University of Copenhagen

Abstract

Three types of black ink are attested in the textual sources pertaining to the manufacture of black pigments in the ancient Mediterranean: “carbon ink”, “mixed ink” and “iron-gall ink”. A discussion of the well-known accounts by Vitruvius, Pliny and Dioscorides is expanded with a study of the formulae for black ink found in the Greek Magical Papyri, and an examination of the textual evidence from late-period Egypt and beyond. It is demonstrated that the ingredients mentioned in the reviewed texts were employed regularly in ancient Egyptian and Mediterranean pharmacology. Further, it is argued that the soot and charcoal for “mixed inks”, i.e. carbons inks that contain metalloids, were obtained as by-products of metallurgy, glaze and glass production. The article is supplemented with a glossary of selected Arabic, Coptic, Egyptian, Greek and Latin technical terms.

Black ink is the established and time-honoured way in which man commits his words to writing and communicates his thoughts and experiences over short and vast distances of space and time. Surprisingly, this ground-breaking invention has received only limited scholarly attention from ancient historians and conservators of manuscripts alike; 2 in marked contrast to the medium on which it was most regularly employed in the ancient Mediterranean, namely the papyrus-manuscript, which for decades has been the subject of scholarly debate and experimental archaeology. 3 That the subject of ink-manufacture has been treated “step-motherly” is probably due to the scarcity of ancient sources pertaining to its production; however at least a dozen of them exist – unlike for the making of papyrus-manuscripts, on which only the account of Pliny the Elder in the Historia naturalis and a few references by Theophrastus in the Historia plantarum have survived. 4

1 I would like to sincerely thank the CoNeXT project, University of Copenhagen, and, in particular, Prof. Kim Ryholt and Prof. Sine Larsen for their support of my ongoing research on ancient inks and papyri. I am grateful to Prof. Adam Bülow-Jacobsen, Dr. Ira Rabin and Prof. Poul Erik Lindelof for their very helpful remarks and suggestions. Finally, I am indebted to MA Lena Tambs for carefully proof-reading the article and double-checking the quotes and references.


There can be no doubt that the ancient Greeks, as they persistently state, obtained the technology of writing from the Egyptians. Although the texts pertaining to writing in ancient Egypt are legio, there exists – besides a few passing references – no detailed descriptions of how the inks used by the ancient Egyptians were produced. The main sources describing the manufacture of inks and paints in the ancient world were written by Vitruvius, Pliny and Dioscorides in the first century CE. Moreover, formulae for ink can be found in Greek magical and alchemical papyri from the third-fourth centuries CE.

The Greek and Latin words for “black ink,” μέλαν and atramentum, can be used not only for black ink per se, but also for various black substances applied as pigments; on occasion μέλαν can further be modified by other words to simply mean ink, e.g. Τυφωνίου μέλανος γραφή (writing with Typhonian ink, i.e. red ink). In ancient Egyptian a similar term is ry.t, which covers both the raw material and the resulting substance compounded with gum and water. In most cases it refers to black ink used in writing, though occasionally to the red employed for rubrication, i.e. ry.t wsd.t (red ink).

Three different types of black ink are attested in the written history of the Hellenistic period: “carbon ink,” “mixed ink” and “iron-gall ink”.

1. Carbon ink is based on carbon compounds obtained from the burning or macerating of organic and inorganic materials, e.g. wood, oil, earth, etc. Carbon is the oldest ink material known and its use for writing can be traced back to the Predynastic period, i.e. c. 3200 BCE, Petrie having found dozens of pottery jars with ink inscriptions of a date “probably half-way back in the dynasty before Mena.”

---

5 E.g. Pl. Phdr. 274d-275b, where the invention of letter writing is ascribed to the Egyptian god of wisdom Theuth (Thoth). Later in the dialogue, 276c. μέλαν, used in the sense “black ink,” is attested in ancient Greek for the first time, when Socrates says: “Then he (the philosopher) will not, when in earnest write them (ideas) in ink (γράψει μέλανι), sowing them through a pen (διὰ καλάμου) with words which cannot defend themselves by argument and cannot teach the truth effectually”

6 Cf. E. Iversen, Some Ancient Egyptian Paints and Pigments: A lexicographical Study (Copenhagen 1955); J. Harris, Lexicographical Studies in Ancient Egyptian Minerals (Berlin 1961) 141-162

7 PGM XII. 96-101; a heading for a formula for red ink

8 A. Erman and H. Grapow, Wörterbuch der ägyptischen Sprache, 7 vols. plus 5 vols. (Leipzig 1926-1963) 2.399.10-11; Harris (n. 5) 147-148

9 For ry.(t) wsd.(t) as an ancient Egyptian euphemism for red ink, see J. Quack, “Mit grüner Tinte Rot schreiben,” Göttinger Miscellen: Beiträge zur ägyptologischen Diskussion 165 (1998) 7-8


11 W.M.F. Petrie, Abydos I (London 1902) 3; the oldest surviving papyrus roll (uninscribed) was found in the tomb of Hemaka, an important official during the long reign of the first dynasty king Den, cf. W.B. Emery, Excavations at Saqqara. The Tomb of Hemaka (Cairo 1938) 13-14 (cat.#:429)
2. Mixed ink consist of the same main ingredients as carbon ink, but whereas the first is based entirely on carbon compounds, then metal bearing minerals (copper, iron, lead) have been added to the second. It is not known, when mixed ink first made its appearance in ancient Egypt, but its use is attested in the third century BCE.

3. Iron-gall ink is made by mixing primarily oak galls (containing gallotannic acid) with an iron sulphate (FeSO₄•7H₂O), which produces a writing fluid (ferrous gallotanate) that on exposure to air turns black through oxidation. The first textual attestation of the use of what may be termed a “sympathetic” iron-gall ink is found in the Belopoeica by Philo of Byzantium, which dates to the late third century BCE.

All three types of ink are later admixed with a binding agent and normally suspended in water; at times in another fluid, e.g. vinegar. Almost invariably the binding agent in ancient Egypt seems to have been gum Arabic from the acacia nilotica (L.), collected in forest-like formations along the Nile. This tree, which was also used in ritual, medicine and cosmetics throughout the ancient Near East and the Mediterranean, was named šnd.t (Coptic: qonte) in Egyptian and its sap kmì(t), kms (Coptic: kommi, komme), from which Greek χέμμα, Latin gummi, and English “gum” etc. is derived.

---

12 Though the exact nature of the chemistry of the black ink on the two fragments from the Herculaneum papyri is nowhere stated explicitly in the available studies, Brun et al. (n. 2) 3751-3754 and Tack et al. (n. 2) 1-7, it is evident that the ink should be classified as what in this article is called a “mixed ink”; in this case meaning a carbon ink to which lead (Pb) has been added.

13 Delange et al. (n. 1) 213-216, cf. the discussion below under “mixed ink.”


15 Ph. Bel. 4.77; for this type of ink, cf. Zerdoun Bat-Yehouda (n. 2) 91-95

16 In the middle ages very mild acidic solutions of dilute vinegar and yoghurt were used to arrest or slow down the formation of mould in the ink, cf. M. Levey, “Mediaeval Arab Bookmaking and Its Relation to Early Chemistry and Pharmacology,” TAPS 52, no. 4 (1962) 7

17 R. Newman, M. Serpico, “Adhesives and Binders,” in Nicholson and Shaw (n. 3) 476-477; Gettens and Stout (n. 14) 27-28

18 For the use of the acacia in ancient Egyptian pharmacology (and cosmetics), cf. H. Von Deinen and H. Grapow, Wörterbuch der Ägyptischen Drogennamen (Berlin 1959) 500-503; L. Manniche, An Ancient Egyptian Herbal (London 1989) 65-67; for its use in Coptic pharmacology, cf. W.C. Till, Der Arzneikunde der Kopten (Berlin 1951). Theophrastus mentions that the Egyptians used acacia instead of gall for tanning (Hist. pl. 4.2.8); Pliny, who copied extensively from Theophrastus, adds that the best gum was that of the Egyptian acacia (HN 13.20.66). For all questions relating to names, identifications and synonyms for plants in the Roman world, cf. J. André, Les Noms de Plantes dans la Rome antique (Paris 1985)

19 Erman and Grapow (n. 8) 4.521; Crum, Dict. 573a-b

20 Erman and Grapow (n. 8) 5.39; Crum, Dict. 110b

21 W. Westendorf, Kopt. Handwörterbuch 64; G. Takács, “Proto-Afro-Asiatic origin of ‘gum’?,” BSOAS 63, no. 1 (2000) 96-99; J. Kramer, “Zur wortgeschichte von Gummi, APF 57.1, 62-64. It can be applied both to true gums and gum-resins, Harris (n. 6) 158-159. Gum (Arabic), like the acacia, is well-attested in both ancient and medieval Egyptian medicine, Deinen and Grapow (n. 17) 516-519; Till (n. 17) 62
Carbon Ink

Results by analytical means show that the majority of ancient papyri are inscribed with amorphous carbon – presumably also pyrolusite (MnO$_2$) and magnetite (Fe$_3$O$_4$) – in the form of soot, charcoal or bone black, called in ancient Egyptian $d^\text{f}b.t$ (Coptic: $\mathbf{XBB\epsilon C}$). The products obtained were rarely pure carbons and most samples analysed so far contain various mineral impurities. The coarseness of some specimens indicates that the “soot/charcoal” was at times collected from calcined masonry and plaster surfaces, which could explain the term, “soot/charcoal from stone” ($d^\text{f}b.t$ n.t inb), found in ancient Egyptian medical papyri from the New Kingdom. An ostracon found in Deir el-Medina from the Ramesside period (c. 1200 BCE) possibly contains the earliest reference to the making of black ink in ancient Egypt, since $ry.t$ (pigment) occurs on it in connection with $ht \, dd(l)$, a particular type of wood (pine?) – from which a fine “soot/charcoal” ($d^\text{f}b.t$) for writing seems to have been produced.

As already stated, no detailed descriptions of the manufacture of black ink are attested before the Roman period, when Pliny provides the most comprehensive account of the different procedures, whereby the carbon compounds (soot/charcoal) used for black ink/paint were obtained. In a section of the thirty-fifth book of the “Natural History,” which is devoted to the different pigments employed in ancient Mediterranean paints, inks and dyes, he writes the following about atramentum:

Black pigment will also be classed among the artificial colours (atramentum quoque inter facticios erit), although it is also derived from earth in two ways; it either exudes from the earth like the brine in salt pits, or actual earth of a sulphur colour is approved for the purpose. Painters (pictores) have been known to dig up charred remains from graves thus violated to supply it. All these plans are troublesome and new-fangled; for black paint can be made in a variety of ways from the soot produced by burning resin or pitch, owing to which factories have actually been built with no exit for the smoke produced by this process (fit enim e fuligine pluribus modis, resina vel pice exustis, propter quod etiam officinas aedificavere fumum eum non emittentes). The most esteemed black paint is obtained in the same way from the wood of the pitch-pine (laudatissimum eodem modo fit e taedis). It is adulterated by mixing it with the soot of furnaces and baths, which is used as a material for writing (adulteratur fornicium balinearumque fuligine quo ad volumina scribenda utuntur).

23 Leach and Tait (n. 3) 238
24 Erman and Grapow (n. 8) 5.537; Harris (n. 6) 160; Lucas and Harris (n. 22) 339
25 J. Černý, Catalogue des ostraca hiératiques non littéraires de Deir el Médineh (Nos 1 à 113) (Cairo 1935) plate 35, 1.10-11; Harris (n. 6) 147, 160
A few lines later he gives a less circumspect way of procuring the black colour:

A black is also produced with dyes from the black florescence which adheres to bronze pans (\textit{fit etiam aput infectores ex flore nigro, qui adhaerescit aereis cortinis}). One is also made by burning logs of pitch-pine and pounding the charcoal in a mortar (\textit{fit et ligno e taedis combusto tritisque in mortario carbonibus}).

He concludes by stating that:

The preparation of all black is completed by exposure to the sun, black for writing ink receiving an admixture of gum and black for painting walls an admixture of glue (\textit{omne autem atramentum sole perficitur, librarium cumme, tectorium glutino admixto}). Black pigment that has been dissolved in vinegar is difficult to wash out (\textit{quod aceto liquefactum est, agere eluitur}).

Like Pliny, Vitruvius in the seventh book of the \textit{De architectura}, which deals with “interior decoration” or “finishing,” gives an overview of the artificial colours used in the ancient Mediterranean. His more succinct account of the manufacture of black ink/paint (\textit{atramentum}) in the main agrees with the statements made by Pliny, besides that it provides a detailed description of the “factories” used for producing carbon compounds of the most esteemed kind (\textit{laudatissimum}):

A vaulted apartment is built like a sweating chamber, and is covered carefully with a marble facing and smoothed down (\textit{namque aedificatur locus uti laconicum et expolitur marmore subtiliter et levigatur}). In front of it a small furnace is built with outlets into the chamber, and the mouth of the furnace is carefully enclosed so that the flame does not escape (\textit{ante id fit foracula habens in laconicum nares, et eius praefurnium magna diligentia conprimitur, ne[c] flamma extra dissipetur}). Resin is placed in the furnace. Now the fiery potency burns it and compels it to emit soot through the outlets into the chamber. The soot clings round the walls and vaulting of the chamber. It is then collected and in part compounded with gum and worked up for the use of writing ink; the rest is mixed with size and used by fresco-painters for colouring walls (\textit{inde collecta partim componitur ex gummy subacta ad usum atramenti librarii, reliquum tectores glutinum admiscentes in parietibus utuntur}).

It is likely that the place, which Vitruvius says is built like a “sweating chamber” or a “Spartan sauna” (\textit{laconicum} i.e. Spartan, \textit{sc. balneum}, bath), is an “area of production” rather than a large oven, since Pliny explicitly uses the word \textit{officina} in his description of the procedure, literally meaning “workshop, factory or laboratory.” Further, in chapter 161 of the fifth book of the

\begin{footnotesize}
\begin{itemize}
\item \textsuperscript{26} Plin. \textit{HN} 35.41-43 [trans. by H. Rackham, \textit{Pliny, Natural History, Volume IX: Books 33-35} (Cambridge 1952) 291-293]
\item \textsuperscript{27} Vitr. \textit{De arch.} 7.10 [trans. by F. Granger, \textit{Vitruvius, On Architecture, Volume II: Books 6-10} (Cambridge 1934) 121-123]. Since it is evident from Dioscorides chapter on \textit{μέλαν} (\textit{Materia Medica} 5.162) that painters’ soot (= \textit{tectorium}) should be mixed with bulls’ hide glue, cf. below, the \textit{glutinum} used for \textit{atramentum tectorium} is likely animal glue; for the use of animal glue as a binding medium in ancient Egyptian paints, cf. for instance H.A.M. Afifi, “Analytical Investigation of Pigments, Ground Layer and Media of Cartonnage from Greek Roman Period,” \textit{Mediterranean Archaeology and Archaeometry} 11, no. 2 (2011) 95
\item \textsuperscript{28} OLD 1243; Vitruvius does not use a particular designation for the area in which the carbon compounds for \textit{atramentum} are procured, he in an earlier passage, which is devoted to the extraction of mercury from cinnabar, uses the word \textit{officina}; “When the ore has been collected in the workshop, because of the large amount of moisture, it is put
\end{itemize}
\end{footnotesize}
Materia Medica, which concerns “soot” (ἀββόλη) and its medicinal uses, Dioscorides states that: “the soot that painters use (ἡ ζωγράφοι χρώνται) is taken from glass-making factories (ἐκ τῶν ἱδρομεγέων), for this is the best.”

The possible relation of pigment production to different types of ancient workshops (ἐργατηρία officinae) will be addressed below; for the moment, the different ingredients stipulated in the surviving formulae for black ink from the Hellenistic period will be in focus.

Like Pliny, Vitruvius also ends his description with providing the reader with simpler ways in which black ink/paint could be manufactured:

But if this cannot be obtained, we must satisfy our requirements without holding back the works by the delay involved. Brushwood or pine-chips must be burnt, and when they are charred they are to be pounded in a mortar with size (sarmenata aut taedae scidiae comburantur; cum erunt carbones, extinguantur, deinde in mortario cum glutino terantur). Thus the fresco-painters will have a not unpleasant black colour. Again, a black colour even more pleasant than this is produced if the dregs of wine are dried and burnt in a furnace, and applied to the walls after being ground with size. The use of the finer wines will allow us to imitate not only black but indigo (non minus si faex vini arefacta et cocta in fornace fuerit et ea contrita cum glutino in opere inductur, super quam atramenti suavitatis efficiet colorem; et quo magis ex meliore vino parabitur, non modo atramenti, sed etiam indici colorem dabit imitari).

The last chapter of Dioscorides’ aforementioned herbal is devoted to μέλαν, because it apparently was considered a good application for gangrene and useful in scalds. In it he describes two types of black ink, a carbon and a mixed ink respectively. Concerning the first, he writes:

The black ink with which we write is made from soot collected from torches (μέλαν, ὧ γράϕομεν, σκευάζεται ἐκ λιγνύου καὶ ἄρχομεν ἐκ διδίων). Three oun giai (i.e. ounces) of soot are combined with one oun gia of gum. It is also made from soot of pine resin and from the painters’ soot mentioned above (σκευάζεται δὲ καὶ ἀπὸ τῆς ῥητῆς λιγνύου καὶ ἐκ τῆς προειριμένης ζωγραφικῆς ἀββόλης).

From the three descriptions provided by Pliny, Vitruvius and Dioscorides of the manufacture of carbon black ink, it is clear that the necessary compounds could be obtained through a variety of different procedures, but also that a certain type of fine soot, considered the best for both writing and painting, was procured through the careful pyrolysis of resin or pitch in “factories” (officinæ ἐργατηρία). A similar resinous substance, i.e. “myrrh” (ζμύρνα), is the principal ingredient in the formulae for black ink found in the later Greek and Demotic Magical Papyri,

in the furnace to dry (hae glaebae, cum collectae sunt in officinam, propter umoris plenitatem coiciuntur in fornacem)” Vitr. De arch. 7.8 [trans. by Granger (n. 27) 115]
29 [trans. by L.Y. Beck, Pedanius Dioscorides of Anazarbus, De materia medica2 (Hildesheim 2011) 405]
30 Vitr. De arch. 7.10 [trans. by Granger (n. 27) 123]; Pliny reports on the same phenomena: “sunt qui et vini faecem siccatat excoquant adfirmentque, si ex bono vino faex ea fuerit, Indici speciem id atramentum praebere (some people calcine dried wine-lees, and declare that if the lees from a good wine are used this ink has the appearance of Indian ink)”, Plin. HN 35.42 [trans. by Rackham (n. 26) 292-293]
31 Dioscorides, Materia Medica 5.162 [trans. by Beck (n. 29) 405]
where important phrases or potent symbols should be written with “myrrh” or using “myrrh ink” (Greek: ζμύρνομέλαν; Demotic: ry(.t) n ḫl).\textsuperscript{33}

The manufacture of black ink from incense was a time-honoured practice in Egypt, as can be inferred by the repeated instructions in medical and funerary papyri from the early New Kingdom (c. 1550 BCE) onwards, which state that prescriptions and spells should be “written with frankincense” (ṣḥṣ m ʿntyw).\textsuperscript{34} Similarly, in Spell 164 of the Book of the Dead, a picture is “to be drawn (ṣḥṣ) on a red bandage with dry frankincense (m ʿntyw ṣw) and fresh incense (ḥr snṭr ṣḏḥ), and coloured (wḥm) with ink (m ry.t).”\textsuperscript{35} Moreover, the abovementioned Egyptian word for “soot/charcoal” (ḏb.t) is found in certain offering lists accompanying pigments in the form “soot/charcoal of anet” (ḏb.t ʿn.t)\textsuperscript{36} and in one instance “soot” is described “as being anet” (ʿn.t pw).\textsuperscript{37} The interpretation of this expression remains doubtful, but it seems possible that anet is an abridged writing of the word anetyu (ʿntyw), “frankincense,” and that it refers to a carbon black obtained through the pyrolysis of resins.\textsuperscript{38}

As evidenced by the following recipe recorded in 1921, the use of incense as a source of soot for the inks of holy books was still standard practice in the Coptic Church in Egypt at the turn of the last century:

Put a quantity of incense on the ground, and round it place three stones or bricks, and resting on these an earthenware dish, bottom upwards, covered with a damp cloth; ignite the incense. Carbon is formed and is deposited inside the dish, from which it is removed and made into ink by mixing with gum arabic and water.\textsuperscript{39}

In the Greek Magical Papyri there is a handful of elaborate formulae for carbon-ink, which besides “myrrh” lists a series of further ingredients to be added; for instance in the following

\textsuperscript{32} PGM I. 1-42; IV. 850-929, 930-1114; passim
\textsuperscript{34} E.g. P.Edwin Smith, J.H. Breasted, The Edwin Smith Surgical Papyrus: Published in Facsimile and Hieroglyphic Transliteration with Translation and Commentary in Two Volumes (Chicago 1930) plate 19, l. 10; P.BM EA 10477, BD 101, G. Lapp, The Papyrus of Nu (London 1997), plate 79, l. 9. antyw has for a long time been taken to mean myrrh, but according to É. Chassinat, Le mystère d’Osiris au mois de Khoiak I (Cairo 1966) 217-223, who made an extensive investigation of the texts from the Ptolemaic period, the word, unlike Demotic ḥr/ḥl, has a wider meaning, and includes gum resins from several boswellia and probably also other resins from the Red Sea region. The literature on this problem has been collected by G. Charpentier in Recueil de matériaux épigraphiques relatifs à la botanique de l’Égypte antique (Paris 1981) 161-165 (ʿntyw) and 552-523 (ḥry; Demotic ḥr/ḥl; Coptic ωχάι); cf. further M. Smith, Papyrus Harkness (MMA 31.9.7) (Oxford 2005) 99-100. For the use of ṣntyu in ancient Egyptian pharmacology, see Deinen and Grapow (n. 18) 99-104
\textsuperscript{35} E. Naville, Das Aegyptische Todtenbuch I (Berlin 1886) plate CXIII, 1.18-19
\textsuperscript{36} W. Wolf, Das schöne Fest von Opet (Leipzig 1931) 44
\textsuperscript{37} G. Daressy, “Une inscription d’Achmoun et la géographie du nome libyque,” ASAE 16 (1916) 225; cf. writings of antyw. Erman and Grapow (n. 8) 1.206.7f.
\textsuperscript{38} Harris (n. 6) 159-160
\textsuperscript{39} A. Lucas, “The Inks of Modern and Ancient Egypt,” Analyst 47 (1922) 13-14
“memory spell” (μνημονική), where some divine names should be inscribed on a hieratic papyrus with a Hermaic myrrh ink (λαβὼν χάρτην Ιερατικόν γράψον τὰ προκείμενα ήνόματα ζυμρομέλαιν Ἐρμαϊκῷ) consisting of:

- myrrh troglitis (τρωγλίτις ζυμώνα), 4 drams
- 3 karian figs (ἰςχάδας Καρικάς)
- 7 pits of Nikolaus dates (φοινίκων Νικολάων δστέα)
- 7 dried pinecones (στροβίλια ἀβροχα)
- 7 piths of the single-stemmed wormwood (ἀρτεμισίας μονοκλώνου καρδίας)
- 7 wings of the Hermaic ibis (ἵβεως Ἐρμαϊκῆς πτερά)
- spring water (ὕδωρ πηγαῖον)

- When you have burned the ingredients, prepare them and write. 

It is only in this ink formula that a specific variety of myrrh is prescribed. The term τρωγλίτις is a form of τρωγλοδύτις, “cave dweller,” and Pliny uses this word, trogodytica, for the highest grade of myrrh, which comes from the Cave Dwellers’ land that he locates on the Red Sea coast. He says it “is distinguished by its thickness and because it is rather dry and dusty and foreign in appearance, but has a stronger scent than the other sorts.”

Both (Karian) figs, the stones of (Nicolaus) dates and wormwood are used in other elaborate formulae in the corpus, while dried pinecones are only applied in this spell. Common denominators are that they, like myrrh, are well-attested as medicaments in the pharmacological literature of the period and that they were used throughout the ancient Mediterranean and Near East in a broad variety of religious, funerary and honorific contexts. While the reason for the admixture of most of these ingredients in ink remains obscure, then the infusion of wormwood seems to have served a practical purpose, since both Pliny and Dioscorides note that it prevents mice from eating up the

---

40 As shown by the papyri from the Tebtunis temple library, Hieratic was only employed for important ritual texts in the Roman period and as a consequence, unlike Demotic, was generally not written on reused papyri. Therefore, the recurring instruction in the PGM to use a “Hieratic papyrus” could mean that the papyrus should be blank, cf. J.F. Quack, “Die hieratischen und hieroglyphischen Papyri aus Tebtynis – ein Überblick,” in K. Ryholt (ed.), The Carlsberg Papyri 7: Hieratic Texts from the Collection (Copenhagen 2006) 1-7
42 Plin. HN 6.189
44 For wormwood, pinecones and myrrh in the PGM, cf. LiDonnici (n. 33) 61-91. For the pharmaceutical use of figs (ⲙⲕⲃ) in the ancient Mediterranean, cf. Dioscorides, Materia Medica 1.128; in ancient Egyptian they were named either ṓsib or kni (Coptic: κνητε) and they were used in medicine throughout Egyptian history, see Deinen and Grapow (n. 18) 571-572; Manniche (n. 18) 102-103; Till (n. 18) 56. Dates, Egyptian bnr (Coptic: ṅἈΝϹ), were employed for similar purposes and are attested in the same corpora, Dioscorides, Materia Medica 1, 109; Deinen and Grapow (n. 18) 172-179; Till (n. 18) 52; of this specific species (Nicolaus) nothing is known besides that it was of an exceptional size, cf. Plin. HN 12.45
The decrepit and worm-eaten state of the majority of papyri that survive from antiquity amply demonstrates the threat that pest-attacks posed for the preservation of manuscripts. Whatever the *raison d'être*, dried pinecones and seeds of dates were still regularly employed in the manufacture of carbon ink in the medieval Arab world. This is evident from the famous treatise on “bookmaking” of Al-Mu‘izz ibn Bādīs – fourth ruler of the Zirids in Ifīqiya – from the beginning of the eleventh century CE, where both are listed as essential ingredients in the first chapter of the work entitled “on the making of the kinds of soot ink (*midād*)”. In one of two complex recipes for “India ink” that Ibn Bādīs provides in this chapter, he states that pinecones advantageously could be added to a certain type of “mixed ink”:

Take two parts of cedar (*abzar*) or dried fruit of the pine (*tamr al-ṣanawhar al-yābas*), or of them together. Put it into a new clay vessel (*jarrah*) and put it into an oven (*furn*) until it becomes charcoal (*faḥm*). It is taken out the next morning and pulverized a day on a stone (*ṣalābah*). It is soaked with water of cooked myrtle (*ās*) and a little of vitriol (*zāj*), made according to the mentioned description. It is completely pulverized with water of myrtle, and pulverized with water of gum in such quantity that there is for every *raṭl* (12 ounces) of pulverized charcoal ink two ounces of water of gum. If a little more is added, it is not harmed. If it is too hard, take the gum from it and knead it. Put it in layers and leave it in the shade. It comes out beautifully.

Though water of myrtle is not mentioned in any of the preserved descriptions of ink manufacture from the Hellenistic period, Dioscorides says that myrtle (*μυρίνη*) – besides being applied in the treatment of ulcers, inflammations and erysipelas – is used to dye the hair black. This might be what Celsus hints at, when he reports that the best way to cure baldness is to recurrently scrape the skin of the affected spot with a razor and thereafter smear a certain type of black ink (*atramentum scriptorium*) upon it. Concerning the seeds of the dates (*οἱ δὲ πυρῆνες τῶν φοινίκων*) Dioscorides writes:

---

45 Plin. *HN* 27.52; Dioscorides, *Materia Medica* 3.23; that the ἀρτεμία of the *PGM* spells can be equated with the ἄψινθια of Pliny and Dioscorides is convincingly argued by LiDonnici (n. 33) 83-87

46 For instance, nine mouse/rat nests built out of hundreds of small strips of Egyptian and Greek papyri were found during the 2015 excavations of the temple precinct of Soknebtynis, see G. Gallazzi, “Appendice,” in G. Gallazzi and G. Hadji-Minaglou (eds.), *Tebtynis VI: Scripta Varia* (Cairo, in press)

47 Levey (n. 16) 15-18; *midād* (derived from *madd*, to stretch out [i.e. the ink]) indicates a paint type of ink whose most important ingredient is soot, while *ḥibr* (derived from *ḥabar*, to write) refers to an ink that reacts chemically with paper or parchment, i.e. usually a gall-vitriol type of ink, cf. A. Gacek, *The Arabic Manuscript Tradition: A Glossary of Technical Terms and Bibliography* (Leiden 2001) 27-28 (*ḥibr*), 133 (*midād*); A. Gacek, *The Arabic Manuscript Tradition: A Glossary of Technical Terms and Bibliography – Supplement* (Leiden 2008) 14 (*ḥibr*), 72 (*midād*)

48 Probably *zāj* meant green vitriol, i.e. melanterite (FeSO₄•7H₂O), though it was frequently confused with blue vitriol, *qalqant*, i.e. cupric sulphate pentahydrate (CuSO₄•5H₂O), cf. Gacek (n. 47) 62, 32 (supplement); and below under “mixed ink”

49 Levey (n. 16) 16

50 Dioscorides, *Materia Medica* 1.112. In the fifth book (160) he reports that a type of bituminous earth called *Ampelitis* in a similar way “is used for painting eyelids and eyelashes, for coloring hair ...” [trans. by Beck (n. 29) 405]; cf. further Plin. *HN* 35.194

51 Celsus, *Med.* 6.4
Date pits are burned in an unfired earthen vessel (ἐν ὠμῇ χύτρᾳ), like everything else, and then after they have been quenched with wine, they are washed and used as vegetable ash (εἰς ἄντιςτοδε). They are suitable for paints of the eyelids and eyelashes (εἰς καλλιβλέφαρα) and if burned insufficiently the process is repeated\textsuperscript{52}

In the already cited chapter on soot inks, Ibn Bādīs provides a recipe for a “Kufic” and a “Persian” ink respectively. Both inks are based on the careful pyrolysis of seeds of dates (tamr) that are placed in a sealed (clay) vessel, which is heated in a furnace (atūn):

Take what you wish of the seed of dates. Then put it in a vessel (qilla) and lute its mouth. Put it in a warm furnace a day and a night until it is burned. Then take it out. When it is cooled, open the vessel and take out the seed which has become like ash (ramād). It is well pulverized and sieved with the thick burned material. Then gum is taken and kneaded with it twice every day. It is made into cakes and then dried in the shade.

Take the seed of the date that has been ripened in vinegar. Put it in a clay vessel. Take as much as you wish. Lute the vessel with clay of the art (ṭin al-ḥikmah).\textsuperscript{53} The luting is done after a cloth has been put over the mouth. It is set down until it is dried a little. Then, if it is desired, the firewood is lit. It is shaken from morning to night. If it is desired, it is introduced into the furnace for the two kinds of glass (atūn al-zajāj). When it is taken out of the fire, it is set down until it is cold. Then it comes out black like charcoal. It is then made into cakes as desired.\textsuperscript{54}

In the Greek Magical Papyri there are three further formulae for carbon ink, which are structured in a similar manner to the already cited formula and require many of the same components, but also differ in some respects. The first simply states that the mentioned botanicals should be pulverised and mixed:

- 3 dried figs
- 3 stones of the Nicolaus date
- 3 fragments of wormwood
- 3 lumps of myrrh\textsuperscript{55}

The second dispenses with the figs and the seed of dates, but adds cinquefoil: “In a purified container burn myrrh and cinquefoil and wormwood; grind them to a paste, and use them (ἐμύρναν καὶ πεντεδάκτυλον βοτάνη καὶ ἄρτεμιαν καύσας ἄγνως λειοτρίβησον καὶ χρῶ")\textsuperscript{56}

The third formula includes vetch (κατανάγκη), branches of the male date palm (θαλλὸι φοίνικος ἁρκενικοῦ) and instead of myrrh prescribes “soot from a goldsmith” (αἰθάλη χρυσοχοίϰη).

\textsuperscript{52} Dioscorides, Materia Medica 1.109 [trans. by Beck (n. 29) 79]
\textsuperscript{53} Used by medieval Arabic alchemists and chemists to make an apparatus air- and water-tight, Levey (n. 16) 17n98
\textsuperscript{54} Levey (n. 16) 16-17
\textsuperscript{55} PGM VII. 993-1009 [trans. by Betz (n. 41) 144]
\textsuperscript{56} PGM II. 1-64 [trans. by Betz (n. 41) 13]
- Composition of the ink with which it is necessary to write …
  ● single-stemmed wormwood
  ● vetch
  ● 3 pits of Nicolaus date palms
  ● 3 Karian dried figs
  ● soot from a goldsmith
  ● 3 branches of a male date palm
  ● sea foam (ἀφρός θαλάςσης)\(^{57}\)

Like the other botanicals, vetch and cinquefoil were used in medicine in the ancient Mediterranean,\(^{58}\) but unlike myrrh, wormwood, pinecones and seeds of dates, they are only attested as components of carbon ink in the Greek Magical Papyri. The same holds true for “soot from a goldsmith” – although it is mentioned again in the corpus in two further formulae for carbon ink.

Both are structured in a dissimilar manner to the already cited formulae. The first simply states that the ink consists of the blood of a serpent and soot of a goldsmith (ἀίμα δρακόντειον καὶ αιθάλη χρυσοχοῖκη).\(^{59}\) In the second formula “soot of a goldsmith” is listed in an instruction for a spell of attraction (ἀγωγή) that should be inscribed on three different writing surfaces with three types of soot dissolved in the blood of three different animals:

The hide is inscribed with blood of an ass from the heart of a sacrificial victim, with which is mixed the soot of a coppersmith (καταγράφεται δὲ ὁ μὲν ὕμην ἀίματι ὀνείῳ ἀπὸ καρδίας ἐσφαγμένου, ὃς συμμίγεται αιθάλη χαλκέως). But the leaf of flax is inscribed with falcon’s blood, with which is mixed the soot of a goldsmith (τὸ δὲ τῆς καλπάκου φύλλον ἀίματι ἰερακείῳ, ὃς συμμίγεται αιθάλη χρυσοχόου). But the leaf of the hieratic papyrus is inscribed with eel’s blood, with which acacia is mixed (τὸ δὲ τοῦ ἱερατικοῦ χάρτου ἀίματι ἐνχέλεως, ὃς συμμίγεται ἀκακία).\(^{60}\)

As with the wings/feathers of the Ibis in the first ink formula cited from the Greek Magical Papyri, the purpose of mixing different types of animal blood into carbon ink is undoubtedly to ensure the efficaciousness of the given spell. Perhaps, these ingredients, together with the recurring “magic” numbers in the formulae (3, 4, 6, 7, 9 (3x3)), should be taken cum grano salis, but it ought to be recalled that the snake, the falcon and the eel were viewed as abodes of gods and, like so many other animals in late period Egypt, were mummified on an industrial scale.\(^{61}\) Moreover, the blood of a wide variety of animals (including the snake and the ass) was used in medicine throughout

---

\(^{57}\) PGM IV. 3172-3208 [trans. by Betz (n. 41) 100]

\(^{58}\) Dioscorides, *Materia Medica* 4.42 (cinquefoil), 4.131 (vetch)

\(^{59}\) PGM IV. 1928-2005

\(^{60}\) PGM IV. 2006-2125 [trans. by Betz (n. 41) 75]

\(^{61}\) D. Kessler, *Die Heiligen Tiere und der König. I: Beiträge zu Organisation, Kult und Theologie der spätzeitlichen Tierfriedhöfe* (Wiesbaden 1989). In late period Egypt the ass was seen as a representative of the diabolic/chthonic god Typhon (Seth) and the blood is therefore specified as coming “from the heart of a sacrificial victim”, cf. in general D. Wortmann “Das Blut des Seth,” *ZPE* 2 (1968) 227-230; also J.G. Griffiths, *Plutarch’s De Iside et Osiride* (Cardiff 1970) 276, commenting on *De Is. et Os.* 6, 353B
Egyptian history in the preparation of drugs designed to treat different ailments. Therefore, these ingredients hardly represent “exotic” or unconventional commodities, but – like the botanicals mentioned above – could be acquired at market places and specialised workshops in the cities and larger towns of late period Egypt.

Like the “glass-working factory” (ὑελουργεῖον, LSJ9 1840) from which Dioscorides said that “the soot that painters use (ἡ οἱ ζωγράφοι χρῶνται)” were taken – workshops of gold and copper smiths are well-attested in Greek documentary and literary evidence from late period Egypt. It is therefore worthy of note that the majority of the Theban Greek(-Demotic) papyri were acquired together with the Leiden-Stockholm (al)chemical treatises by the Alexandrian merchant and antiquarian Giovanni Anastasi not long before 1828 and that they undoubtedly derived from the same ancient archive/library. These texts contain, among recipes for manipulating metals, dying techniques and counterfeiting precious stones, detailed formulae for the manufacture of silver and gilded inks; for instance, Papyrus Leiden X describes the preparation of a gilded ink based on a certain amount of gold, which is melted in a “goldsmiths’ crucible (χῶνον χρυσοχοίχον).”

While the link between the instruments used by the early alchemists and the tools and workshops utilised by the “Greco-Egyptian” craftsmen is still debated, then the overlap between the practitioners, whom the Greek Magical Papyri address, and certain ἑργατήρια/ officinae is evident from the different spells or rituals in the corpus that guarantee profitable activity to unspecified workshops; in one case the magical papyri describe the manufacture of a red (Typhonian) ink, which is prepared inside an ἑργατήριον. This relation between pigment production, workshops and early alchemy, will be developed a bit further in the following section devoted to the few preserved written sources from the ancient Mediterranean that pertain to the manufacture of “mixed ink,” i.e. a carbon ink to which metallic substances have been added.

62 Deinen and Grapow (n. 18) 444-448 (Egyptian snf), Till (n. 18) 51 (Coptic: CNOJ)
63 For availability and expense of some of the botanicals mentioned in the PGM, cf. LiDonnici (n. 33) 61-91. An ethno-historical parallel of the use of blood as a binding medium in carbon based black pigment is provided by the rock paintings of the Chumash Indians from the south-central coastal zone of California, who utilized the blood of humans and pronghorn antelopes as binding agents in the black pigments they applied in their ritual “art”, D.A. Scott et al., "Blood as binding medium in a Chumash Indian pigment cake,” Archaeometry 38, no. 1 (1996) 103-112. doi: 10.1111/j.1475-4754.1996.tb00764.x
64 Dioscorides, Materia Medica 5.161
66 G. Fowden, The Egyptian Hermes: A Historical Approach to the Late Pagan Mind (New Jersey 1993) 168-176
69 See e.g. PGM VI. 2359-72, VIII. 54-64
70 PGM XII. 96-101; the papyrus reads ἱματζέου and therefore this recipe can perhaps be ascribed to the fourth-century physician Himerios, cf. K. Preisendanz Papyri Graecae Magicae. Die griechischen Zauberpapyri II (Leipzig 1931) 64
Mixed ink

The second part of the already cited formula by Dioscorides for the preparation of black ink (μέλαναν) reads:

You must take one mna of soot, one and one-half litra gum, one and one-half litra bulls’ hide glue, and one and one-half litra copper sulfate (δεὶ δὲ τῆς μὲν ἀϲβόλης μνᾶν μίαν λαμβάνειν, κόμμεως δὲ λίτραν μίαν ἡμίειαν, ταυροκόλλης οὐγγίαν μίαν ἡμίειαν, χαλκάνθου οὐγγίαν μίαν ἡμίειαν).

Besides χάλκανθου/χαλκανθές (LSJ 1972) the ingredients prescribed has already been addressed in the section on carbon ink. From the descriptions of χάλκανθου/chalcanthon provided by Dioscorides and Pliny it appears to be a (solid) residue in water, which possessed not only the appearance of, but also the virtues of blue vitriol or cupric sulphate pentahydrate (CuSO₄•5H₂O). However, the same substance, chalcanthon, is by Celsus and Pliny identified with “shoemakers’ black” (atramentum sutorium), i.e. a dye for leather. This has led to some confusion in the history of vitriols, since a black dye cannot be obtained by tannic acid reacting with copper sulphates, but only with iron sulphates or green vitriol (FeSO₄•7H₂O). Therefore, both the Greek and Latin terms must on occasion – besides blue vitriol – have been used for green vitriol (coppersas) as well. That the two were often confused, was probably due to the fact that both vitriols – as was the case with almost all other chemicals used in antiquity – were found only in an impure state.

The ancient Egyptian term “black stone” (inr km) can designate two quite different substances, namely black granite and vitriol. In demotic (iny km) and Coptic (Anikam) the word always refers to the second substance and seems, like χάλκανθον, to connote both cupric sulphate and green vitriol (atramentum sutorium/μέλαντηρία). The use of iny km in a black ink/paint is attested in a demotic mortuary papyrus from the first century CE, where the mummy bandages of the deceased, Tanwerou, are said to have been: “drawn (tk) with the water of the fruit of the carob tree (demotic: mw t-ir.t; Coptic: MÛØY MTTXIE¹PE)” and “coloured (whm) in vitriol (iny km).”

---

71 Dioscorides, *Materia Medica* 5.162 [trans. by Beck (n. 29) 405]
72 Plin. *HN* 34.123-127; Dioscorides, *Materia Medica* 5.98; for a discussion of its properties and an evaluation of the classical sources, cf. Bat-Yehouda (n. 2) 357-362
73 Celsus’ and Pliny’s atramentum sutorium (chalcanthus) is reminiscent of Dioscorides description of μέλαντηρία (blacking), which could indicate that he distinguished between two types of vitriol: χάλκανθον/χαλκανθές then being blue vitriol and μέλαντηρία green vitriol, cf. Celsus, *Med.* 5.1, 5.7-8; Plin. *HN* 34.123-127; Dioscorides, *Materia Medica* 5.101
75 Bat-Yehouda (n. 2) 360-362; Levey (n. 16) 16n88
76 Harris (n. 6) 74
77 Crum, *Dict.* 12a; Till (n. 18) 98-99; Smith (n. 34) 98-99
78 For the medicinal use of the juice of this plant in Coptic pharmacology, cf. Till (n. 18) 67; for tk as a late period Egyptian word meaning to draw/paint/dye, see K. Ryholt, “A hieratic list of book titles,” in Ryholt (n. 40) 152-153
A similar type of black ink is attested in the already cited work of Ibn Bādīs, where both “water from the fruit of the carob tree (kharnūb)” and “vitriol (zāj)” are enumerated in a formula for the preparation of a black tannin ink (ḥibr):

Preparation of another powdered dry ink. Gallnut (ʿafṣ), gum arabic, vitriol, and acacia in equal parts are taken. All are pulverized with water of fresh St. John’s bread (i.e. fruit of the carob) until it is dried. It is then removed and dissolved with the necessary amount of gum water when it is needed. Write with it.

The demotic word for vitriol, iny km, also occurs in a list of stones and plants from the Roman period together with such items as wt, “green eye paint,” mstmy, “black eye paint,” and iny n ss-wr, “great protection stone,” a substance employed in a manner similar to copper sulphate. Besides, as a component of black inks, paints and dyes, ANIKAM (iny km) is attested in both demotic and Coptic medical treatises, specifically in the treatment of tumours and abscesses, while chalcanthum/atramentum sutorium – according to Celsus and Pliny – was applied partly in caustic and exedent medicaments and partly in salves designed to arrest hemorrhage and to clean wounds. It should be noted that not only ANIKAM (iny km) is used to designate sulphate of copper or iron in demotic and Coptic, but also the Greek χάλκανθον (Coptic: KAAKANOC). An early example of the use of this loanword in Egyptian is a demotic/hieratic medical compilation from the second century CE, where a powder for removing an abscess consists of a concoction of “heated copper? (mSy), ¼, orpiment (knw), ¼, qerekehentes-vitriol (krkhnts) […]” is “pulverised and mixed.” Like the arsenic sulphide orpiment (As₂S₃) (para-)realgar (As₄S₄) mentioned in this medical recipe – which was regularly employed as a yellow/orange pigment in ancient Egyptian funerary papyri from the New Kingdom onwards – “shoemakers’ black” seems to have been highly toxic on occasion, since Cicero, in an undated letter to Papirius Paetus, writes that Gnaeus Carbo (the elder), when prosecuted by Marcus Antonius, poisoned himself using atramentum sutorium.

---

79 P.MMA 31.9.7 (Papyrus Harkness), Smith (n. 34) col.1, 1.6; M. Smith, Traversing Eternity: Texts for the Afterlife from Ptolemaic and Roman Egypt (Oxford 2009) 279  
80 Levey (n. 16) 20  
81 P.Berlin 8769, W. Spiegelberg, Demotische Papyrus aus den königlichen Museen (Leipzig 1902) plate 98  
82 Harris (n. 6) 179, 234; Smith (n. 34) 99  
83 E.A.E Reymond, From the Contents of the Libraries of the Suchos Temples in the Fayum, Part 1: A Medical Book from Crocodilopolis (Vienna 1976) plates 3, 6; Till (n. 18) 98-99  
84 Celsus, Med. 5.1, 5.7-8; Plin. HN 34.123-127  
85 It is also attested in the Demotic Magical Papyri, where it is written g̣lsgments and glossed in old Coptic KAAKANONI.  
86 P.Wien D 6257, Reymond (n. 82) col. x+9, l. 14, plate 3; cf. the translation of the passage by F. Hoffmann and J.F. Quack, “Demotische Texte zur Heilkunde,” in B. Janowski and D. Schwemer (eds.), Texte zur Heilkunde (Gütherloh 2010) 302  
87 L. Lee and S. Quirke, “Painting Materials,” in Nicholson and Shaw (n. 3) 115-116; Di Stefano and Fuchs (n. 22) 230-233  
88 iam pater eius accusatus a M. Antonio sutorio atramento absolutus putatur, Cic. Fam. IX.21
Related to χάλκανθον is χάλκιτις (chalcitis), which according to Pliny and Dioscorides is a fossil substance, impregnated with the minerals σώρι (sori) and μίςυ (misy). Only conjectures can be made about the exact chemistry of these compounds, but it seems that chalcitis was a chalcopyrite (CuFe$_2$), while sori and misy respectively were the decomposed copper and iron sulphides contained within the fossil. The first two minerals are not attested as components of black ink, but both χάλκανθον and μίςυ are mentioned in one of the Greek Magical Papyri, where the following formula for the preparation of a “mixed ink” is provided:

- The formula (ἡ ἀναγραφή):
  - 1 dram of myrrh
  - 4 drams of truffle (μίςυος δρακμαὶ)
  - 2 drams of blue vitriol (χαλκάνθου ...)
  - 2 drams of oak gall (χαλκάνθου ...)
  - 3 drams of gum arabic (χόμεως ...)

While it is possible to translate μίςυ with “truffle,” as is done in Betz’s edition of the corpus, it seems a more probable alternative to equate it with the misy discussed above, since the only attestation given in LSJ for this word as a term for a specific variant of truffle is a fragment (n. 137) of Theophrastus. This is the choice of the first editor of the Greek Magical Papyri, Preisendanz, who renders it “Vitriolerz”. Because copper and iron vitriols are mixed with oak galls (containing tannic acid), the few researchers, who has commented on the formula classified the ink as being an “iron-gall ink”. However, myrrh, the primary ingredient of carbon ink in the Greek Magical Papyri, is added as well. Consequently, it should be categorised as a “mixed ink” according to the principles outlined in the introduction above.

It is noteworthy that two different metal bearing minerals are included in the formula, since chemical analyses undertaken at the Louvre in the late 1980s of the black ink of five bilingual (Demotic/Greek) papyri from the Ptolemaic period, which were studied using proton induced X-ray emission (PIXE), demonstrated that all the Greek texts, besides one, were written with a type of “metallic ink,” which in the literature is referred to as being either an “encre métallogallique” or an “iron-gall/mordant ink,” while all the demotic texts were written with carbon ink. The contents of these metallic inks were surprising in that besides iron (Fe), copper (Cu) and lead (Pb) they contained traces of titanium (Ti) and zink (Zn), which suggested to the researchers that the inks had

---

89 Plin. HN 34.117-122; Dioscorides, Materia Medica 5.99-102
90 Goltz (n. 74) 154-157; Bat-Yehouda (n.2) 321-322 (chalcitis), 337-339 (misy), 351-352 (sori)
91 PGM XII. 397-400 [trans. by Betz (n. 41) 167]
92 LSJ 1138
93 Preisendanz (n. 70) 83
94 Bat-Yehouda (n.2) 94-95; M. Fackelmann, Restaurierung von Papyrus und anderen Schriftträgern aus Ägypten (Zutphen 1985) 28. For the use of gall-nuts in Mediterranean and Egyptian pharmacology, cf. Celsus, Med. 5.6-7; Dioscorides, Materia Medica 1.107; Plin. HN 16.26-27; Till (n. 17) 58
95 Delange et al., (n. 2) 213-217; Leach and Tait (n. 3) 238; Bülow-Jacobsen (n. 4) 18
been made from many different metallic components. Another significant finding was that unlike the iron-gall ink from the Middle Ages and the pre-Modern era, which shows a substantial amount of Fe and sulphur (S), these ink samples had a marked lack of S. There was also a predominance of Cu in the samples as opposed to Fe, while the relation between the two elements is normally vice versa. This in turn led to speculation about the method of ink manufacture and the effects of ageing and it has been suggested that carbonates were used instead of sulphates, or that the S may have been incorporated into a gas or liquid compound, which could have disappeared over time.

PIXE is not sensitive to carbon (Z≥ atomic number 11) and a pertinent question, in light of the ink-formulae cited above, is whether these and other black metallic inks with similar characteristics should not be classified as mixed inks, rather than iron-gall inks? A possible explanation of the atypical chemistry of these ink samples could be that they were prepared from impure vitriols mixed with the charcoal or soot of burned botanicals. Alternatively, the black pigment might have been obtained as by-products from different workshops involved in the working of metals or the manipulation of vitreous substances, which again would explain the presence of metals in the ink, e.g. “the soot of a coppersmith (αἰθάλη χαλκέως)” or the soot “from glass-making factories (ἐκ τῶν υελουργείων).”

In order to answer these questions with any kind of certainty further chemical analyses of the papyri in Louvre would be needed, but concerning the last point, which briefly has been touched upon above, it is worthy of note that Dioscorides (and Ibn Bādīs a thousand years later) in his formula for mixed ink prescribes soot that derives from glassmaking factories, since also another copper bearing pigment, “Egyptian blue,” undoubtedly was manufactured in production areas, where both glass and blue/green faience were made. This pigment consists mainly of cuprorivaite (CaCuSi$_4$O$_{10}$) – containing variable amounts of wallonite (CaSiO$_3$), Cu-rich glass and cuprite (Cu$_2$O) or tenorite (CuO) – that is heated in a furnace at constant high temperatures (ca. Z ≥ 900 ºC). Moreover, two alchemical recipes, which are preserved in the two Syriac manuscripts from the sixteenth century and are ascribed to the first century philosopher (Pseudo-)Democritus, a

---

97 Leach and Tait (n. 3) 238
98 E.g. the black ink found in the Herculaneum papyri, where small amounts of lead (Pb) have been mixed with the carbon compounds that constitute the major components of the pigment, cf. Brun et al. (n. 2) 3751-3754; Tack et al. (n. 2) 1-7
99 *PGM* IV. 2006-2125; Dioscorides, *Materia Medica* 5.161
contemporary of Dioscorides, prescribe that products closely related to the manufacture of mixed ink, misy and copper, should be processed in “a glass-blowers furnace (qamyna dzgwgya).”

Like the Leiden and Stockholm papyri discussed above, both Democritus’ œuvre and the Corpus alchemicum graecum in general concern dying techniques and the making of gold and silver by treating base metals and the counterfeiting of precious stones. It is clear that each of these τεχναι, like ancient Mediterranean pharmacology, was based on the use of specific tools and ingredients and related to the activity of specialised craftsmen, whom from the textual sources reviewed so far, in one way or the other seem to have been involved in the manufacture of inks, paints and dyes. The dyeing of clothes were done by the βαφείς and the working of metals by different craftsmen, such as the χρυσόχοι (experts at working gold), the ἀργυροχόποι (experts at working silver) and the χαλκεῖς/χαλκουργοί/χαλκοτύποι (experts at working copper/bronze). Another particular expertise was necessary for producing fake precious stones, which were based on the dyeing of white quartz by means of different minerals; procedures clearly linked to the traditional Egyptian skill of producing glazed quartz and manipulating vitreous substances, which must be connected to the activity of glass-makers, whose furnaces are often mentioned in the alchemical texts. All these activities are attested in ancient Egypt since time immemorial and were often related to temple workshops. Furthermore, archaeological investigations have discovered different evidence of the continuity of such craftsmanship well into the Hellenistic, Roman and Byzantine periods.

Iron-gall ink

When parchment in the early fifth century CE started to supersede papyrus as the primary carrier medium for written communication, the first definite formulae for iron-gall mixtures were elaborated and adopted as a new form of writing ink. Because of the different nature of the support, another, more adherent, ink was required. Thereafter, different types of iron-gall inks became the standard for writing on parchment (and later on paper) throughout the middle Ages and the Renaissance. However, as already shown in the section on “mixed ink,” the chemical reaction between metallic salts (Fe/Cu?) and extracts of tannic acid was known long before it was regularly used in the manufacture of black ink.

102 M. Berthelot, La Chimie au Moyen Age II (Amsterdam 1967) 57.2-6 (Syriac text) and 102.1-7 (French translation); 58.14-21 (Syriac text) and 104.7-18 (French translation); for a description of the manuscripts, see R. Duval, “Notice sur le manuscrits d’alchimie,” in Berthelot (n. 102) XLVI-XLVIII
103 A general inquiry into Egyptian craftsmen in the Roman period is undertaken by P. van Minnen in Urban Craftsmen in Roman Egypt (1987) 31-87
105 M. Beretta, The Alchemy of Glass. Counterfeit, Imitation and Transmutation in Ancient Glassmaking (Sagamore Beach 2009)
106 Martelli (n. 65) 271-290
107 Fackelmann (n. 94) 28; Brun et al. (n. 1) 3751
The oldest ink formula, which employs both gallnuts and vitriol, was penned in the late second century BCE by Philo of Byzantium in the Belopoeica. In this work, Philo refers to an invisible ink, which could be used to send hidden messages during the siege of a town. It may be considered an unfinished or “sympathetic” ink and was composed of powdered gallnuts dissolved in water. As the mixture dried, the writing turned invisible and the letters only became legible again, when the writing was washed off with a sponge dipped in a solution of “vitriol” (\(\chi\alpha\lambda\kappa\o\nu\delta \varepsilon \acute{\alpha}ν\nuς = \chi\alpha\lambda\kappa\a\nu\theta\o\sigma\)).\(^{108}\) Again \(\chi\alpha\lambda\kappa\a\nu\theta\o\sigma\)/\(\chi\a\lambda\kappa\a\nu\theta\o\sigma\) likely refers to green vitriol or ferrous sulphate rather than blue vitriol or cupric sulphate. This being said, it seems that at least basic copper acetate or copper carbonate could be used for similar purposes, since Pliny reports that the best way to detect whether verdigris (\(\alpha\varepsilon\rho\u\ro\gamma\u\u\gamma\o\o\)) has been adulterated is “by means of a papyrus previously steeped in an infusion of plantgall, as this, when smeared with genuine verdigris at once turns black (\(\pi\a\pi\ro\gamma\o\o\) \(\gamma\a\la\kappa\n\a\nu\lambda\o\) \(\pi\a\pi\ro\gamma\o\o\) \(\mu\a\ce\a\ro\))”).\(^{109}\)

A “sympathetic” ink manufactured in a similar way to the one already described by Philo of Byzantium is preserved in the work Φιλοσοφούμενα, also known as refutatio omnium haerasium, which is normally attributed to Hippolyt of Rome, who lived in the third century CE. In the fourth book of this work, which deals with diviners and magicians, it is described how a person, who wishes to consult a god or a demon, is advised by the magician (\(\mu\a\gamma\o\o\)) to write his message to the deity, without informing the magician of the nature of his request, with a tincture or a decoction of gallnuts. Unbeknownst to the client, the magician thereafter immerses the document in a solution of vitriol and in this way becomes aware of its content:

And he having put copperas in the libation bowl and when the drug is dissolved sprinkling with it the paper which had forsooth been discharged of writing, he compels the hidden and concealed letters again to come to light, whereby he learns what the enquirer has written:

And if one writes with copperas and fumigates it with a powdered gall-nut, the hidden letters will become clear (\(\kappa\i\a\i\a \tau\o \chi\a\l\a\k\a\n\o\b\o\nu\ \d\'\ \tau\e\i\ \varepsilon\ \gamma\a\r\a\f\e\i\ \kappa\i\a\i\a \k\i\r\i\d\o\c\o\ \u\p\o\b\u\r\u\m\a\c\e\i\e\ \l\e\l\i\e\w\m\e\n\e\ \f\a\n\e\r\a \g\e\n\o\c\i\c\i\ e\n \t\a \k\e\k\r\u\r\m\e\n\a \g\r\a\m\m\a\c\a\)). Also if one writes (with milk) and the paper is burned and the ash sprinkled on the letters written with the milk, they will be manifest (\(\kappa\i\a\i\a \gamma\a\l\a\k\a\i\c\a\i\i\ \d\'\ \varepsilon\ \gamma\a\r\a\f\e\i\ \tau\i\\i\ \\i\c\a\u\s\c\a\i\ \k\a\l\i\w\c\a\c\ \e\p\i\p\a\c\a\s\ \t\r\i\f\e\i\(\e\n\) \e\p\i \t\o\i \t\o \gamma\a\l\a\k\a\i\ \g\e\g\a\m\m\e\n\o\c\i\e\g\r\a\m\m\a\c\i\e, \e\c\e\t\i\ \p\r\o\d\h\i\la\)). And urine

\(^{108}\) Ph. Bel. 4.77; the text reads: γράφονται δ' οι ἐπιστολαί εἰς καυσίαν καίνην (α) εἰς τὸν χρῶτα κηρίδος ὑδατείςς καὶ υδάτι βραχείςς, οἱ ἐπαίνεις ἤ ὑμποδημάκες λελειμμένης, φανερά γένοιτ' ἄν τὰ κεκρυμμένα γράμματα. Also if one writes (with milk) and the paper is burned and the ash sprinkled on the letters written with the milk, they will be manifest (καὶ γάλακτι δ' εἰ γράφει τις, ἢτο χάρτιν καύσας καὶ λείωςας ἐπιπάςας τριτεί(είς) ἐπι τοῖς τῷ γάλακτι γεγραμμένοις γράμμασιν, ἐσταὶ πρόθελα). And urine

\(^{109}\) Plin. HN 34.112
and *garum* also and juice of the spurge and of the fig will have the same effect (*καὶ οὖρος δὲ καὶ γάρον καὶ τιθυμάλου υπὸς καὶ εὐκῆς ποιεῖ τὸ δημιον*). \(^{111}\)

As with many of the other formulae for ink manufacture discussed in this article, counterparts for some of the curious “sympathetic” inks described by Hippolyt can be found in the eighth chapter, “on recording secrets,” of the later work by Ibn Bādīs:

White vitriol (*shabb*)\(^{112}\) is used to write with. Then water of gallnut is smeared on. Or, water of gallnut is used to write with, and vitriol is smeared on. The well pulverized vitriol is sprinkled on and the writing appears … Description of writing with milk. Write with yoghurt (*laban ḥalib*) on paper and send it to whom it is desired. The other man will sprinkle on it ashes of *qarāfīs*: this is from the burning of paper; its ashes are sprinkled.\(^{113}\)

**Conclusion**

The review of the textual sources pertaining to the manufacture of black ink presented in this paper, conform to the analytical record in as much as the bulk of the cited material cluster around carbon ink. The most common black pigments, lamp black of various sorts and natural black earth, are only briefly mentioned in the sources. Their preparation was too well known to be discussed. The major difference among the carbon inks is the botanical material from which the soot is prepared. Some ingredients are mentioned time and time again, e.g. resin, pine, incense and myrrh, while others are attested primarily in the Greek Magical Papyri, e.g. the seeds of dates, (dried) figs, pinecones, etc. Many of these ingredients were still used in the manufacture of ink by the Arabs of North Africa in the eleventh century CE as evidenced by the treatise of Ibn Bādīs.

By-products of metallurgy, glaze and glass production, which seem in some way to be connected with early alchemy and the production of cosmetics, provided the raw material (soot) for some of the more “refined” black inks.\(^{114}\) Formulae for mixed ink, where either copper/iron vitriol or related compounds should be added to a carbon ink, are preserved in an Egyptian funerary papyrus (P.MMA 31.9.7), the *Materia Medica* and the Greek Magical Papyri. Mixed ink can be considered a precursor for iron-gall ink, two formulae for which are provided by Philo of Byzantium and Hippolyt of Rome respectively.

When the gall-nut and ferrous sulphate inks described by these two authors were first applied in written communication proper cannot be inferred from the textual sources, but it is beyond doubt that the chemical reaction between tannic acid and iron sulphate (II) was well-known in the Hellenistic period. Further chemical analyses are needed to ascertain, when iron-gall ink first

---

110 A sauce made of brine and small fish


112 This is probably alum mixed with green vitriol, cf. Gacek (n. 47) 40 (supplement)

113 Levey (n. 16) 35

appeared on a writing medium in the ancient Mediterranean, since it is impossible to discern with our current knowledge of the chemistry of ancient black inks, whether the following description of a documentary papyrus from Oxyrhynchus, dating to 269 BCE, pertains to a mixed ink or the earliest preserved instance of the use of an iron-gall ink on a papyrus:

The ink used is of the reddish-brown variety commonly used in the Byzantine period for literary texts and sometimes for documents. It is interesting to find so early a dated instance for its use.\(^{115}\)

Gum Arabic was the most common additive in the inks, but glair seems also to have been employed – in the formulae from the Greek Magical Papyri, the blood of different animals are also used. Mild solutions of diluted vinegar or wormwood were added to arrest mould and prevent pest attacks. The water applied to the inks is only mentioned, when the source is exceptional, e.g. spring water and sea foam. The common denominator for all the ingredients mentioned in the reviewed textual sources, is that they, besides in the manufacture of black inks, were used in ancient Egyptian and Mediterranean pharmacology.

\(^{115}\) E. Lobel, E.P. Wegener and C.H. Roberts, *The Oxyrhynchus Papyri XX* (London 1952) 142n1 (n° 2269)
<table>
<thead>
<tr>
<th>Arabic</th>
<th>English</th>
</tr>
</thead>
<tbody>
<tr>
<td>ʿafṣ</td>
<td>gallnut</td>
</tr>
<tr>
<td>abzar</td>
<td>cedar</td>
</tr>
<tr>
<td>tamr</td>
<td>date</td>
</tr>
<tr>
<td>jarrah</td>
<td>clay vessel</td>
</tr>
<tr>
<td>hibr</td>
<td>gall-vitriol ink</td>
</tr>
<tr>
<td>kharnāb</td>
<td>carob tree</td>
</tr>
<tr>
<td>ramād</td>
<td>ash</td>
</tr>
<tr>
<td>zāj</td>
<td>vitriol</td>
</tr>
<tr>
<td>shabb</td>
<td>white vitriol</td>
</tr>
<tr>
<td>salābah</td>
<td>fruit of the pine</td>
</tr>
<tr>
<td>sanawbar</td>
<td>clay of the art</td>
</tr>
<tr>
<td>ṭin al-ḥikmah</td>
<td>charcoal</td>
</tr>
<tr>
<td>fahm</td>
<td>oven</td>
</tr>
<tr>
<td>ḥibr</td>
<td>vitriol</td>
</tr>
<tr>
<td>kharnūb</td>
<td>carob tree</td>
</tr>
<tr>
<td>ḍabt</td>
<td>a particular type of wood</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Greek</th>
<th>English</th>
</tr>
</thead>
<tbody>
<tr>
<td>αἰβάλη χρυσοχοίχη</td>
<td>goldsmith</td>
</tr>
<tr>
<td>αἰβάλη χρυσοχού</td>
<td>soot of a goldsmith</td>
</tr>
<tr>
<td>αἰβάλη χαλκέως</td>
<td>soot of a coppersmith</td>
</tr>
<tr>
<td>αλμα δραχόντειον</td>
<td>snake blood</td>
</tr>
<tr>
<td>αλμα ιεράξιος</td>
<td>falcon blood</td>
</tr>
<tr>
<td>αλμα ἔνχλειος</td>
<td>eel blood</td>
</tr>
<tr>
<td>αλμα ἄνειος</td>
<td>blood of an ass</td>
</tr>
<tr>
<td>ἀκακία</td>
<td>acacia</td>
</tr>
<tr>
<td>ἀντιπόδιον</td>
<td>vegetable ash</td>
</tr>
<tr>
<td>ἀργυρόκοπος</td>
<td>silversmith</td>
</tr>
<tr>
<td>ἀρτεμία</td>
<td>single-stemmed wormwood</td>
</tr>
<tr>
<td>ἀρτεμία μονοκλώνος</td>
<td>wormwood</td>
</tr>
<tr>
<td>ἀς</td>
<td>charcoal/soot</td>
</tr>
<tr>
<td>ῥητική</td>
<td>workshop</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coptic</th>
<th>English</th>
</tr>
</thead>
<tbody>
<tr>
<td>ἀνίκαμ</td>
<td>blue/green vitriol</td>
</tr>
<tr>
<td>βννε</td>
<td>date</td>
</tr>
<tr>
<td>κντε</td>
<td>fig</td>
</tr>
<tr>
<td>κόμμι</td>
<td>gum</td>
</tr>
<tr>
<td>κομμι. κόμμιε</td>
<td>water of the fruit of the carob tree</td>
</tr>
<tr>
<td>κόμμι</td>
<td>blood</td>
</tr>
<tr>
<td>κόμμι</td>
<td>blood</td>
</tr>
<tr>
<td>κόμμι</td>
<td>blood</td>
</tr>
<tr>
<td>κόππος</td>
<td>myrrh</td>
</tr>
<tr>
<td>κόμμι</td>
<td>acacia</td>
</tr>
<tr>
<td>κόμμι</td>
<td>charcoal/soot</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Egyptian</th>
<th>English</th>
</tr>
</thead>
<tbody>
<tr>
<td>iny km</td>
<td>blue/green vitriol</td>
</tr>
<tr>
<td>inr km</td>
<td>granite/vitriol</td>
</tr>
<tr>
<td>ʿntyw</td>
<td>frankincense</td>
</tr>
<tr>
<td>ʿn.t</td>
<td>frankincense?</td>
</tr>
<tr>
<td>ῥt</td>
<td>green eye paint</td>
</tr>
<tr>
<td>bnr</td>
<td>date</td>
</tr>
<tr>
<td>mw t-ir.t</td>
<td>water of the fruit of the carob tree</td>
</tr>
<tr>
<td>nstmy</td>
<td>black eye paint</td>
</tr>
<tr>
<td>mšy</td>
<td>copper?</td>
</tr>
<tr>
<td>ry.t</td>
<td>(black) ink/pigment</td>
</tr>
<tr>
<td>ry.t w3d.t</td>
<td>red ink/pigment</td>
</tr>
<tr>
<td>ῥή/Ḥl</td>
<td>myrrh</td>
</tr>
<tr>
<td>ȝt ḍḏ(l)</td>
<td>a particular type of wood</td>
</tr>
<tr>
<td>ṳfr</td>
<td>blood</td>
</tr>
<tr>
<td>ṳfr</td>
<td>incense</td>
</tr>
<tr>
<td>ṳfr</td>
<td>acacia</td>
</tr>
<tr>
<td>ṳfr</td>
<td>gum</td>
</tr>
<tr>
<td>ṳfr</td>
<td>opiment</td>
</tr>
<tr>
<td>ṳfr</td>
<td>fig</td>
</tr>
<tr>
<td>ṳfr</td>
<td>blue/green vitriol</td>
</tr>
<tr>
<td>ṳfr</td>
<td>fig</td>
</tr>
<tr>
<td>ṳfr</td>
<td>charcoal/soot</td>
</tr>
<tr>
<td>ṳfr</td>
<td>charcoal/soot from stone</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Egyptian</th>
<th>English</th>
</tr>
</thead>
<tbody>
<tr>
<td>ὅραμος</td>
<td>myrrh</td>
</tr>
<tr>
<td>ἆργαφος</td>
<td>myrrh ink</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>painter</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>branch</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>dried fig</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>Karian dried fig</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>pen</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>paint for the eyelids and eyelashes</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>flax</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>vetch</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>fresh skin</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>gallnut</td>
</tr>
<tr>
<td>ἄφινθια</td>
<td>gum</td>
</tr>
</tbody>
</table>
λείωϲιϲ
μάγοϲ
μέλαν
μελαντηρία
μέλανοϲ
μερινηϲ
όπαϲ
όττενοϲ
όυροϲ
πεντεδάκτυλοϲ ροϲτάνη
πτερόν ἰβεϲ Ἑρμαίκηϲ
πυρ ρή
ῥητίνη
στροβίλωϲ ἄβροχοϲ
συϲη
σύϲον
σώϲιϲ
σώϲιϲ
ταυροκόλλα
τύϲμαλλοϲ
τρυγλίτιϲ ξύϲρα
τρυψιδοτιϲ
Ὑϲφωνίου μέλανοϲ
ὑδώ ρηγαίϲον
ὑλοϲτρυγγεϲον
ὑϲｍηϲ
φάληϲ
φοίνιϲ
φοίνιϲ ἀρϲενιϲοϲ
φοίνιϲ Νικολάοϲ
φύϲοϲ
χάλκανθοϲ/χάλκανθεϲ
χάλϰευϲ
χάλϰιϲτϲ
χάλϰοϲ ἄνθοϲ
χάρτηϲ
χάρτηϲ ἰερατιϲοϲ
trituration
magician
(black) ink/pigment
blacking/green vitriol?
iron sulphide?
myrtle
juice
stone/seed
urine
cinqufoil
wing/feather of the Hermaic ibis
dried pinecone
fig-tree
fig
copper sulphide?
bulls’ hide glue
spurge
myrrh troglitis
Typhonian ink/red ink
spring water
glass-working factory
skin
libation bowl
date palm/date
male date palm
Nikolaus date
leaf
blue/green vitriol
coppersmith
chalcopyrite
cf. χάλϰανθοϲ
papyrus
hieratic papyrus
χρυϲόχοϲ
χύτρα ωμηϲ
χύϲον χρυϲοϲχοϲιϲοϲ
χρυϲόχοϲ
goldsmith
unfired earthen vessel
goldsmiths’ crucible
Latin
aerea cortina
aerugo
atramentum
balnerius
carbo
facticius
faex vini
fornacula
fornax
fuligo
fumus
glutinum
gummi (arabicum)
infectio
laconicum (sc. balneum)
librarium (atramentum)
mortarium
officina
pictor
pix
resina
sarmenta
schidia
scriptorium (atramentum)
sutorium (atramentum)
taeda
tectorium (atramentum)
Syriac
qamyna dzgwgya
glass-blowers furnace
Second part: archaeometric studies
Chemical characterization of black and red inks inscribed on ancient Egyptian papyri: the Tebtunis temple library

* Thomas Christiansen, David Buti, Anna Vila, (Kim Dalby), Poul Erik Lindelof, Kim Ryholt

1. Introduction

The present paper reports on the first analysis of inks used to inscribe ancient Egyptian papyrus manuscripts from the “Tebtunis temple library”. This library constitutes the largest homogenous collection of cultic, literary and scientific texts that have survived from Ancient Egypt and arguably ranks among the most important assemblages of papyri ever discovered in Egypt (Ryholt, 2005; von Lieven, 2005; Quack, 2006). The research is part of a wider project that seeks to study the chemical composition of ancient Egyptian inks through non-invasive analysis and, in particular, to what extent their composition or structural “finger-prints” can be used to map manuscripts geographically and chronologically. It is an interdisciplinary effort carried out in collaboration between the University of Copenhagen and several partners, and the teams include chemists, physicists, conservation scientists, and Egyptologists. The present research was carried out in collaboration with the Centre for Art Technological Studies and Conservation (CATS) at the National Gallery of Art (SMK), Copenhagen, on papyrus manuscripts from the Papyrus Carlsberg Collection. The aim was to explore the extent to which different inks might have been used within a small and well-defined social context, i.e. the discrete circumstances afforded by the priestly community at the temple of Soknebtunis at Tebtunis in the first-second centuries CE, and possible implications of either positive or negative results. The analytical results are compared to three other ancient assemblages (Pathyris in Egypt, Qumran in Palestine, and Herculaneum in Italy), which are deliberately selected to reflect non-related cultural contexts, time periods, or geographical regions.

1.1. The Tebtunis temple library

The Tebtunis temple library is the only large-scale institutional library to have survived from ancient Egypt. The assemblages include some 300-400 papyrus manuscripts which span the first through the early third century CE, with the bulk dating to the late first and second century CE. It was discovered within two small cellars inside the main temple precinct at Tebtunis, modern Umm el-Breigât, which is located in the south of the Fayum depression some 100 kilometers south-west of Cairo. The dry and brittle manuscripts are all poorly preserved and broken into several thousand smaller fragments. Whole columns or pages are only rarely preserved, and the difficult and time consuming process of sorting and identifying fragments of specific manuscripts is still ongoing. Published texts indicate that on average less than 10% of a manuscript is likely to have been preserved.

The circumstances of their discovery are complex (Gallazzi and Hadji-Minaglou, 2000; Ryholt, 2005). Excavations of the temple’s interior was first undertaken by the British Grenfell and Hunt in December of 1899 and then again by German Otto Rubensohn in March/April of 1902. Both missions brought to light parts of the library. However, the bulk of the papyri were not excavated until 1930 during illicit activities at the site. The emergence of these papyri on the antiquities market prompted the Italian mission then working at the site to search for their source,
which they located and completely excavated on the 10th of March 1931. No detailed archaeological report of any of these early missions was ever published and there are several cellars within the temple precinct. Recently, a specific identification has been proposed on the basis of archival evidence by Claudio Gallazzi, who has directed the current Franco-Italian excavations since 1988 (Gallazzi, in press).

The bulk of the manuscripts from the cellars pertain directly to the temple and the cult of the main local deity, Soknebtunis, and many of the manuscripts were written by the same scribes. However, their exact nature remains uncertain. The manuscripts might have been kept there when the temple was still in use, have been deposited there when it was abandoned, or have been collected for re-use; we feel more inclined towards the second of these options. For the purposes of the present paper, the exact nature of the archaeological context has limited relevance. More relevant here is the fact that the papyri were found in rock-cut cellars and were found covered in sand, since this relates to the potential for contamination of the samples and needs to be taken into consideration in the interpretation of the analytical data (§ 1.2.).

The papyri selected for analysis all belong to the Papyrus Carlsberg Collection for which they were acquired between 1931 and 1938 (Hagen and Ryholt, in press). Many of the fragments were conserved by Hugo Ibscher in Berlin, while others were conserved by Aksel Volten in Copenhagen. There is no detailed documentation on the method of conservation, but it usually consisted of a simple process where the papyri were moistened with water and then flattened by being placed within blotting paper or some other form of folders under a weight of some kind. Dirt would usually have been mechanically removed from the surface of the papyrus, with a staple brush or a sharp instrument, either when wet or dry.

1.2. Sources of contamination and pollution

The analysis of ink used on papyrus manuscripts needs take into account the archaeological context or environment in which the material objects were found. Much analysis has been carried out on Books of the Dead which are visually impressive and frequently well preserved (§ 1.4.). Virtually all these papyri were found within tombs, often in coffins or even inside mummy wrappings. By contrast, papyri deriving from settlement contexts have usually been covered and thus brought into direct and long-term contact with sand or soil which will, to a smaller or greater degree, have embedded particles in the fiber structure of the papyrus. The chemical composition of such contamination of the sampled papyrus will potentially affect the markers. In order to discern between constituents intrinsic and extrinsic to the inks, we have therefore performed point analysis and area scans, where both areas covered by ink, blank areas on the papyrus support next to the ink, and areas far away from the ink have been analyzed.

The papyri contain more information than the preserved texts. As physical objects they carry information both on technologies pertaining to their production and in most cases also the environment in which they were later kept. Traces of the production and contamination from the environment are preserved in the foreign organic and inorganic compounds in the inks and the papyrus fabric. While contamination can distort the analysis of the ink itself, it may at the same time be useful in determining the origin of specific papyrus samples. If affected by contamination, it must be expected that a group of papyri found in the same archaeological context will be likely to share the same specific signatures. This consideration was confirmed during our testing where, in
addition to the ink itself, the contamination of papyrus samples from Tebtunis and papyri from other archaeological contexts can be shown to display distinct signatures (§ 4.).

Contamination by salt is characteristic of many Egyptian objects (Moussa et al., 2009). On papyrus the presence of this kind of pollution manifests itself as crystals on the surface, where it can be seen with the naked eye or through a microscope as small encrustations embedded in the material. When salt particles effloresce, due to the absorption of moisture from the air, it is very detrimental to papyrus, since the particles form within the physical structure of the material, thus destroying the surrounding tissue (Nielsen, 1985; Leach and Tait, 2000; Neate et al., 2011). The fact that the soil of the Fayum is especially high in salt content was demonstrated as early as 1902, when investigations into the soil and water of the Fayum Province were undertaken for agricultural purposes (Lucas 1902; Monson, 2013). It was found that the soil contained sodium chloride and sodium sulfate at concentrations of up to 5.3 per cent, over 0.5 per cent being considered injurious to crops. The analysis concluded that the irrigation water in the Fayum was not the source of salt in the soil, but rather the desert sand, and the limestone and clays that underlie it.

1.3. Description of the samples

A multi-analytical approach using different imaging and spectroscopic techniques was applied to 22 fragments from 13 manuscripts stemming from the Tebtunis temple library (see Table 1 at end). All the samples belong to the Papyrus Carlsberg Collection and are inscribed with either black ink or a combination of black and red ink. This was standard practice in ancient Egypt, where black was used for the main body of the text, while red was used to mark headings or important phrases (rubrication). The black inks fasten to the papyri in different ways; some are entirely stable, while others display cracking. Most are stable in water, but others are soluble (Lau-Lamb, 2010). It is to be expected that these differences are due to variations in their composition, i.e. in the way in which they were prepared.

The fragments chosen for the analytical campaigns all derive from manuscripts that are representative of the different genres typically attested in manuscripts stemming from the library: divinatory literature (ten fragments from four manuscripts: 7, 11, 18-21, 22), medical literature (five fragments from one manuscript: 12-16), narrative literature (four fragments from two or more different manuscripts: 1, 2, 3, 17) and ritual literature (three fragments from three manuscripts: 4, 5, 6). Some of the texts were written on the blank backside of Greek administrative papyrus rolls, which did not originally concern the temple library but had been acquired as “scrap paper” for later re-use (8 fragments from six manuscript: 1, 2, 3, 6, 11, 18-21). The ink used to write these Greek texts has also been analyzed, but will not be discussed in any detail in the present context, where the focus is the temple library itself. Black ink is used on all the 22 numbered papyri, while red ink is found on 11 out of 22 fragments that represent seven manuscripts (4, 6, 7, 8-9, 11, 12-15, 22). Since the papyri from the library are generally very fragmentary, groups of fragments, which have been assigned to specific manuscripts on the basis of content, paleography, and other criteria, was analyzed in order to determine whether the individual fragments would display similar traits or differ significantly from each other. We have selected three such examples; five fragments from a medical treatise (12-16), four from a divinatory text concerning dream interpretation (18-21), and three from another divinatory text concerning astrology (8-10).
The majority of the papyrus samples display clearly distinct types of hand-writing, but three fragments (1, 2, 3) are written in a characteristic hand that is assumed to represent a single prolific scribe who wrote about two dozen of the literary texts found in the library (Ryholt, in press; Quack, in press). There are literally hundreds of smaller and larger fragments from the library in this hand, as a result of the manner in which it was excavated (§ 1.1), and their sorting pose immense difficulties. The three fragments here sampled have not yet been assigned to any specific original manuscript and are therefore designated P. Carlsberg SN 1-3 (sn = sine numero, without number). The same is the case with P. Carlsberg SN 4-5 which clearly derive from two other manuscripts.

1.4. History of the studies

Previous analysis of ink used on Egyptian papyri show that the black pigments are almost invariably based on amorphous carbon in the form of soot (“lamp black”), charcoal, or bone black (Lucas and Harris, 1962; Lee and Quirke, 2000; Di Stefano and Fuchs, 2011). Water was added twice in the process of the manufacture of carbon inks. First, in the production of the dry ink, soot was mixed with a binder dissolved in small amounts of water. Then the mixture was dried and pressed into pellets which could be stored or carried by the scribe. When the scribe was ready to write a text, he would prepare a fluid ink by mixing the ink pellet with another quantity of water. The binding agent seems almost invariably to have been gum Arabic from the acacia nilotica (L.), but the occasional use of different types of glair cannot be ruled out, since they were applied regularly in ancient Egyptian paints (Afifi, 2011).

Different types of black inks often described as “metallic” seem to have been applied as a writing fluid in ancient Egypt and by extension in the ancient Mediterranean at an early date ( Bülow-Jacobsen, 2009). A type of iron/metal-gall ink (encre métallogallique) was detected during chemical analyses undertaken at the Louvre in the late 1980s (Delange et al., 1990). The black inks of papyri written in both Demotic and Greek, dating to c. 250-100 BCE, were analyzed using proton induced X-ray emission (PIXE). The results showed that all the Demotic texts were written with carbon ink and that all the Greek texts, besides one, were written with a type of metallic ink. The iron-gall inks that are attested from the 5th century CE until the pre-modern era are made from a mixture of tannic acid, typically extracted from oak trees, and iron sulfates (II).

The black inks of three papyrus fragments from Qumran, discovered in Cave 4, were analyzed in the mid-1990’s using X-ray fluorescence (XRF). Both Cu and Pb were detected in relative low amounts in black inks of an otherwise carbonaceous nature. The same elements were found in an unspecified number of parchment fragments from Qumran and especially in the Genesis Apocryphon (1QapGen), where the ink seems to have reacted with the support (i.e. the physical manuscript) and caused severe patterns of degradation. The study concluded that Cu and Pb likely had their origin in the bronze inkwells employed by the scribes who wrote the fragments, because Roland de Vaux, who excavated the area between 1951 and 1956, discovered an inkwell of bronze in Locus 30, called “The Scriptorium” (Nir-El and Broshi, 1996a) (A second inkwell was made of clay; de Vaux, 1954: 214, pl. Xb). Another more recent study of a carbon black pigment on a fragment from the Thanksgiving Scroll (1QHodayot 2) – using a combination of XRF, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) – indicated that gall extracts were used in ink preparation already in the 1st century CE (Rabin et al., 2009).
A so far unique black pigment based on powdered galena (PbS) has been proposed in a Book of the Dead from c. 1400 BCE using SEM-EDS (Wagner et al., 2007). Recently, the black ink on two fragments from the Herculaneum papyri (1st century CE) has been the object of close scrutiny at the European Synchrotron Radiation Facility in Grenoble, where they were analyzed using a combination of µXRF, X-ray absorption near edge spectroscopy (XANES) and µX-ray diffraction (µXRD). It demonstrated that the ink was based on amorphous carbon and small amounts of lead whose origin has not been fully understood (Brun et al., 2016; Tack et al., 2016).

The black ink used in ancient Egypt and in the Mediterranean has generally received less attention than colored pigments, perhaps because of the complexity and experimental difficulties posed by carbon (Winter, 1983), and is still in need of systematic studies. The different types of red pigments applied as inks and paints on funerary papyri and their distribution in time have been well established through multi-instrumental analysis of the palette of illustrated papyri: polarized light microscopy (PLM), XRF, µXRF, XRD, SEM-EDS and PIXE (Lee and Quirke, 2000; Olsson et al., 2001; Calza et al., 2008; Leach and Parkinson, 2010; Di Stefano and Fuchs, 2011; Munro and Fuchs, 2015). The source of the red pigment is, with rare exceptions, haematite (Fe₂O₃). A brighter red (closer to orange) could be obtained with orpiment (As₂S₃) or realgar/pararealgar (As₄S₄) that are attested as pigments from the New Kingdom to the Roman period (Daniels and Leach, 2004). Minium (Pb₃O₄) and cinnabar (HgS) were in use in Egypt in the Greco-Roman period. Finally, XRF and XRD analyses performed on the red ink of four fragments from the Dead Sea Scrolls demonstrate that they were made from cinnabar (Nir-El and Broshi, 1996b).

In ancient Egypt, pink was also based on haematite with or without the addition of a white pigment, typically chalk (CaCO₃) or gypsum (CaSO₄•2H₂O). An atypical red/pink paint in a Book of the Dead from c. 300 BCE, has been found to contain haematite and a white compound identified mineralogically with XRD as potassium lead chloride (KPb₂Cl₅). This compound is presumably a secondary product formed by the reaction of lead white [(PbCO₃)₂•Pb(OH)₂] with potassium chloride (KCl) from the earth (Di Stefano and Fuchs, 2011).

2. Experimental

2.1. Experimental approach

Besides digital microscopy, near infrared reflectography has been used for a first characterization of the materials used in the inks and their distribution. Elemental analysis was carried out by means of X-ray fluorescence (XRF). Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and molecular investigation by micro-Raman spectroscopy have been used to corroborate and complement the XRF results.

2.2. Non-invasive analytical methods

2.2.1. Imaging

Microphotographs with incident light on the dark field (DF) were taken using a Leica DM4000M microscope with Leica Application Suite 4.1 software using 5x and 10x objectives. Near infrared (NIR) images of the black inks were made using VideometerLab 3, a spectral imaging instrument, at the Arnamagnaeanc Institute, University of Copenhagen.
2.2.2. X-ray fluorescence

X-ray fluorescence (XRF) measurements were carried out on at least 3 different areas of the black and/or red inscriptions of each of the 22 investigated fragments, as well as a minimum on at least 3 different areas of the papyrus support. All measurements were made with a Bruker ARTAX 400 spectrometer equipped with an Rh tube, a 200 μm collimator and a Si drift detector; using 50 kV and 700 μA with an acquisition time of 100-200 seconds (live-time). Helium was utilized in a feasibility study in order to ensure that light elements were not missed using the abovementioned conditions. A procedure fitting was employed for calculating the net counts for each element. X-ray emission peaks were fitted with the Bayesian deconvolution method in the Bruker ARTAX software and the data expressed as counts.

2.2.3. Scanning electron microscopy-energy dispersive spectroscopy

Backscattered electron (BSE) images were collected of several areas of three fragments of papyri (1, 2, 12). Two samples were written by the same scribe (1, 2). EDS microprobe was applied for qualitative and semi-quantitative analysis as well as mapping the distribution of elements in the investigated areas of the papyri. The images and the spectra were acquired with a FEI Quanta 3D FEG equipped with Oxford Instruments’ Inca EDS at the Nano-Science Center, University of Copenhagen. The measurements were carried out at an accelerating voltage of 10 kV (1, 2) and 20kV (12); pressure of 1.1kPa in H2O vapor; secondary electron (SE) mode with BSE. On each fragment SEM images, elemental maps and EDS map sum spectra were acquired from two areas inscribed with black and/or red ink. As a minimum 20 individual EDS spectra for each of the analyzed areas were obtained through micro-probing both the ink and the support.

2.2.4. Raman spectroscopy

Raman analyses were carried out with a Bruker Senterra spectrometer configured with an Olympus microscope and a thermoelectrically cooled charged-coupled device (CCD) detector. Analyses were recorded alternatively with a 785 nm and 532 nm laser line for excitation. The laser beam was focused on the different areas of the samples using an LD50x objective and a laser power between 1-10 mW for the red laser and between 0.2-2 mW for the green laser. A 400 lines/mm grating and ca. 9-18 μm lateral resolution was used, and in each spot the acquisition time was between 10-60 scans and 1-2 accumulations.

3. Results and discussion

3.1. Imaging analysis

Examples of digital microscopy images of black and red inks are reported in Figures 1 and 2 respectively. Visually, the black inks show different color and material consistency. From the microscopic point of view, the ink layer in samples 16 and 15 (Fig. 1a and b) appear very compact although characterized by several cracks which follow the direction of the papyrus fibers. Further, they have a greasy appearance with fine grains. Diversely, samples 22, 19, 20 and 11 (Fig. 1a, d, e
and f) have a dry and coarse appearance. The same greasy consistency characterizes samples 9, 10 and 12 (Fig. 1g, h and i) but the ink layer is thinner than in the other samples and more transparent, allowing the papyrus support to be seen through the pigment. Furthermore, sand particles that are attached to the ink layer can be seen in the images, e.g. sample 16, 11 (very fine) and 12 (very coarse).

Concerning the red inks, visually they range from deep burgundy (samples 12 and 15, Fig. 2a and b) to orange red (samples 9 and 10, Fig. 2c and d). Only two cases can be considered outsiders: sample 4 (Fig. 2e), which has a pink color with random yellow grains, and sample 22 (Fig. 2f), which has a pale yellow color almost similar to the papyrus support. As for consistency, samples 12 and 15 (Fig. 2a and b) show a very thick ink layer with a dull compact greasy appearance; samples 9 and 10 (Fig. 2c and d) are brighter and with a very thin transparent appearance; samples 4 and 22 (Fig. 2e and f) have a very coarse and dry consistency.

A blackish “patina” can be seen on the surface of samples 12 and 15 (Fig. 2a and b). It is not possible to firmly state by visual means, if it is a degradation of the red pigment or a dirty deposit after contact with the soil. Type of pigment, type and amount of binding medium, particle size, archaeological context and conservation history are all factors contributing to the visual and material appearance of the inks.
All the black inks discussed in this article appear black at 970 nm and show no signs of transparency in NIR region, as observed for other black materials such as iron-gall ink (Havermans et al., 2003a; Havermans et al. 2003b). This suggests that the pigments used are carbon-based black pigments. It is important to note that the black “cracking” inks of a brownish hue found on two manuscripts (5, 12-16) show the same NIR behavior as the other inks, thus indicating that they are based on similar black compounds.

3.2. Elemental and molecular analysis

The elemental composition of the analyzed fragments is reported in Table 1. The results recorded on the support were compared with those from the black and red inks in order to highlight characteristic markers of the inks. In some cases Raman and SEM analysis was applied, providing molecular and complementary elemental information about the black and red pigments. The results will be discussed according to the following arrangement: support, black ink and red ink.

The black inks are divided into two groups: carbon ink and mixed ink. Mixed ink connotes an ink that is primarily based on amorphous carbon, but to which metallic substances are also added, e.g. containing Fe, Cu and Pb (Zerdoun Bat-Yehounda, 1983). The latter are not metallic inks in the
traditional sense of a ferrous-gallotannate compound, where it is not the carbon compounds that provides the black color, but a process of oxidation by exposure to air.

3.2.1. Support

XRF spectra from the papyrus support show in general presence of calcium (Ca), iron (Fe) and chlorine (Cl) in relatively medium amounts, silicon (Si) and potassium (K) in relatively low amounts, and titanium (Ti), strontium (Sr), sulfur (S), aluminum (Al), manganese (Mn), and phosphorus (P) in relatively very low amounts. As can be read in Table 1 - where the elements are listed in decreasing order of abundance - the composition slightly varies from one fragment to the other in terms of relative amounts. This is seen also in fragments from the same document (Fig. 3) and reflects contamination of the individual papyrus fragments by the soil in which they were buried (§ 1.2). Therefore, the elemental composition of the support mainly depends on the elements occurring in the archaeological context and is present on the fragments as contaminants or polluting agents.

The main polluting agent is Ca, which seems to exist on papyri most probably as its carbonate (Flieder and Delange, 2001). However, the presence of small amounts of sulfate or phosphate cannot be excluded, since S and P were sometimes detected. Furthermore, also an exogenous origin of Ca cannot be ruled out. It is present in the cell wall of plants and it is also known to occur as calcium oxalate after reaction with oxalic acid, another constituent of vegetal cells (Wiedeman and Bayer, 1983). Cl is consistently detected in all the measurements carried out on the support in relative medium amounts indicating salt as the probable polluting agent. K, which is present on all the papyri, could be either associated with the salt or natural earth pigments. Si, which is mainly present on all the samples in the form of quartz grains from the sand, could also be associated with Fe, Mn and Al in earth pigments.
The SEM-EDS analysis confirms the XRF results. The origins of these agents are likely the soil in which the papyri were found, but can also derive from the temporary hardness of the water used to conserve the papyri (Flieider and Delange, 2001). Connected with the residues of soil is Si, probably in the form of a mixture of quartz and earth, characterized further by the presence of Al and Fe, and salts, indicated by the presence of Na which is correlated with Cl and perhaps also with K.

3.2.2. Black ink

3.2.2.1. Carbon ink

XRF elemental analyses on the black ink of samples 1, 2, 3, 4, 6, 7, 11, 17, show the same elemental composition detected on the papyrus support. Also, in this case different fragments are characterized by slight differences in their relative elemental abundance (see the elements listed in Table 1). The absence of key heavy elements in the X-ray fluorescence spectra of the black inks on the abovementioned samples, suggests the use of carbon-based black pigments.

Raman spectroscopy carried out on the same papyri confirms the presence of such pigments. The spectra are characterized by two bands placed at ca. 1355 and 1600 cm$^{-1}$ which are known respectively as D and G bands of carbon materials (Fig. 4) (Bell et al., 1997; Tomasini et al., 2012). The higher energy peak (G band, from “graphite”) is assigned to the in-plane stretching vibration mode and it is related to ordered carbon in crystalline graphitic structures. The lower energy peak (D band, from “disorder”) is connected to carbon in disordered graphite (that is to a reduced structural symmetry). In amorphous carbon the two Raman bands are broad; furthermore they can vary in relative intensity and width in relation to the degree of disorder or crystallinity, thus providing structural information on the compound and its preparation.

Fig. 4 Raman spectra of black inks representative of the three groups: sample 10 belonging to the Pb-based mixed ink group (green line), 19 belonging to the carbon-based ink group (blue line) and sample 14 belonging to the Cu-based mixed ink group (black line). The spectra, all showing the features typical of carbon-based materials, are vertically translated.
The SEM-EDS measurements confirm the results obtained by the XRF analysis, but add some important elemental characteristics to the inks. The chemical composition of the black pigments used on samples 1 and 2 show significant chemical variation and it is unlikely that they belong to the same manuscript – although they were written by the same scribe, no contrast can be observed between the ink and the papyrus in the SEM-BSE images of sample 1 – suggesting that soot or finely pulverized charcoal was used to manufacture the pigment (Winter, 1983). In sample 2 a cluster of particles clearly demarcating the ink can be observed on the SEM-BSE images (Fig. 5).

A comparison of the EDS elemental maps and spectra of the two papyri, show that main element of the granular particles observed in the ink of sample 2 is Si, while micro-probing reveals that it is further characterized by Fe, Ca and Al. Perhaps sand was stuck to ink, because of a solubilized binder.

![Fig. 5 SEM-BSE images of two regions containing black pigment on sample 2. Trails of coarse particles following the ink strokes are marked by yellow lines.](image)

### 3.2.2.2. Mixed ink

The same elements present on the papyrus support can be seen in the XRF spectra of black ink on samples 5, 12-16, 18-21 and 22. At the same time, relative low amounts of Cu were detected only when measuring the black letters, providing a marker for the black pigments used to inscribe the four manuscripts. The absence of any Fe marker and the relative low amounts of Cu detected in all the samples show that they should not be classified as “iron/metal gall inks” (Goltz, 2012). Therefore, it is likely that the black pigments on the samples are primarily based on carbon compounds, as suggested by the imaging analysis (§ 3.1.). Carbon-based black was detected by Raman spectroscopy on all the fragments. The graph reported in Figure 4 clearly shows the presence of the D and G bands (Bell et al., 1997; Tomasini et al., 2012). The simultaneous presence of Cu in the pigments indicates the use of what was classified as “mixed ink” in § 3.2. It is important to stress that the experimental results match the philological analysis, since samples 12-16 – all assigned to the same medical text (P. Carlsberg 172) – are characterized by the presence of relatively low amounts of Cu.
No contrast between the ink and the papyrus could be observed in the SEM images of the black pigment on sample 12 (P. Carlsberg 172). Relatively very low amounts of Cu could be detected by micro-probing the bright particles on the scanned areas. The complementary SEM-BSE images show that the Cu particles in the pigment detected by the XRF analysis are likely of sub-micron size.

The only outliers are samples 18-20, which on the basis of paleography and content has been assigned to the same divinatory text as sample 21 (P. Carlsberg 649). Unlike sample 21, which contains relatively very low amounts of Cu in the black pigment, either no trace or only insignificant amounts of Cu were detected in samples 18-20. Further, Ca and Fe in sample 18 were found to be more abundant in the inked regions than in the net papyrus. This could indicate that the scribe used different inks, when he copied the text over a longer period of time or that he wrote the same text on multiple manuscripts. Finally, it is possible that the fragments have been assigned incorrectly to P. Carlsberg 649.

It is important to note that Pb was not found together with Cu in the abovementioned samples, besides in sample 22, where relative very low amounts of Pb were detected together with Cu. However, Pb was seen also in one of the measurements carried out on the support of the sample and its presence on the surface of the papyrus is likely due to the “migration” of Pb particles from the red letters, which was used to mark a chapter heading on the fragment (§ 3.2.3). Therefore it seems unlikely that the Cu in this group of samples originated in a metallic ink-well, which has been suggested as the source for Cu and Pb elements found in the black ink of a number papyrus and parchment fragments from the Dead Sea Scrolls (§ 1.4.).

A review of the few preserved written formulae from the Roman period pertaining to the manufacture of black pigments suggests that by-products of metallurgy, glaze and glass production provided the raw material (soot) for some of the more “refined” black inks used in the ancient Mediterranean (Christiansen, submitted). Bearing this in mind, it should be taken into account that different Cu-containing and Pb-containing compounds were used as colorants in ancient Egyptian pigments, dyes and glasses, which were produced at workshops connected to the local temple and its officiating priests (Ogden, 2000; Nicholson, 2000; Shortland, 2009).

Another “mixed ink” was detected on samples 8-10, which have been assigned to a divinatory text concerning astrology (P. Carlsberg 86). The XRF spectra show the same elemental composition as the support (Ca, Fe, Cl, K, Mn, Si, Sr), but the inked areas are characterized by the presence of relatively low amounts of Pb. In addition, carbon-based black pigment was identified by Raman (Fig. 4). It is important to mention that Pb was detected also in the red ink used on samples 9 and 10. In 9 the two inks are characterized by the same amounts of Pb, while in 10 the red pigment shows slightly higher counts than the black ink. Possible contamination due to the use of the same writing implement for both the black and red inks has to be taken into consideration. However, the red pigment shows substantially higher counts of Fe than in the black areas, where no contrast is observed between ink and support (cf. § 3.2.3.). Therefore, the origin of Pb in the red pigment is more likely to be contamination from the black ink than the other way around. It should be mentioned that relatively low amounts of Pb was detected also in the Greek text written on the front of sample 11.

If it is indeed intrinsic to the black pigment (cf. § 1.4.), the Pb detected in the samples is probably made out of galena (PbS) or cerrusite (PbCO₃), which was the principal lead ores in
ancient Egypt. They could easily be melted using simple charcoal and wood fire (Ogden, 2000) and were used in mineral form as colorant in the manufacture of black eye paint throughout ancient Egyptian history (Hardy et al., 2006; Shortland, 2009).

3.2.3 Red ink

Unlike black ink, not all the investigated fragments contain letters written in red ink (§ 1.3.). XRF elemental analysis, apart from detecting the same elements seen in the papyrus support, shows also the occurrence in the red pigments of variable amounts of Fe and Pb. The relative amounts of iron and lead can be seen in the bar graph shown in Figure 6. The presence of Fe indicates that probably reddish iron earth pigments, red ochre/hematite (Fe₂O₃), were used – as traditionally in ancient Egypt (§ 1.4.). On the other hand, Pb suggests the use of minium/red lead (Pb₃O₄). It has been demonstrated that in the Roman period red lead was used to paint linen cloths intended for funerary use at Hawara, which is located at the entrance to the Fayum region (Walton and Trentelman, 2009). In the wider Roman world, a few scattered occurrences of red lead has also been noted in polychrome sculpture, incorporated into wall paintings at Pompeii, and formulated into cosmetic rouges. However, in many of the analyzed pigments, the presence of other lead-based pigments, such as litharge/massicot (PbO), cerussite and hydrocerussite ([PbCO₃]₂•Pb[OH]₂), cannot be excluded.

Pb is the marker for the red ink in samples 4, 7 and 22, while Fe is the marker in sample 6. Mixtures of Fe- and Pb-based pigments were detected in samples 9-10, 11 and 12-15 (Fig. 6a). The challenges in clearly identifying the origin of lead in both the red and black inks on samples 9 and 10 have been discussed in the previous paragraph (§ 3.2.2.2.). Sample 11 shows variable amounts of Fe and Pb, ranging from relatively low to relatively high. The two elements are also characterized by a 1:1 ratio and they follow the same trend in three measurements; the more pronounced the intensity of the Fe peak, the higher the Pb count. This trend is further stressed by a good linear correlation between the fitted peaks of the two elements as shown in Figure 6b.

As for the four samples with red ink from P. Carlsberg 172, a medical text, sample 12 shows relatively high to medium amounts of Fe with relatively medium to low amounts of Pb; sample 13 high amounts of Fe together with relatively medium amounts of Pb; sample 14 relatively high to medium amounts of Fe with relatively medium to low amounts of Pb; and sample 15, relatively high amounts of Fe with relatively medium amount of Pb. It is possible to notice two subgroups in the manuscript, where fragments 12 and 14 are characterized by a correlation between the fitted peaks of Fe and Pb (Fe and Pb ratio respectively around 3:1 in 12 and around 4/5:1 in 14) (Fig. 6c and d) while an absence of the same correlation can be seen in fragments 13 and 15 (data not shown).
The good correlation between Fe and Pb counts in many of the samples could indicate that the scribes employed red ink cakes that had been mixed together by Fe and Pb containing compounds. For the sake of completeness, it should be mentioned that due to the experimental conditions and the fragility of the fragments, no good Raman spectra have been obtained to firmly identify the Fe and Pb compounds used in the red inks.

The SEM-EDS results obtained from the area of red ink on sample 12 assigned to the medical treatise P. Carlsberg 172 (12-16) confirm the XRF elemental analysis, which shows that the pigment is based on Fe and Pb. Besides Fe and Pb, the elemental maps show that the inked area contains relatively higher amounts of Ca, P, S and Al than the background, as seen in Figure 7. Al can be correlated with the red ochre (Fe₂O₃) on which the pigment is likely based, while the presence of Ca and S could indicate that gypsum (CaSO₄•2H₂O) was added as a toner. There is no obvious explanation for the presence of P in the pigment, but it could be associated with the binder or perhaps a drying agent applied to the ink (cf. Christiansen et al., 2016).
4. Comparisons with black inks from Pathyris

Using the same experimental setup and conditions specified above, we have started studying Egyptian and Greek papyrus fragments deriving from the military camp of Pathyris, located at modern Gebelein some 30 kilometers south of Luxor and about 600 kilometers south of Tebtunis by the Nile. The manuscripts from this site mainly consists of legal documents, accounts, and letters from private archives belonging to the Egyptian soldiers who, together with their families, lived at this community in the late second and early first centuries BCE. Pathyris was destroyed in 88 BCE during a civil war and thousands of papyri have been preserved in the ruins until modern times and are now preserved in papyrus collections around the world (Vandorpe and Waebens, 2009).

Since the study is still ongoing, only some general observations can be made at this point. In addition to carbon ink, it is noteworthy that also “mixed ink” is attested at Pathyris. Thus, for instance, a letter written in demotic is written with a carbon ink that contains lead (Pb) as shown in Fig. 8.
The letter predates the eruption of Mount Vesuvius by nearly two centuries and is one of the earliest attestations in the ancient Mediterranean of the deliberate addition of metalloids during the manufacture of a black ink (c. 100 BCE). The fact that the same type of ink is attested at Herculanum and Tebtunis shows that similar strategies of ink manufacture were employed throughout the Mediterranean and for an extended period of time. Besides lead-bearing carbon inks, also copper-bearing carbon inks are attested at Pathyris. A mixture of both Cu and Pb has been detected in the mixed black inks of the Dead Sea Scrolls and in a single fragment from Tebtunis (sample 22), but none of the samples from Pathyris analyzed until now contain a mixture of these two elements.

Despite their distance in time, space, and social context, the black inks of Pathyris and Tebtunis reveal similar traits and few distinctive features. The materiality of the manuscripts do, however, differ in another significant manner. All samples from Pathyris, analyzed thus far, were found to contain potassium (K) in relative medium amounts and chlorine (Cl) in relative low amounts in the papyrus texture itself, while the relation between the two elements in the samples from Tebtunis is always the opposite (cf. § 3.2.1.). We assume that these elements represent some form of contamination and that the papyri from Tebtunis and Pathyris have been affected by the different local environments. None of the papyri from the two sites contain traces of bromine (Br), which has been detected in papyri of Memphite and Theban provenance and in the Dead Sea Scrolls (Flieder and Delange, 2001; Wolff et al., 2012).

5. Conclusions

Among the conclusion that may be drawn from the analyses present above, the following seem to us particular important:

1. Two types of ink previously undocumented in the analytical record have been analyzed and described: a black “mixed ink” containing Cu and a red ink contained a mixture of Fe and Pb.

2. Raman spectroscopy has been applied with very limited success, and it has not been possible to ascertain the exact nature of metal compounds. Raman also did not provide information on the contaminants found on the samples. The latter was instead achieved through XRF and SEM-EDS, which shows the importance of using a multi-instrumental approach for the study of the inks.

3. A specific community would not necessarily use just one primary type of (black) ink. While this may seem an obvious possibility, very little is known about how papyrus and ink was procured. An account belonging to a head of the local notarial office at Tebtunis in the first century CE shows that he acquired both papyrus and ink from different people, but it is unclear whether they were the direct providers or simply middlemen (Boak, 1933: 98-100). The samples here analyzed demonstrate how one scribe used two different inks for two manuscripts (sample 1, 2) and another, more significantly, used two or three different inks to write out different sections of the same text on a single papyrus (samples 18-21). This observation complicates the mapping of inks, but might facilitate the identification of which fragments belong to a single manuscript or sections thereof.
Acknowledgements

The project Ancient Ink as Technology forms part of CoNeXT: Fertilizing the ground and harvesting the full potential of the new neutron and X-ray research infrastructures close to Copenhagen University (dir. Prof. Sine Larsen) under the UCPH Excellence Programme for Interdisciplinary Research (conext.ku.dk). The CATS gratefully acknowledge VILLUM FONDEN and VELUX FONDEN for infra-structural financial support.

Author Contribution

T.C. wrote the manuscript, assisted in processing the data, and participated in the experiments. D.B. and A.V. ran the acquisition of XRF, Raman and microscopy data, processed the data and participated in writing the manuscript. P.E.L. participated in the data acquisition, in the interpretation of the results and in writing the manuscript. K.R. participated in the interpretation of results and in writing the manuscript. K.D. ran the acquisition of the SEM-EDS data and participated in the interpretation of the results.

References


Tack, P., Cotte, M., Bauters, S., Brun, E., Banerjee, D., Bras, W., Ferrero, C., Delattre, D., Mocella, V., Vincze, L., 2016. Tracking Ink Composition on Herculaneum Papyrus Scrolls:
Quantification and Speciation of Lead by X-ray Based Techniques and Monte Carlo Simulations. Scientific Reports 6. DOI: 10.1038/srep20763.


Table 1 – Summary table showing the analysed samples and their elemental composition.

<table>
<thead>
<tr>
<th>Inventory no.</th>
<th>Sample Image</th>
<th>Size (cm)</th>
<th>Elemental Composition</th>
<th>Marker</th>
</tr>
</thead>
</table>
| P. Carlsberg SN 1 | 1 | 4.7 x 3.2 | **Support:** Ca, Cl, Fe (K, Sr, Si, Mn, Ti?)  
**Black Ink:** Ca, Fe, Cl (K, Sr, S, Mn, Si, P, Ti?, Al?) | / |
| P. Carlsberg SN 2 | 2 | 4 x 2.4 | **Support:** Ca, Cl (Fe, K, Si, Mn, Sr)  
**Black Ink:** Ca, Cl (Fe, K, Si, Mn, Sr, Ti?, P?) | / |
| P. Carlsberg SN 3 | 3 | 6.6 x 4.1 | **Support:** Ca, Cl, Fe (K, Si, Mn, Sr)  
**Black Ink:** Ca, Cl, Fe (K, Si, Mn, Ti) | / |
| P. Carlsberg SN 4 | 4 | 3.7 x 2 | **Support:** Ca, Fe, Cl (Si, Pb, K, Sr, S, Ti, Mn)  
**Red Ink:** Pb, Ca, Fe, Cl (K, Si, Al, Ti, Mn?) | Pb |
| P. Carlsberg SN 5 | 5 | 3 x 5.5 | **Support:** Ca, Cl (Fe, K, Si, Mn, Sr?)  
**Black Ink:** Ca, Cl (Fe, Cu, K, Si, Mn, Ti?) | Cu |
| P. Carlsberg 53 | 6 | 3.8 x 2 | **Support:** Ca, Cl (Fe, K, Si, S, Ti, Mn?, Ti?)  
**Black Ink:** Ca, Cl, Fe (Si, K, Sr, S, Mn, Ti?)  
**Red Ink:** Fe, Ca (Cl, S, K, Si, Sr, Al, P) | Fe |
| P. Carlsberg 66 | 7 | 14.6 x 4.8 | **Support:** Ca, Fe (Si, Cl, K, S, Sr, Ti, Al)  
**Black Ink:** Ca, Fe (Si, Cl, K, S, Sr, Ti, Al?) | / |
| P. Carlsberg 86 | 8 | 3.7 x 3.5 | **Support:** Ca, Fe (Cl, K, Mn, Sr, Ti)  
**Black Ink:** Ca, Fe (Cl, Pb, K, Mn, Sr, Ti) | Pb |
| P. Carlsberg 86 | 9 | 2 x 1.8 | **Support:** Ca, Fe, Cl (K, Mn, Si)  
**Black Ink:** Ca, Fe, Pb (Cl, K, Mn, Sr, Si, K)  
**Red Ink:** Fe, Ca, Pb (Cl, K, Mn) | Fe, Pb |
| P. Carlsberg 86 | 10 | 2 x 1.4 | **Support:** Ca (Fe, Cl, K, Mn, Si)  
**Black Ink:** Ca, Fe, Pb (Cl, K, Mn, S, Ti?)  
**Red Ink:** Fe, Ca, Pb (K, Cl, Si, Ti?) | Pb |
| P. Carlsberg 99 | 11 | 5.7 x 5.2 | **Support:** Ca, Cl (Fe, S, K, Si, Mn, Al?)  
**Black Ink:** Ca, Cl, Si, Fe, K, Mn, Al?  
**Red Ink:** Fe, Ca, Pb (Cl, Si, K, P, Mn, Al, Ti?, Cu?) | Fe, Pb |
| P. Carlsberg 172 | 12 | 6 x 2.3 | **Support:** Fe, Pb (Ca, K, Cl, S, P)  
**Black Ink:** Ca, Cl (Fe, K, Si, Cu, S, P, Al, Ti)  
**Red Ink:** Fe, Pb (Ca, K, Cl, S, P, Si, Al, Sr, Ti) | Cu, Pb |
<table>
<thead>
<tr>
<th>Page</th>
<th>Image</th>
<th>Dimensions</th>
<th>Support:</th>
<th>Black Ink:</th>
<th>Red Ink:</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td><img src="image13.png" alt="Image" /></td>
<td>10.4 x 5.6</td>
<td>Ca (Cl, Si, Fe, K, Sr, S, Mn)</td>
<td>Ca (Fe, Cl, K, Si, Cu, S, Mn, Sr, Ti)</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe (Ca, Pb, K, S, Si, P, Sr, Ti, Al)</td>
<td>Fe, Pb</td>
</tr>
<tr>
<td>14</td>
<td><img src="image14.png" alt="Image" /></td>
<td>3.8 x 2.4</td>
<td>Ca, Cl (K, Fe, Si, S, Sr, Mn, Al?)</td>
<td>Ca, Cl (Fe, K, Si, Cu, S, Mn, Ti?)</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe (Ca, Pb, S, K, Cl, Si, P, Al, Sr, Ti?)</td>
<td>Fe, Pb</td>
</tr>
<tr>
<td>15</td>
<td><img src="image15.png" alt="Image" /></td>
<td>4.8 x 2.9</td>
<td>Ca (Fe, K, Mn, Ti, Si?, Sr?)</td>
<td>Ca (Fe, Cu, K, Cl, Mn, Ti)</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe, Pb, Ca (K, Cl, S, Sr, Mn, Ti)</td>
<td>Fe, Pb</td>
</tr>
<tr>
<td>16</td>
<td><img src="image16.png" alt="Image" /></td>
<td>5 x 3.1</td>
<td>Ca (Fe, K, Cl, Mn, Sr, Si)</td>
<td>Ca (Fe, Cl, K, Cu, Sr, Mn, Si, Ti)</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td><img src="image17.png" alt="Image" /></td>
<td>3.8 x 3</td>
<td>Ca, Cl (Fe, Si, K, Sr, Mn, S?)</td>
<td>Ca, Cl (Fe, Si, K, Sr, S, Mn, Ti)</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td><img src="image18.png" alt="Image" /></td>
<td>6.4 x 2.7</td>
<td>Ca, Cl, K, Fe, Si, Mn, Ti, P, S</td>
<td>Ca, Fe</td>
<td>Ca, Fe</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td><img src="image19.png" alt="Image" /></td>
<td>3.9 x 3.7</td>
<td>Ca (Cl, Fe, K, Mn, Sr?, Ti?, S?)</td>
<td>Ca (Cl, Fe, K, Mn, Ti, S, Sr)</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td><img src="image20.png" alt="Image" /></td>
<td>3 x 2</td>
<td>Ca (Cl, K, Mn, Ti, Sr, S, Cu?)</td>
<td>Ca, Fe (K, Cl, S, Mn, Ti, Sr, Cu?, Pb?)</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td><img src="image21.png" alt="Image" /></td>
<td>9.5 x 5</td>
<td>Ca, Fe, Cl (K, Mn)</td>
<td>Ca, Fe, Cl (K, Ti, Cu, Mn)</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td><img src="image22.png" alt="Image" /></td>
<td>8.5 x 10.8</td>
<td>Ca, Cl (Fe, K, S, Mn?)</td>
<td>Ca, Fe, Cl (Pb, K, Sr, Ti, Mn, Cu)</td>
<td>Cu, Pb</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pb</td>
<td>Pb</td>
</tr>
</tbody>
</table>
Copper-containing carbon inks from ancient Egypt: a µXRF and µXANES study
*

Thomas Christiansen, (Marinne Cotte), (René Loredo Portales), Sine Larsen, Poul Erik Lindelof, Kell Mortnensen, Kim Ryholt

The chemistry of the black inks used in the ancient world has been only scantily studied so far. This leaves gaps in our knowledge of one of the crucial inventions in the history of civilization. Thus, until recently, it was assumed that the ink used for writing was carbon-based at least until the fourth to the fifth century CE. However, µX-ray analyses of two papyrus fragments from Herculaneum have shown that lead compounds were added to black ink at an early date, thereby modifying our knowledge of ink manufacture in Antiquity (1, 2).

In this experiment the chemical composition of 12 papyrus fragments from ancient Egypt was studied using X-ray fluorescence (XRF) and X-ray absorption near edge structure spectroscopy (XANES). The fragments form parts of larger manuscripts that today are housed in the Papyrus Carlsberg Collection and can be divided into two groups.

The first group comes from southern Egypt and consists of the private papers of an Egyptian soldier, Horos, who was stationed at the military camp of Pathyris, located at modern Gebelein some 30 kilometers south of Luxor. Pathyris was destroyed in 88 BCE during a civil war and thousands of papyri have been preserved in the ruins until modern times and are now conserved in papyrus collections around the world. The archive consists of 57 Greek and Egyptian papyri that date to the late second and early first centuries BCE. They were bought on the antiquities market in 1924 by the manuscript collector Elkan Nathan Adler (1861-1941), who reports that they were stored in a sealed jar, which had been unearthed by locals during clandestine excavations of the ancient settlement (3). This is the only archive from Pathyris that have come down to posterity more or less intact (4).

The second group derives from the only large scale institutional library to survive from ancient Egypt, namely the Tebtunis temple library. This assemblage includes some 300-400 papyrus manuscripts which span the first through the early third century CE, with the bulk dating to the late first and second centuries. It was discovered within two small cellars inside the main temple precinct at Tebtunis, modern Umm el-Breigât, which is located in the south of the Fayum depression some 100 kilometers south-west of Cairo. The dry and brittle manuscripts are all poorly preserved and broken into several thousand smaller fragments, which are preserved in papyrus collections around the world, including Copenhagen, Florence, Berlin, London and Yale. Whole columns or pages are only rarely preserved, and the difficult and time consuming process of sorting and identifying fragments of specific manuscripts is still ongoing. Published texts indicate that on average less than 10% of a manuscript is likely to have been preserved. The papyri selected for analysis were acquired for the Papyrus Carlsberg Collection between 1931 and 1938 on the antiquities market in Cairo (5, 6).

To resolve the composition of the black inks found on the fragments, µXRF and µXANES experiments were performed at the ID21 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Via this technique it was possible to detect many of the principle elements present in the inks and on the papyri, the only notable exceptions being carbon and oxygen. The fragments are of a light brown color and the inks range from deep black to light grey or brown. They are approximately 0.5 mm thick and made of two layers of papyrus strips – in one
instance, where two sheets overlap, of four layers. They were scanned using X-ray beams of different sizes, from a sub-millimeter to a micrometric scale. The different acquisition parameters are described in Method.

Results and discussion

Figure 1 shows a comparison between high-resolution scans, microscope pictures and XRF maps obtained for four fragments of papyri – two from Pathyris (fig. 1 A) and two from Tebtunis (fig. 1 B). The four fragments stand apart from the rest of the analyzed papyri in as much as they contain variable amounts of copper (Cu) in the inked areas. The levels of concentration in the inks imply that copper-bearing material was intentionally introduced in the ink during the manufacturing process. These copper-containing carbon inks are otherwise unattested in the analytical record that pertains to ancient ink manufacture and will be described more closely, following a general overview of the elemental composition of the analyzed fragments.

Fig. 1 Images showing microscope pictures and XRF maps obtained for four fragments of papyri from Pathyris and Tebtunis respectively at the ESRF, beamline ID 21. The red frame inserts demarcate the areas analyzed with µXRF. XRF maps were normalized by the incident flux and are in arbitrary units. The two fragments in A were found in Pathyris; they are written in Greek and date to the late second century CE (inv. P. Adler G. 1 = P. Carlsberg 828 and inv. P. Adler G. 12 = P. Carlsberg 839). The fragments in B are written in Demotic and derive from the Tebtunis temple library; they date to the first/second century CE (inv. P. Carlsberg 79 and inv. P. Carlsberg 649).

Like all the black inks on the analyzed fragments, the copper-containing carbon inks appear black at an IR illumination of 970 nm wavelength and show no signs of transparency, as observed for other black pigment materials such as iron-gall ink (6, 7, 8). This suggests that the inks used are of a carbonaceous nature, which is confirmed by Raman spectroscopy carried out on the same papyri, where the spectra are characterized by two broad bands placed at ca. 1322 and 1588 cm⁻¹, known as D and G bands of carbon materials respectively (6, 9, 10).
The support of the analyzed papyrus fragments is characterized primarily by relatively high amounts of calcium (Ca) and iron (Fe). The fragments from Pathyris are characterized further by high amounts of potassium (K) and low amounts of chlorine (Cl), while the relation between the two elements in fragments from Tebtunis is always the opposite, i.e. high amounts of Cl and low amounts of K. Moreover, the fragments contain medium to low amounts of sodium (Na), magnesium (Mg), aluminium (Al), silicium (Si), phosphor (P), sulfur (S), manganese (Mn), and very low amounts of titanium (Ti), strontium (Sr) and lead (Pb). These elements reflect contamination of the individual papyrus fragments, primarily by the soil in which they were buried. In other words, the elemental composition of the support mainly depends on the elements occurring in the archaeological context and is present on the fragments as contaminants.

The main contaminant is Ca, which seems to exist on papyri as its carbonate. However, the presence of small amounts of Ca sulfate or phosphate cannot be excluded. Cl and Na, which is consistently detected in all the measurements carried out on the support indicates salt, sodium chloride, as the most probable polluting agent. On papyrus the presence of this kind of contamination manifests itself as crystals on the surface, where it can be seen with the naked eye or through a microscope as small encrustations embedded in the material. When salt particles effloresce, due to the absorption of moisture from the air, it is very detrimental to papyrus, since the particles form within the physical structure of the material, thus destroying the surrounding tissue (11, 12). K, which is present on all the papyri, could be associated with salt particles, but the papyri from Pathyris that contain high amounts of K, all have very low Na contents. Si mainly appears on the samples in the form of quartz grains.

The fragments are either characterized by no contrast between the inked areas and the papyrus support, indicating the use of soot or finely powered charcoal, or by the presence of Cu or Pb compounds in the black pigments. Like the “metallic inks” revealed in the Herculaneum papyri, the lead-containing carbon pigments from Tebtunis show a clear correlation between Pb and P as seen in figure 2. The nature of this correlation remains to be explained (2). It is unlikely that galena (PbS) is the main metalloid constituent of the ink, since – unlike Pb and P – no co-distribution of Pb and S can be observed at macro- and micro-scale.

XANES measurements performed at Pb-L$_3$ edges of the Herculaneum papyri have shown that the Pb in these inks is very similar to that of lead acetate (II) with a partial contribution of PbS (up to 45%) (2). Egyptian kohl or black eye-paint, which seems closely related to the manufacture of lead-containing carbon inks, were made from the principal lead ores found in ancient Egypt, galena (PbS) and cerrusite (PbCO$_3$), which could be easily melted using simple charcoal and wood fire (13). It is likely that the lead-containing carbon pigments were manufactured as byproducts during similar processes and later admixed with a binding agent and water. Alternatively to the use of a lead based pigment it has been suggested that lead could have been introduced in the ink as a drier, since litharge (PbO) was used in Antiquity as an oil drier (14). As PbO is very prompt to react, e.g. with oil or another reactive such as soil, the detection of PbO in nuce with µXRF and µXANES is rendered improbable (2).
In the four fragments, where Cu was detected in the inks, it is present also in very low amounts along the fibrous structure. A possible explanation for the phenomena is the conservation history of the fragments. There is no detailed documentation on the method of conservation applied to the fragments, but it usually consisted of a simple process, where the papyri were moistened with water in order to unfold them. From the XRF maps it is clear that the copper is concentrated in the letters from where it seems to diffuse out in the papyri (cf. fig. 1). Therefore it would seem that copper-containing carbon inks, unlike both carbon ink and lead-containing carbon ink, are unstable and that some Cu compounds are susceptible to migrate, if water is applied during conservation. In this respect copper-containing carbon ink is similar in nature to iron-gall ink, which being an acidic product, ferric gallotannate, is less stable than carbon black (15).

Besides Cu, the inks on the four fragments contain higher amounts of some of the same elements detected on the papyrus support – besides in the hoariest of the fragments, a Greek contract from Pathyris dating to the 17th of September 134 BCE, where Cu is not co-localized with any other element. This is thus far the oldest dated document from the ancient Mediterranean in which the addition of metalloids to a black ink has been detected. Figure 3 displays the Cu-K XANES of the Cu in the fragment, compared to several known reference compounds (16, 17). The ink shows features characteristic of cuprite (Cu2O[Cu1+]), a mixture of Cu1+ and Cu2+ species (fig. 3 B). The XANES collected on a single Cu bearing grain shows the presence of chalcopyrite (CuFeS2), while spectra obtained from the fibers indicate that malachite (Cu2CO3[OH]2) is the main component (fig. 3 C, D). In general the linear combination fits (LCFs) have good R-factors (cf. the appendix). However, the fitted shapes are not entirely good, indicating that there might be other Cu
compounds present, which are not in the standards. In general the LCFs could be improved by using a better standard for malachite (the spectrum is noisy) and reducing the number of points taken in the averages.

Fig. 3 Greek papyrus from Pathyris dated to the 17th of September 134 BCE (inv. P. Adler G. 1 = inv. P. Carlsberg 828). The blue frame insert marks the area that was scanned with a focused beam (160x100 steps of 5µm) and the black circles the regions from where XANES data was obtained: the ink (B), the fibers (C) and single particles (D).

In the second fragment from Pathyris, another Greek contract, which dates to the 16th of October 101 BCE, Cu is partially correlated with the following elements in the macro XRF maps listed in decreasing amounts of abundance: K, Mn, Cl, Si, Al, Pb and S. At high resolution Cu is not associated with any other element. The Cu is also present as a mixture of Cu¹⁺ and Cu²⁺ species, but is characterized further by the contribution of copper acetate and tenorite (CuO[Cu²⁺]). XANES measurements on the ink suggest that azurite (Cu₃[CO₃]₂(OH)₂) is the main component (fig. 4 B). In single copper-bearing grains two distinct types of XANES spectra can be observed: one with a “shoulder”, which resembles azurite and chalcopyrite, and another type without a shoulder, which shows tenorite and Cu acetate as components (fig. 4 E-F). In Cu XANES taken along the fiber azurite, cuprite and malachite are the main constituents (fig. 4 C), while malachite is not present in XANES spectra obtained from fibers far removed from the ink (fig. 4 D).
Fig. 4 Greek papyrus from Pathyris dated to the 16th of October 101 BCE (inv. P. Adler G. 12 = P. Carlsberg 8XX). The red frame insert marks the area that was scanned with a focused beam (390x330 steps of 5 µm) and the yellow circles on the red XRF map the regions from where XANES data was obtained: the ink (B), the fibers (C-D) and single grains (E-G). In the grains (E) two distinct XANES spectra can be observed: one displays a shoulder (F), red region, which resembles azurite and chalcopyrite, and another type without a shoulder (G), green region, which shows tenorite and Cu acetate as partial components.

In the first fragment from Tebtunis, written in Demotic and dated to the first/second century CE on the basis of paleography, Cu is in the macro scans co-localized with Ca, Mn, P and Al. In micro-scale Cu is partially correlated with Ca, K and M – as shown in fig. 5 – which could indicate that earth pigments were used during the manufacture of the ink. XANES taken from the ink show that the principle Cu compounds are cuprite and azurite. As in the fragments from Pathyris chalcopyrite was detected in individual copper-bearing grains, but is not associated with the organic form of Cu acetate as in the second fragment from Pathyris.
Fig 5 Egyptian papyrus dating to first/second century CE found at Tebtunis (inv. P. Carlsberg 79). The blue frame insert marks the area that was scanned using a focused beam (100x100 steps of 5 µm). The correlation plots show that Cu is partially co-localized with Ca, K and Mn (B).

In the second fragment from Tebtunis, also written in Demotic and dated to the first/second century CE on the basis of paleography, Fe, K, Si, Cu, S, Al and P seem to be co-localized. However, Cu is not correlated with any other element at very high resolution. As seen in figure 6, the XANES data show that cuprite and azurite are the main components present in the ink (fig. 6 B). Probing individual Cu grains revealed that they contain Fe, which is explained by a significant contribution of chalcopyrite in the relevant areas (fig. 6 C). As in the fragments from Pathyris, the presence of malachite was detected in the fibrous structure (fig. 6 D).

Fig. 6 Egyptian papyrus dating to first/second century CE found at Tebtunis (inv. P. Carlsberg 649). The red frame inserts mark the areas that were scanned using a focused beam (159x581 steps of 5 µm and 52x69 steps of 2 µm). The main components present in the ink are cuprite and azurite (B). The black circles demarcate the regions in a single Cu and Fe rich grain from which XANES data were extracted (C-D).
In conclusion Cu in inked areas of the four fragments is present principally as azurite and cuprite. Further, chalcopyrite was detected in individual grains on the fragments. In the fibers malachite also occurs as one of the main components, while the shoulder present in some of the XANES measurements of the second fragment from Pathyris is explained by the contribution of azurite and chalcopyrite. Though they share similar traits, none of the four inks analyzed are completely identical, which could indicate that the scribes either procured or concocted their own inks. However, it should be recalled that the papyri in question were written over a period of 300 years and that the composition and fabrication of ink are likely to have evolved during this time-span.

As for the source of the Cu found in the inks and along the fibrous structure, a review of the few preserved written formulae from the Hellenistic Period pertaining to the manufacture of black ink suggest that by-products of metallurgy, glaze and glass production provided the raw material (soot) for some of the more “refined” carbon inks used in the ancient Mediterranean (18). For instance, Dioscorides records in “On Pharmacy and Medicine (V161, 162)” that a superior ink used for writing and painting can be made from a mixture of soot collected from glass-factories (19), while a Greek papyrus from the third century CE states that a spell should be written with the soot of a coppersmith (20).

Another copper-bearing pigment in Egypt, namely the so-called Egyptian blue, was manufactured from scrap or by-product copper obtained at temple workshops that either melted copper or produced glass and faience (13). Egyptian blue (CaSi₂O₅•CuSi₂O₅) was made by mixing cupric oxide with sand, soda and lime, which thereafter was roasted at about 850-900°C to sintered crystalline aggregates rather than glass (21, 22). Looking at the elements present in the four inks, it seems likely that the soot/charcoal of copper-containing carbon inks were obtained during related manufacturing processes, e.g. the extraction of cupric oxide from sulfurous ores like chalcopyrite. This finds some confirmation in the fact that Egyptian kohl or black eye-paint, which seems closely related to the manufacture of lead-containing carbon inks, as mentioned above, was produced in workshops, where vitreous materials were manipulated (23).

Finally, it seems that copper-containing carbon inks are less stable than carbon inks and that some copper compounds are susceptible to migrate along the fibrous structure, if water is applied to the manuscript during conservation. This phenomenon calls for further scientific analysis, if better methods for conservation of the earliest black inks that contain metalloids are to be developed.

Methods

Samples were sandwiched between two 4 µm thick ultralene foils (Spec, Certiprep). Due to the motorization of the microscope the direction of the writing is inverted in the figures (cf. the appendix for the correct orientation).

XRF microbeam measurements were performed at X-ray microscopy beamline ID21 at the ESRF (Grenoble, France). The primary beam energy was tuned by the use of a Si (111) monochromator. To define the beam spot size on the samples for general overview mapping a pinhole of 100µm was used. An incident beam flux monitoring pin diode was used continuously to correct for intensity variations. An average beam flux of 1 x 10¹⁰ ph/s, 1.3 x 10⁹ ph/s, 2.7 x 10¹⁰ ph/s and 6.3 x 10⁹ ph/s were obtained during the measurements of the samples. The sample detector chip distance was set
to 3 cm. Scans were performed by moving the sample through the X-ray beam with an energy of 9.05 KeV and 3+9 KeV, acquiring a XRF spectrum at each step. Acquisition times of 500 and 100 ms per step were used. High resolution spatially resolved XRF measurements were performed using progressively smaller pixel size, the beam being focused down to ~0.4 x 0.7µm² with a Kirkpatrick-Baez mirror system.

The microscope was operated under vacuum and samples were placed under an angle of 62º with respect to the primary X-ray beam. The XRF (and scatter) radiation was detected using a Bruker (Germany) XFlash 5100 silicon drift detector (SDD), equipped with a Moxtex AP3.3 polymer window (24), mounted under 69º with respect to the primary X-ray beam. An additional ultralene foil (4 µm) covers the detector. XRF spectra were processed using PyMCA (24) as well as the AXIL and IDL based Microxrf2 software packages (26, 27).

XANES acquisitions were performed at ID21, at the copper K-edge (calibrated using a metallic Cu foil). XANES spectra were recorded in XRF mode (same set-up as above), with a beam of 80, 20, 10, 5 and 2 µm diameter. The XANES were acquired from 8.9 to 9.15 KeV with 260 steps of 0.3 eV at Cu-K edge. Linear combination fitting was performed to identify and quantify mixtures of pure copper compounds, which were prepared as powder pressed into pellets and measured in transmission mode.

References
(6) Christiansen, T., Buti, D., Vila, A., Dalby, K., Lindelof, P.E., Ryholt, K. (in preparation) Chemical characterization of black and red inks inscribed on ancient Egyptian papyri: the Tebtunis temple library


Acknowledgements
The project Ancient Ink as Technology forms part of CoNeXT: Fertilizing the ground and harvesting the full potential of the new neutron and X-ray research infrastructures close to Copenhagen University (dir. Prof. Sine Larsen) under the UCPH Excellence Programme for Interdisciplinary Research (conext.ku.dk). The scientific committee of the ESRF is thanked for granting 48 hours of beamtime and Marine Cotte for providing additional in-house beamtime. Great thanks go out to P.J. Veiga for providing us with XANES spectra for azurite, chalcantite, malachite and tenorite.

Author Contribution
T.C. wrote the manuscript, processed the XRF and XANES data and participated in experiments at ID21. M.C. ran the acquisition and processing of the XRF and XANES data, and participated in the interpretation of the results. R.L.P. processed the XANES data and participated in the interpretation of the results. S.I., P.E.L., K.M. and K.R. assisted in the acquisition of XRF and XANES data at ID21 and participated in the interpretation of the results and in writing the manuscript.
Appendix

XANES data and calculations in tabular models

<table>
<thead>
<tr>
<th></th>
<th>Azurite Cu₃(CO₃)₂(OH)₂</th>
<th>Chalcantinite Cu₃SO₄·5H₂O</th>
<th>Cuprite Cu₂O</th>
<th>Malachite Cu₉CO₃(OH)₂</th>
<th>Chalcopyrite CuFeS₂</th>
<th>R-Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 points on ink</td>
<td>29.6</td>
<td>5.8</td>
<td>32.8</td>
<td>31.7</td>
<td>0</td>
<td>0.003</td>
</tr>
<tr>
<td>6 points on fiber</td>
<td>28.3</td>
<td>1.4</td>
<td>34.4</td>
<td>35.8</td>
<td>0</td>
<td>0.004</td>
</tr>
<tr>
<td>5 points on grain</td>
<td>0</td>
<td>22.1</td>
<td>27.1</td>
<td>19.6</td>
<td>31.2</td>
<td>0.003</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Azurite Cu₃(CO₃)₂(OH)₂</th>
<th>Chalcantinite Cu₃SO₄·5H₂O</th>
<th>Tenorite CuO</th>
<th>Cuprite Cu₂O</th>
<th>Malachite Cu₉CO₃(OH)₂</th>
<th>Cooper Acetate CuAc</th>
<th>Chalcopyrite CuFeS₂</th>
<th>R-Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 points on ink</td>
<td>56.2</td>
<td>0</td>
<td>29.6</td>
<td>0</td>
<td>0</td>
<td>8.3</td>
<td>5.9</td>
<td>0.004</td>
</tr>
<tr>
<td>10 points on ink</td>
<td>55.7</td>
<td>0</td>
<td>34.2</td>
<td>0</td>
<td>0</td>
<td>10.1</td>
<td>0</td>
<td>0.006</td>
</tr>
<tr>
<td>4 points on ink with shoulder</td>
<td>72.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>27.6</td>
<td>0.002</td>
</tr>
<tr>
<td>6 points on ink without shoulder</td>
<td>21.2</td>
<td>2.5</td>
<td>47.3</td>
<td>0</td>
<td>0</td>
<td>29.1</td>
<td>0</td>
<td>0.009</td>
</tr>
<tr>
<td>3 points on grain</td>
<td>70.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.4</td>
<td>0</td>
<td>22.9</td>
<td>0.003</td>
</tr>
<tr>
<td>4 points on grain</td>
<td>6.9</td>
<td>9.8</td>
<td>49.6</td>
<td>0</td>
<td>0</td>
<td>33.7</td>
<td>0</td>
<td>0.010</td>
</tr>
<tr>
<td>3 points grain with shoulder</td>
<td>62.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>33.1</td>
<td>0</td>
<td>4.7</td>
<td>0.001</td>
</tr>
<tr>
<td>6 points on grain without shoulder</td>
<td>31.6</td>
<td>0</td>
<td>33.1</td>
<td>0</td>
<td>0</td>
<td>35.4</td>
<td>0</td>
<td>0.009</td>
</tr>
<tr>
<td>15 points on fiber</td>
<td>30.8</td>
<td>0</td>
<td>33</td>
<td>30.1</td>
<td>0</td>
<td>6</td>
<td>9</td>
<td>0.003</td>
</tr>
<tr>
<td>24 points on ink</td>
<td>43.9</td>
<td>0</td>
<td>34.5</td>
<td>12.5</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>0.002</td>
</tr>
<tr>
<td>45 points on fiber</td>
<td>34</td>
<td>0</td>
<td>43.6</td>
<td>0</td>
<td>0</td>
<td>22.4</td>
<td>0</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>Azurite $\text{Cu}_2(\text{CO}_3)_2(\text{OH})_2$</td>
<td>Tenorite $\text{Cu}_2\text{O}$</td>
<td>Cuprite $\text{Cu}_2\text{O}$</td>
<td>Malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$</td>
<td>Chalcopyrite $\text{CuFeS}_2$</td>
<td>R-Factor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------------------------------------</td>
<td>---------------------------------</td>
<td>-------------------------------</td>
<td>---------------------------------</td>
<td>-------------------------------</td>
<td>----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 points out of ink</td>
<td>18.8</td>
<td>0</td>
<td>39.6</td>
<td>21.7</td>
<td>19.9</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 points on concentrated ink</td>
<td>30.6</td>
<td>10.3</td>
<td>29.1</td>
<td>0</td>
<td>30.1</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 points in ink</td>
<td>27.7</td>
<td>0</td>
<td>32.6</td>
<td>18.6</td>
<td>21.1</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Azurite $\text{Cu}_2(\text{CO}_3)_2(\text{OH})_2$</th>
<th>Cuprite $\text{Cu}_2\text{O}$</th>
<th>Malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$</th>
<th>Chalcopyrite $\text{CuFeS}_2$</th>
<th>R-Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 points on Cu and Fe rich grains</td>
<td>31.5</td>
<td>32.5</td>
<td>10.5</td>
<td>25.3</td>
<td>0.002</td>
</tr>
<tr>
<td>6 points on Cu but not Fe rich grains</td>
<td>18</td>
<td>37.6</td>
<td>21.6</td>
<td>22.8</td>
<td>0.005</td>
</tr>
<tr>
<td>10 points on ink</td>
<td>17.9</td>
<td>29.6</td>
<td>36.6</td>
<td>16</td>
<td>0.004</td>
</tr>
<tr>
<td>18 points on fiber</td>
<td>16.70</td>
<td>32.5</td>
<td>33.5</td>
<td>17.2</td>
<td>0.003</td>
</tr>
</tbody>
</table>
Postlude
**Experiment title:**
Study of the composition of various types of ink on ancient Egyptian papyri – determination of provenance

<table>
<thead>
<tr>
<th>Experiment number:</th>
</tr>
</thead>
<tbody>
<tr>
<td>HG84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Beamline:</th>
<th>Date of experiment:</th>
<th>Date of report:</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID21</td>
<td>from: 13/4-2016</td>
<td>07/9-2016</td>
</tr>
<tr>
<td></td>
<td>to: 15/4-2016</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Shifts:</th>
<th>Local contact(s):</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Marine Cotte</td>
</tr>
</tbody>
</table>

**Names and affiliations of applicants** (* indicates experimentalists):

- PhD fellow Thomas Christiansen* (Egyptology, UCPH)
- Dr. Marine Cotte* (Beam-line responsible ID 21, ESRF)
- Prof. Sine Larsen* (Chemistry, UCPH)
- Prof. Poul Erik Lindelof* (Science, University of Copenhagen)
- Prof. Kell Mortensen* (Science, UCPH)
- Prof. Kim Ryholt* (Egyptology, UCPH)

**Report:**

In the spring of 2016, we were granted 48 hours of beam-time at ID21, ESRF, to study the chemical composition of ancient Egyptian inks and papyri from the Papyrus Carlsberg Collection. During the 48 hours we analyzed a group of 12 carefully selected papyrus fragments using µX-ray fluorescence (XRF) and µX-ray absorption near edge structure spectroscopy (XANES). We made macro and micro XRF-maps of all the fragments at Cu K-edge (9.05 KeV). We primarily focused on the black ink, though we also analysed the red ink present on three fragments at 3(+9) KeV – so as to get a good signal for S, Cl, Fe and Pb. The manuscripts that we analyzed can be subdivided into two groups.

One group comes from southern Egypt and primarily consists of the private papers of an Egyptian mercenary solider, Horus, who was stationed at a small military outpost in southern Egypt, Pathyris, located some 30 kilometers south of modern Luxor. Today this archive consists of 51 larger Greek and Egyptian papyri that date to the late second century BCE. Though thousands of papyri from Pathyris are preserved in papyrus collections around the world, this is the only archive from the military camp that have come down to posterity more or less intact.

The other group derives from the only large scale institutional library to survive from ancient Egypt. This assemblage includes some 300-400 papyrus manuscripts which span the first through the early third century CE with the bulk dating to the late first and second century CE. It was discovered within two small cellars inside the main temple precinct at Tebtunis, modern Umm el-Breigât, which is located in the south of the Fayum depression some 100 kilometers south-west of Cairo. The dry and brittle manuscripts are all poorly preserved and broken into several thousand smaller fragments. Whole columns or pages are only rarely preserved, and the difficult and time consuming process of sorting and identifying fragments of specific manuscripts is still ongoing.

As seen in figure 1, our synchrotron results were surprising, in as much as we encountered a hitherto unknown type of ink in a number of fragments coming from both Pathyris and Tebtunis, namely a copper containing carbon ink. The preliminary analysis of Cu-K edge XANES spectra collected on the inks displayed complex features, characteristic of different species, e.g. cuprite ($\text{Cu}_2\text{O(Cu}^{1+}\text{)}$) and azurite ($\text{Cu}_3[\text{CO}_3]_2[\text{OH}_2]_2$). Further these inks are the earliest examples in the history of writing of the conscious addition of metal compounds during the manufacture of black ink. From our results it seems that the raw
material for some of the “refined” black inks in the ancient Mediterranean were obtained as byproducts of metallurgy, glaze and glass production.

Fig. 1: Greek papyrus fragment from Pathyris dating to the 16th of October 101 BCE. The green and red inserts demarcate areas of the macro and micro XRF maps, which show the distribution of Cu in the sample. The yellow circle indicates the area from where the XANES spectra, seen to the right, were obtained.

In the papyrus fragments, where Cu was detected in the inks, it is present also in very low amounts along the fibrous structure. XANES measurements suggests that the Cu appearing along the fibers consists primarily of malachite ($\text{Cu}_3\text{CO}_3[\text{OH}]_2$). From the XRF maps, as seen in figure 1, it is clear that the Cu compounds are concentrated in the letters from where they seem diffuse out in the papyri. A possible explanation for this phenomena is the conservation history of the fragments. There is no detailed documentation on the method of conservation applied to the papyri, but it usually consists of a simple process, where the papyri are moistened with water in order to unfold them. Therefore it seems that copper containing carbon inks unlike both carbon ink and iron-gall ink are unstable and that particular Cu compounds are susceptible to migrate, if water is applied during conservation. This demonstrates the need for scientific analysis of ancient manuscripts, if better methods of papyrus conservation are to be developed.

The composition of the red inks is unattested in the history of writing. The XRF maps are characterized by the following elements in decreasing amounts of relative abundance: Si, Fe, P, Pb, S, Ca, Al and Cu. P and Pb are strongly co-localized and distributed along the edges of the letter. Micro-metric maps of relevant areas confirmed the correlation between the two elements and revealed further that they formed a cell-like structure. This perhaps indicates the use of an unknown dryer or binding agent in the ink. S seemed correlated with Ca, so likely gypsum ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$) was added as a white toner. The source of the red pigment is probably haematite ($\text{Fe}_2\text{O}_3$), goethite ($\text{FeO(OH)}$) or minium ($\text{Pb}_3\text{O}_4$); to which compounds Si and Al could be related? None of the analyzed black and red inks are completely identical, which could indicate that individual scribes concocted their own inks. However, it should be kept in mind that the papyri in question were written over a period of 300 years and that the composition and fabrication of inks are likely to have evolved over this span of years.

The results obtained so far using the synchrotron radiation from ID21 in the study of the black ink on papyri provide exiting new perspectives on a decisive chapter in the history of science: the invention and evolution of ink. Further, the chemical and structural signatures obtained through the X-ray analysis reflect the physical properties of the manuscripts and thereby address one of the central challenges facing the historian: the fact that the majority of ancient manuscripts lack a recorded archaeological context. It is our expectation that these “finger-prints”, we have found, in the future will contribute to the mapping of characteristic traits of ink and papyrus, which is of importance for their chronological and geographical origin.
Application for beam time at ESRF – Experimental Method

Proposal Summary (should state the aims and scientific basis of the proposal):
We propose to study a group of ancient Egyptian papyri from the Papyrus Carlsberg Collection inscribed with red ink at the ESRF. Fragments that represent a wide variety of archaeological contexts and time-periods would be selected for the analysis. This experiment is a continuation of a previous study, where µXRF and µXANES were successfully applied in an investigation devoted to the composition of ancient Egyptian black inks. The results were surprising, because we encountered an unknown type of ink in a number of fragments, namely a copper containing carbon ink. These inks are the earliest examples in the history of writing of the conscious addition of metal compounds during the manufacture of black ink (1, 2). The chemical and structural signatures obtained through X-ray analysis could resolve one of the central challenges facing the historian: the lack of a recorded archaeological context for the majority of ancient papyri. It is our expectation that these “finger-prints” will contribute to the mapping of the chronological and geographical origins of the papyri.

Scientific background:
Besides black, some of the papyri are inscribed also with red ink, which in ancient Egypt was used to mark headings or important phrases in a text. During the experiment a preliminary study was made of three specimens with red ink, dating to the 1st/2nd century CE. They stem from the only temple library to survive from ancient Egypt, which was discovered within two small cellars inside the main temple precinct at Tebtunis, modern Umm el-Breigât, located in the south of the Fayum depression some 100 kilometers south-west of Cairo. This assemblage includes some 300-400 papyrus manuscripts. The dry and brittle manuscripts are all poorly preserved and broken into several thousand smaller fragments. Due to antiquities trade, the manuscripts from the library are dispersed between papyrus collections around the world, e.g. Copenhagen, Florence, Berlin, London, Yale etc.

The composition of these red inks is unattested in the history of writing. As can be seen in figure 1 where XRF maps of two samples are provided, the macro XRF map is characterized by the following elements in decreasing amounts of relative abundance: Si, Fe, P, Pb, S, Ca, Al and Cu. It is evident that P and Pb are strongly co-localized and distributed along the edges of the letter. Micrometric maps of relevant areas confirmed the correlation between the two elements and revealed further that they formed a cell-like structure. This indicates the use of an unknown dryer or binding agent in the ink. S seemed correlated with Ca, so likely gypsum (CaSO$_4$•2H$_2$O) was added as a white toner. The source of the red pigment is probably hematite (Fe$_2$O$_3$), goethite (FeO[OH]) or minium (Pb$_3$O$_4$); to which compounds Si and Al could be related. The red color might be provided partially also by Cu (I) oxide. Interestingly the Cu in the sample have seeped out along in the fibrous structure of the papyrus – a phenomena that we have observed also in relation to the Cu containing carbon inks as described in our experiment report. This migration of Cu compounds is likely caused by the water that was applied during the unfolding of papyri, and calls for the development of better methods of papyrus conservation.
The red ink shown in figure 1 (A) was analyzed further using μX-ray diffraction (XRD) during a short in-house experiment at ID21. The experiment was first and foremost performed to see, whether μXRD could be successfully applied to the study of ancient red inks. This turned out to be a success in as much as it proved that the technique could be employed in the study, but also raised more questions, than it answered. Thus, the μXRD analysis of the red pigment area revealed no traces of minium, goethite or hematite – as was expected – but instead patterns similar to potassium lead chloride (K Pb\(_2\)Cl\(_5\)). This could mean that white lead has been added to the red pigment as well and that this compound is a secondary product formed by the reaction of lead white \([\text{PbCO}_3\text{•Pb(OH)}_2]\) with potassium chloride (KCl) from the soil in which the papyri were found. This adds to the number of unanswered questions relating to the composition of the red inks. In conclusion, we would like to ascertain the exact nature of the chemistry of these and related red inks. Our study of black inks showed that many different technologies were applied during the manufacture of the black pigments and it will be fascinating to observe whether the same phenomena can be detected in relation to the manufacture of red pigments.

**Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc):**

XRF and XANES with a beam of different sizes, from a sub-millimeter to a sub-micrometric scale and energies 3+(9)KeV and 9.05 KeV, complemented with μXRD analysis. In total we would analyze 12 fragments with red ink from the Papyrus Carlsberg Collection

**Beamline(s) and beam time requested with justification :**

We would require 6 line-shifts at ID 21 to perform the XRF and XANES measurements of the fragments, which we would like to complement thereafter with μXRD analysis. Ideally, the μXRD experiment would be performed at ID13, but could also be executed at ID21. In both cases it would require 3 line-shifts using μXRD to map the characteristic traits of the red pigments’ crystal structure. Our experience shows that it is not possible to unravel the complex composition of the inks using conventional X-ray sources.

**Results expected and their significance in the respective field of research :**

X-ray analysis will provide exiting new perspectives on a decisive chapter in the history of science: the invention and evolution of ink in ancient Egypt. The results would undoubtedly be important for fields like ancient history, papyrology and manuscript conservation. They should be published in journals of high-impact within both the humanities and the sciences.

**References**


(2) Christiansen, T, Cotte, M, Portales, RL, Larsen, S, Lindelof, PE, Mortensen, K, Ryholt, K (in preparation) XRF and XANES disclose the earliest attestations of metalloids in black inks from ancient Egypt
Dansk resumé

Afhandlingen, Select Papyri from Danish Collections:Philological and Archaeometric Studies, består af en indledning, en bog, fire artikler, samt en rapport om et videnskabeligt forsøg ved den Europæiske synkrotron (ESRF) i Grenoble, Frankrig, og en ansøgning om endnu et forsøg ved den samme institution. Bogen præsenterer tekstudgaver af 22 upublicerede begravelses (funerary) manuskripter, hvoraf hovedparten er skrevet på papyri. Den første artikel er en tekstudgave af et brev fra det sene Ny Rige (c. 1100 f.v.t.), hvorpå følger en diskussion og oversigt over skriftlige kilder, der vedrører produktionen af sort blæk i antikkens middelhavs kulturer og to artikler, der udforsker brugen af røntgenstrålings analyser i studiet af old-egyptiske papyri. Fem af bidragene er skrevet i samarbejde med andre forskere. Tilsammen tegner afhandlingens forskellige dele et kort rids over udviklingen og brugen af skriften i det gamle Egypten igennem en cirka 1500 årig periode.

English resume

The thesis, Select Papyri from Danish Collections: Philological and Archaeometric Studies, consists of an introduction, a book, four articles and a rapport on a scientific experiment at European Radiation Synchrotron Facility (ESRF), Grenoble, France, together with an application for another experiment at the same facility. The book presents text-editions of 22 unpublished funerary papyri, primarily written on papyri. The first article is a text-edition of letter from the late New Kingdom (c. 1100). It is followed by a review of the written sources pertaining to the manufacture of black ink in the ancient Mediterranean and two articles that explore the application of X-ray analysis in the study of ancient Egyptian papyri. Five of the contributions are co-authored with other researchers. In total, the thesis provides an overview of the evolution and use of writing in Ancient Egypt, through a period of nearly 1500 years.