Archaeological and Anthropological Sciences (2021) 13: 71
https://doi.org/10.1007/s12520-021-01320-5

ORIGINAL PAPER

Looking for the missing link in the evolution of black inks

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Received: 10 December 2020 / Accepted: 15 March 2021 / Published online: 31 March 2021

Abstract
In the transition from carbon to iron-gall inks, the two documents from the Egyptian Museum and Papyrus Collection in Berlin with shelfmarks P 13500 and P 13501 discussed in this work present an important case. Their inks appear brownish, although they date back to the fourth and third century BCE, when carbon inks are believed to have been commonly if not exclusively used. Using imaging micro-X-ray fluorescence and infrared reflectography, we discovered that the inks in both documents contain a significant amount of copper in addition to carbon. Comparing the extant recipes for black writing inks and the experimental evidence, we suggest that these inks are a transition between the pure carbon and the iron-gall inks. Such inks may have been quite common before the production of iron-gall ink was clearly understood and established.

Keywords Black writing ink · Hellenistic · Papyrus · XRF imaging · NIR imaging

Introduction

It is customary today to distinguish among three main types of historical black writing inks: carbon, plant, and iron-gall ink. The oldest preserved documents are written with carbon inks. Such inks were made by mixing soot, a binder of choice, and water. The second type, plant inks, consists of an aqueous solution of tannins with or without a binding agent. The third kind, iron-gall inks, results from the reaction between tannins and iron ions usually provided by soluble iron salts, with the addition of a binder. The onset of the use of iron-gall inks, which are often easily recognized by their corrosive action on the substrate, has commonly been associated with the spread of parchment as a writing support in the early Middle Ages (Diringer 1982, p.531). By contrast, carbon inks, which were used predominantly on papyri, neither undergo compositional changes with time nor damage the substrates. The fact that most papyri appeared to be penned in carbon ink whereas the majority of the medieval parchment codices are written with iron-gall ink, at least in Europe, seemed to support the strong correlation between the writing surface and the type of the ink. Interestingly, little attention was paid to the transition period from the carbon inks of Antiquity to the iron-gall inks of the Middle Ages. Zerdoun's "Les encres noires au Moyen Age: jusqu'à 1600" is the only monograph that offers insight into that time, based on the linguistic analysis of the extant sources on writing inks. Apart from this remarkable book, there is no systematic overview of the technological evolution of black writing inks. From this point of view, from the very first day of its existence, the collaboration of the Bundesanstalt für Materialforschung und -prüfung (BAM) with the Centre for the Study of Manuscripts Cultures (CSMC) of Hamburg University created a unique multidisciplinary environment perfectly suited to systematically study the technological evolution of inks without neglecting historical recipes and treatises (Brockmann et al. 2014, 2018).

It has to be stressed that the body of experimental work dedicated to various aspects of iron-gall inks focuses mostly on the inks of the medieval period or later, rather than their early history (see, e.g. the collection of papers in Kolar and Strlič 2006). In the last few decades, destructive sampling of historical manuscripts was prohibited, particularly from inscribed areas. For that reason, a significant portion of the literature deals with the development of non-destructive methods for identifying and classifying ink components (e.g. Budnar et al. 2006; Hahn et al. 2004). In addition to articles dealing with conservation and analytical techniques, there are

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many case studies to help address scholarly questions and gain insight into specific writing traditions. The majority of reported cases, though, deal with parchment and paper but not papyrus manuscripts, like the ones presented in this article. For this reason, the first appearance and technological development of iron-gall ink are still obscure. To date, the oldest documents in which iron-gall ink was experimentally identified date back to the third or fourth century CE (Aceto et al. 2008; Ghigo 2020), although ancient recipes provide hints that the reaction between tannins and vitriol, responsible for the black colour of iron-gall ink, was already known at an earlier date (Zerdoun Bat-Yehuda 1983, p. 91-94).

In contrast to the huge number of publications dealing with medieval inks, the published examples of inks from Antiquity that contain metals are rather sporadic and do not offer a homogeneous picture. The discovery exactly thirty years ago of Hellenistic inks containing metals attracted our attention and initiated this line of work. In 1990, Delange and co-authors published a Particle-Induced X-ray Emission (PIXE) study of five bilingual papyri (Greek and Egyptian demotic, shelfmarks N2433, N2429, N2416, N2410, and N2422) and one Greek papyrus (shelfmark N2331) from the Louvre collection and dating from 253 to 98 BCE (Delange et al. 1990). No metal was found in the demotic text, but copper, sometimes associated with traces of lead or iron, was found in the ink of the Greek text on four of the five bilingual papyri and on the Greek papyrus. In the absence of reflectographic analysis, it is not clear whether the inks also contained elemental carbon and belong to the category of mixed ink discussed here. More recently, Rabin et al. published the analysis of an ink containing an elevated amount of copper in a section of P. Laur. Inv. 19655 from the second century CE in the Biblioteca Medicea in Florence, whose ink has visual aspects similar to the ones discussed in this article. This time, elemental carbon was also identified, using near infrared (NIR) reflectography (Rabin et al. 2019). Bonnerot et al. also recently detected copper in inks from several fragments detached from Herculaneum scrolls (Bonnerot et al. 2020). On these fragments, carbon-based pigment is clearly visible in the infrared images collected by Booras and his team (MacFarlane et al. 2007). However, we cannot determine the ink's original visual aspects because the rolls were carbonized by the eruption of Mount Vesuvius in 79 CE. Nir-El and Broshi reported the presence of copper in the carbon inks of the Genesis Apocryphon (1QGenAp) and several other fragments from Qumran, which they attributed to contamination coming from bronze inkwells (Nir-El and Broshi 1996). In the case of the Genesis Apocryphon, no signs of metallic presence could be seen other than a corrosive action that practically destroyed the parchment of the scroll. Neither signs of ink corrosion nor brownish colour could be seen on the several papyri from the Tebtunis temple library dating back to the first-second centuries CE published in 2017, by Christiansen and co-authors. Reporting the results of X-ray fluorescence (XRF), scanning electron microscope with energy dispersive spectroscopy (SEM-EDS), and Raman spectroscopy analysis on inks, they stressed that only "relatively low amounts" of copper could be detected in four of them (Christiansen et al. 2017a). Probably intrigued by this presence of copper, Christiansen and other colleagues conducted a micro-X-ray absorption near edge structure (XANES) experiment on another set of papyri at the European Synchrotron Radiation Facility (ESRF), whose results were published in the same year[1] (Christiansen et al. 2017b). The authors claimed that copper was present in the form of cuprite, together with azurite and malachite, and suggested that these originate from the soot used. Indeed, in another publication (Christiansen 2017), Christiansen cited several recipes for magical ink (from the third and fourth centuries CE) that mention specific sources of soot, such as "goldsmith soot" (αἰθάλη χρυσοχοϊκή) or "coppersmith soot" (αἰθάλη χαλκέως). "Coppersmith soot" might refer to soot collected from copper or bronze vessels, resembling the description by Pliny the Elder in the first century CE (Pliny Naturalis Historia XXXV 25.43).[2] Christiansen also touched upon the "painter's soot" (ἀσβόλη ζωγραφική) mentioned by Dioscorides in his *De Materia Medica*, which is soot collected from glassworks (Dioscorides *De Materia Medica* V 161). While cuprite was indeed probably used in ancient glass manufactures, in particular to obtain red or orange glass (Barber et al. 2009), it is unlikely that azurite and malachite were used in the coloured-glass-making industry, for which the main source of copper was probably scraps of bronze (Freestone 2008).

Besides these examples from Antiquity, copper and carbon have been reported in the inks of three Coptic fragments from the Roca Puig collection (inv. 345, 357, 399) originating from the monastery of Apa Apollo in Bawit and paleographically dated to the seventh–eighth centuries. The inks from these documents visually strongly resemble the ones discussed in the present article (Ghigo 2020). The presence of other metals like iron or lead is sometimes also mentioned (Bonnerot et al. 2020; Brun et al. 2016; Christiansen et al. 2020). It is clear from this short overview that there is a lack of understanding of the transition from carbon to iron-gall inks.

In the present work, combining conservation, papyrology, and natural sciences, we focused our attention on the transition from carbon-based to metal-based inks, in which inks containing copper seem to play a crucial role. Two Greek documents from Elephantine that date back to the early Hellenistic period, preserved in the Egyptian Museum and the Papyrus Collection in Berlin, are inscribed with a corrosive ink that

[1] The new set contained two Greek and two Demotic papyri, dating between the late second and the early first century BCE from Tebtunis and Pathyris. One of the papyri, P. Carlsberg 649, is common to both publications.

[2] All cited Latin and Greek original texts are found, together with their English translation, in the Supplementary Information (SI).

contains copper in amounts far exceeding that reported by Christiansen et al. (2017) for Carlsberg 172.[3] We suggest that a correlation exists between this ink and ancient recipes from the time in question.

The ink on these manuscripts has a distinct appearance, and we hope that the characterization and analysis presented in this paper will help experts studying papyri recognize such inks and collect systematic data on papyri written with inks containing copper. In addition to material analysis and description, we suggest that a correlation exists between this ink and ancient recipes from the time in question.

Provenance of the documents

The two papyri discussed here are very famous Greek documents from the fourth and third centuries BCE, with shelfmarks P 13500 and P 13501, respectively. Each of these manuscripts consists of two certificates, one in the upper part of the papyrus and its copy in the lower part. P 13500 (P Eleph. 1), the oldest surviving Greek document with a date, is a marriage contract between Heracleides and Demetria with a detailed description of the dowry. Dated between July 17 and August 15, 310 BCE, P 13501 (P Eleph. 2) is a will stipulating reciprocal hereditary entitlement between the Greeks Dionysios and Callista. The surviving partner agreed to bequeath the inheritance to the couple's sons. The second document is dated between May 31 and June 29, 284 BCE. Both papyri were excavated by Otto Rubensohn in 1906 on Elephantine Island, located close to the first cataract of the Nile.[4] They were found in a clay pot that contained five papyrus documents in total: a bundle of four documents and a separate manuscript. Both P 13500 and P 13501 were found within the bundle, which was wrapped in a piece of papyrus inscribed with the famous "Drinking Songs" of Elephantine. The remaining two papyri from the bundle, different in their format and folding technique (Rubensohn 1907, pp. 5–7), are now stored in Cairo and were not accessible for inspection. The separate document, which was found inside the pot next to the bundle, belongs to the Berlin Papyrus Collection and, based on observation in visible light, seems to be inscribed with carbon-based ink.

Detailed description of the documents

The documents are written on papyrus whose structure, fineness, and surface finish indicate that this substrate might have been manufactured in Elephantine (Krutzsch 2020, pp. 47–56). These rather thin papyri currently have a very unstable and fragile consistency. The cracks and losses are particularly numerous in the areas where the documents were folded and where the writing is due to folding and ink corrosion. In addition, the papyri display discoloration caused by oxidation and hydrolysis.

The format of both documents is remarkable; both were written transversa charta (i.e. the papyrus was turned 90° before writing) on rolls measuring ca. 40 cm (P 13500) and almost 52 cm (P 13501) in height. P 13500 consists of only two sheets 35 and 35.5 cm wide, while the roll section of P 13501 consists of four much narrower sheets, each about 14-cm wide. Despite this significant difference in the widths of the sheets, the structure of the papyri suggests a common origin. In Fig. 1, we see the exceptional similarity of the papyri in reflected light. In contrast, the photographs in transmitted light clearly show the individual structure and formats of the individual sheets as well as their sheet joins.

Visual analysis of the sheet joins of the two papyri shows that here we are dealing with the manufacture joins of the most common type II (Krutzsch 2017), with three fibre layers. In both papyri, the upper sheets are adhered on top of the lower ones. All the sheet joins are easily recognizable because their colour is slightly darker than the rest of the papyrus. The dark hue is caused by the adhesive used to connect the sheets, which has penetrated into the upper layer of fibres.[5] While the sheet join of P 13500 has the mixed form based on types II and III with a width of ca. 2 cm, the joins in P 13501 belong to the basic form of type II and are 1–1.6-cm wide.

The papyrus P 13501 has a roll-end at the top edge, which consisted of an attached papyrus sheet cut to the width of 2 cm.

P 13501, with its four complete individual sheets, provides enough information for their description. All sheets have trimmed side edges and belong to sheet type II. The surface of the individual sheets of both papyri has the silky sheen on the recto side that is typical of the Elephantine material. The verso, on the other hand, has a matt and blunt surface. Only the lower sheet of P 13500 is of inferior quality, whereas the rest of the single sheets display excellent quality, characterized by a consistent structure, transparency, and silky appearance of the recto side.

Both papyri were folded according to the same basic scheme, but with some variations (Rubensohn 1907, p. 6f). Between the top and the bottom certificates, there is a cut that

[3] Previously analysed by I. Rabin with longer acquisition times with otherwise equal parameters and the same instrument, making a direct comparison possible.

[4] In his publication on the Elephantine finds, Rubensohn did not provide geographical coordinates, but included a hand-drawn map with locations (Rubensohn 1907, p. 3). Based on this map, the approximate DMS coordinates of the find site are: 24° 5′ 6″ N and 32° 53′ 8″ E.

[5] The adhesive used to glue the single papyrus sheets in Antiquity has never been identified.

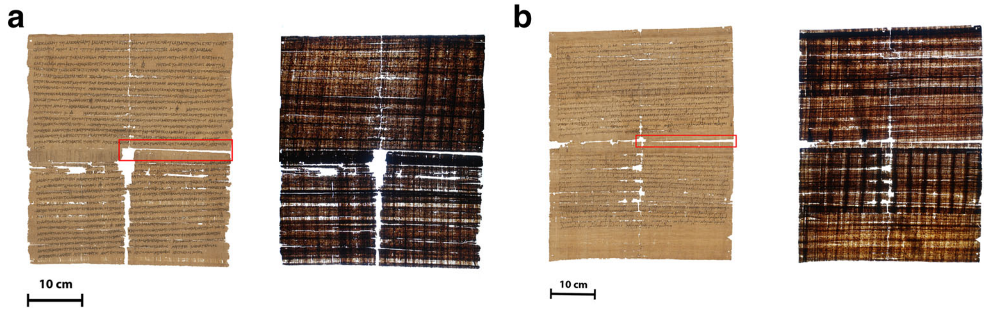


Fig. 1 **a** P 13500 in reflected (left) and transmitted light (right). The cut that runs from the right margin to the middle of the sheet is marked with a red rectangle (© Staatliche Museen zu Berlin, Ägyptisches Museum und Papyrussammlung; scan (left, reflected light), Berliner Papyrusdatenbank, P 13500 (https://berlpap.smb.museum/03734/); photo (right, transmitted light), Myriam Krutzsch). **b** P 13501 in reflected (left) and transmitted light (right) (© Staatliche Museen zu Berlin, Ägyptisches Museum und Papyrussammlung; scan (left, reflected light), Berliner Papyrusdatenbank, P 13501 (https://berlpap.smb.museum/03735/); photo (right, transmitted light), Myriam Krutzsch). The fibres' run and density indicate that the writing surfaces of both papyri were manufactured according to the classic method, i.e. the papyrus stem was cut into strips with a knife. The cut that runs from the right margin to the middle of the sheet is marked with a red rectangle

runs from the right margin to the middle of the sheet (see red rectangles in Fig. 1) that makes it possible to close the documents separately. While the top document was folded and sealed, the bottom copy remained open and, thus, accessible.

The main difference between the ways the two manuscripts are folded corresponds to the folding of the top document. Whereas P 13500 was folded first from top to centre and then halved from right to left, P 13501 is exactly the other way around. Here, the top half was first folded from right to left and, only in a second step, from top to bottom. In both cases, the sealings were attached after the top part of the manuscript was folded (see the red rectangles in Fig. 2). Finally, the bottom part was folded in the same way for both papyri, starting from right to left, then bottom to centre. While P 13500 was folded like a fanfold (in zigzag), P 13501 was folded according to the roll principle. Thanks to the different folding systems, the two manuscripts are characterized by different cross sections.[6]

The sealing differs in the number of clay seals and the number of impressions: P 13500 has two clay seals and four impressions, whereas P 13501 has three clay seals and thirteen impressions (Rubensohn 1907, pp. 10–14).

Experiment

The manuscripts were analysed according to the standard BAM protocol, which involves an initial reflectographic screening followed by spectroscopic analysis (Rabin et al. 2012). This protocol has been developed to analyse and compare inks using exclusively non-destructive and non-invasive techniques. These requirements were crucial for the current work because no invasive sampling was permitted. According to the protocol, the preliminary screening to determine the ink typology is conducted with a Dino-Lite USB microscope (model AD413T-12 V) equipped with built-in near infrared (NIR) and ultraviolet (UV) lights at 940 nm and 395 nm respectively, to which we added an external LED white light source. The principle of differentiation between the three main kinds of ink (carbon-based, plant, iron-gall) is based on the comparison of the ink's opacity in visible and NIR light (Mrusek et al. 1995). In contrast to the constant black colour of carbon ink, plant inks become transparent at the red end of the visible light region, ca. 750 nm, while iron-gall inks only start losing opacity at this wavelength, turning totally transparent at much longer wavelengths (ca. > 1400 nm). UV light is used as a tool to identify tannins or to track texts written with inks containing tannins, which quench fluorescence and enhance the contrast between a fluorescing background and the text (Rabin 2015; Colini et al. 2018). This very property of tannins has been extensively used for text recovery in palimpsests (Albrecht 2014). Though leading to reliable identification of pure ink types, the reflectographic screening is not well suited to recognize the mixed ones, since it will only identify the main component. For example, mixed inks containing carbon with added minor amounts of tannins or iron-gall ink have the optical properties of carbon ink and will be identified as such by this method. To unequivocally identify mixed inks using their optical properties, one must conduct proper IR reflectography at wavelengths beyond 1400 nm, where only the carbon component remains visible. In this work, we used an Osiris Apollo infrared camera, sensitive in the 900–1700 nm range, with a 128 × 128 px InGaAs area sensor, 6 element 150 mm f/5-F45 aperture, and equipped with a long wave pass (LWP) filter at 1510 nm.

Spectroscopic identification of the elemental composition of the papyrus and the inks was conducted using X-ray fluorescence spectroscopy. To obtain spatial maps of element distribution, we used an M6 Jetstream (Bruker GmbH) imaging

[6] For this, see Fig, 2, illustrating the different folds of the two documents.

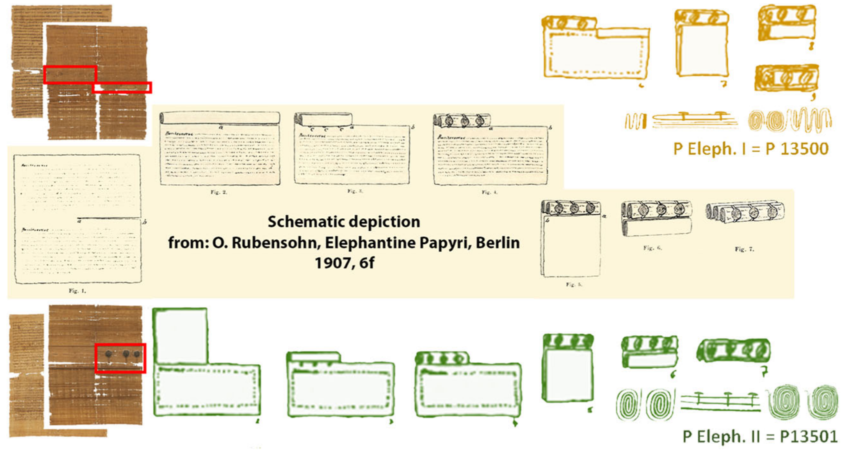


Fig. 2 Illustration of the folding system of P 13500 (top), P 13501 (bottom), and the schematic diagram by O. Rubensohn (middle) (© Staatliche Museen zu Berlin, Ägyptisches Museum und Papyrussammlung; drawings (top and bottom): Myriam Krutzsch)

μ-XRF spectrometer with an adjustable measuring spot ranging from 50 to 650 μm, which is equipped with a low-power Rh X-ray tube, polycapillary X-ray focussing optics, a 50 mm^2 Xflash SDD detector, and two microscopes for positioning. Since scanning is conducted in air atmosphere, only elements heavier than magnesium (Mg) can be securely identified. We conducted a semi-quantitative comparison of the abundance of elements heavier than potassium (K). To get the net peak intensities used for the semi-quantitative analysis, the X-ray emission peaks were fitted using Gaussian deconvolution with the Bruker M6 Jetstream software. All the measurements were performed at 50 kV and 600 μA, with a spot size of 50 μm, an acquisition time ranging from 5 to 10 ms/pixel, and a pixel (step) size of 75 to 150 μm.

Results

Our attention was primarily drawn to the brown colour of the script and the corrosive action of the ink that was used to write the will dated to 284 BCE (P. 13501, Fig. 1b). The ink appears to be cracked and flaking, causing considerable deterioration of the papyrus substrate. As seen in Fig. 1b, there are narrow lacunae coinciding with the lines of text in multiple areas, which is a typical phenomenon associated with corrosion induced by iron-gall inks and by some pigments that contain copper (Banik et al. 1983). Furthermore, the halo around each letter that can be seen in visible light under magnification (Fig. 3C) may also be associated with iron-gall ink corrosion (Reissland 2001).

Figure 3 shows the reflectographic analysis conducted by comparing the micrographs under UV (A), visible NIR (B), and visible (C) illumination. The writing substance appears dark in UV light, and the halos extend further than when registered in VIS. This observation suggests the presence of tannins diffused into the papyrus material (Fig. 3a and c). By contrast, the letters appear to have slimmed down in the NIR micrograph (Fig. 3b): Not only the halos but also part of the brownish ink completely disappears, leaving behind a perfectly legible text in black. This observation suggests the presence of elemental carbon. To prove its presence unequivocally, we used the infrared camera equipped with a long wave pass filter at 1510 nm. Figure 4 shows clearly that the entire textual content of the document remains legible, thereby proving that elemental carbon is one of the ink's constituents.

To address the question of the possible presence of metal components that could be responsible for the corrosion, we used XRF analysis. Correct interpretation of the results was possible only by using imaging XRF, i.e. when spatial maps of the elemental distributions were obtained (Fig. 5). Though both iron and copper produced strong signals, the signal of iron comes from the papyrus rather than from the ink, since the spatial map of iron does not reproduce the text. This displays one of the important characteristics of a papyrus writing surface: its great heterogeneity. Because of the locally iron-rich substrate, we cannot exclude the possibility of small amounts of iron impurities in the ink. Ghigo et al. recently raised the problem of iron identification in the inks of historical papyri (Ghigo et al. 2020). A copper map contrasts with

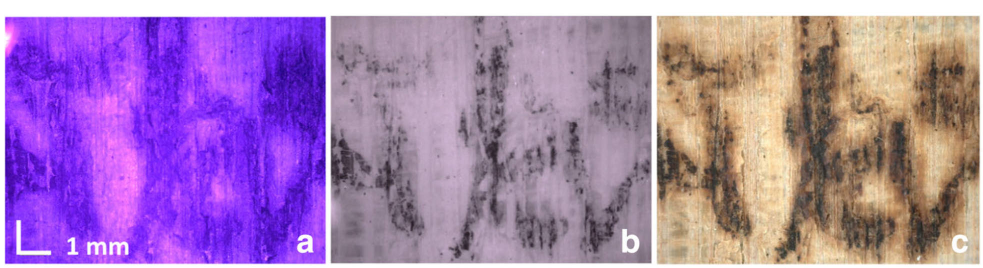


Fig. 3 P 13501 micrographs of the letter κ at 50 times magnification under ultraviolet (**a**), near infrared (**b**), and visible light (**c**)

that of iron, displaying a perfectly legible text, proving that copper is a metallic component of the ink.

To check for the presence of elements other than copper as ink constituents, additional measurements were made on chosen regions of interest. Figure 6 presents the comparison of two regions: inscribed and non-inscribed. The only difference between the stacked spectra shown on the right (Fig. 6b) is the presence of copper in the ink as testified by the peaks at 8.0 and 8.9 KeV, corresponding to the energies of its $K\alpha$ and $K\beta$ lines, respectively. The intensities of the other detected elements (iron, calcium, potassium, and manganese) are not greater in the spectrum corresponding to the inscribed area than in the one of the non-inscribed papyrus, indicating that all the elements are present in the substrate, rather than in the ink. Analogous results were obtained when analysing other areas in both documents, proving that not only the substrate but also the inks share similar features across both papyri. Therefore, inks found on both papyri belong to the same type of mixed inks containing elemental carbon and copper.

Discussion

P 13500, dated to the fourth century BCE, closely followed by P 13501 and the group of Greek texts (Delange et al. 1990), dated to the period from the third to the first century BCE, all containing copper, might indicate the beginning of the transition from carbon to iron-gall inks. We suggest associating this ink with a recipe for sympathetic (invisible) ink reported by Philo of Byzantium. This recipe seems particularly relevant, since it is not only roughly contemporary with our documents but also presents the oldest extant record of the reaction between a substance based on copper and a tannic solution. Even though Philo's ink has been well known to scholars for quite some time, most of the scientists analysing inks became aware of it only after 1983, when Zerdoun first drew their attention to it (Zerdoun Bat-Yehuda 1983, pp. 91–92). The ink produced according to Philo's recipe has not yet been found experimentally. Although the exact date when Philo lived is unknown, specialists think he lived around the end of the third and the beginning of the second century BCE. However, the recipe was transmitted to us only as a part of Byzantine collections of ancient military texts, compiled in the tenth century CE, probably during the reign of Emperor Constantine VII Porphyrogenitus (de Rochas d'Aiglun 1881, pp. 19–21).[7]

The Greek text of the recipe (chapter 77[102]) reads as follows:

Γράφονται δ'αἱ ἐπιστολαὶ εἰς καυσίαν καινὴν <ἢ> εἰς τὸν χρῶτα, κικῖδος θλασθείσης καὶ ὕδατι βραχείσης· ξηρανθέντα δὲ τὰ γράμματα ἄδηλα γίνεται, χαλκοῦ δὲ ἄνθους τριφθέντος ὥσπερ ἐν ὕδατι τὸ μέλαν καὶ ἐν τούτῳ σπόγγου βραχέντος, ὅταν ἀποσπογγισθῇ τούτῳ, φανερὰ γίνεται.

We suggest the following literal translation:

The letters are written on a new kausia,[8] *or on (human) skin, with crushed gallnuts soaked in water; when the characters dry out, they become invisible; when one grinds flower of copper, like black (ink) in water, and moistens a sponge with it, they become visible whenever one wipes them off with it as with a sponge.*

Here, Philo describes how to create a sympathetic ink, made of a solution of gallnuts, that becomes visible only after exposure to "flower of copper". It is the oldest attested recipe for ink using a tannic solution. The juice of gallnut is a very common ingredient for later iron-gall inks, but also for plant inks. It has a very light brown colour and is indeed likely to appear invisible when written on a brownish surface such as a felt hat or skin. The term "flower of copper" ("χαλκοῦ ἄνθος"), the main constituent of the revealing solution, is usually translated as "copper sulphate" in the modern editions of the text (Garlan 1974, 324; de Rochas d'Aiglun 1881). The exact same term (in two separate words) appears in several medical texts in Antiquity, in particular in the Hippocratic Corpus attributed to Hippocrates of Kos (fifth–fourth century BCE).[9] Of more relevance to us are mentions by Dioscorides and Pliny the Elder, both authors from the first century CE, who distinguish "χαλκοῦ ἄνθος" (Dioscorides *De Materia Medica* V 77) or "aeris flos" (Pliny *Naturalis Historia* XXXIV 24.107) from "χαλκανθὲς" (Dioscorides *De Materia Medica* V 98) or "chalcanthum" (Pliny *Naturalis Historia* XXXIV 32.123). The first material is defined as particles flying off melted copper when it is suddenly cooled with water (Dioscorides *De Materia Medica* V 77) or hammered (Pliny Naturalis Historia XXXIV 24.107). It may consist of small particles of metallic copper or of cuprite (copper oxide). The second material is described by Pliny as a blue substance resembling glass, which, when diluted, appears dark and is used to dye leather black (Pliny *Naturalis Historia* XXXIV 32.123). Dioscorides describes it as a solidified liquid (similar to Pliny's description of a material that looks like glass)

[7] The oldest and most complete surviving texts come from BNF MS Grec 2443 (f125v) and from Vat. Gr. 1164 (f164v). Several translations found in the literature, however, are based on BNF MS Grec 2435 (f70v), which is a sixteenth-century Florentine copy of an eleventh-century manuscript. The text of the recipe is remarkably consistent throughout all three manuscripts.

[8] The kausia is a Macedonian flat felt hat.

[9] Flower of copper is mentioned as an ingredient used to treat many ailments, including afflictions of the brain (*De Morbis* II 19, 25), the amygdales (*De Morbis* II 30), the lungs (*De Morbis* II 47, *De Morbis* III 16), and fistulae (*De Fistulis* 4, 5 and 6). It is also mentioned in the context of eyelid surgery (*De Visu* 4 and 6) and for treatments related to menstruation (*De Natura Muliebri* 32) and fertility (*De Morbis Mulierum* III 243).

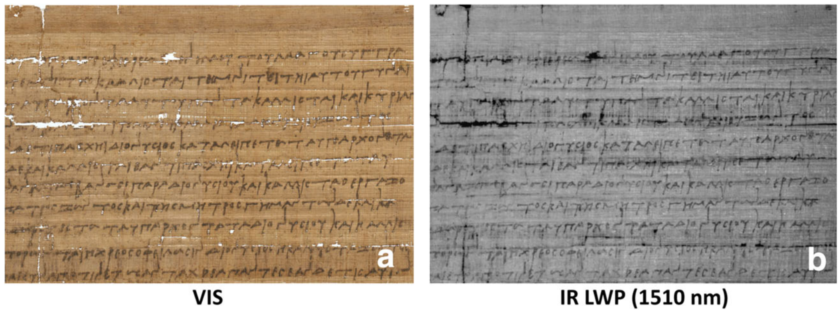


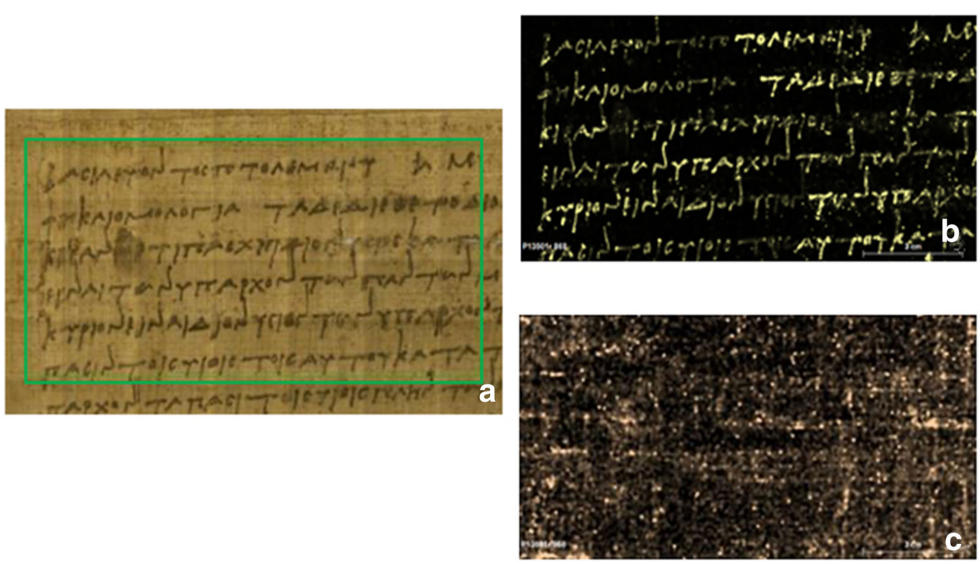
Fig. 4 Portion of P 13501 registered in visible light (**a**) (© Staatliche Museen zu Berlin, Ägyptisches Museum und Papyrussammlung; scan: Berliner Papyrusdatenbank, P 13501 (https://berlpap.smb.museum/03735/)) and infrared region—long wave pass filter at 1510 nm (**b**). The background of Fig. 4b appears black because of the black support used during infrared imaging

existing in three different varieties, before listing its medicinal properties (Dioscorides *De Materia Medica* V 98).

The possible confusion between the two expressions "χαλκοῦ ἄνθος" and "χαλκανθὲς" or "χάλκανθος" was already noted by Zerdoun (Zerdoun Bat-Yehuda 1983, p. 92 note 49), who claims that "χαλκοῦ ἄνθος" in Philo's recipe is correctly translated as "copper sulphate". Philo's flower of copper, reacting with the gallnut solution to reveal the ink, indeed appears more likely to be Pliny's "chalcanthum" than "aeris flos", which would not react with tannins. Nowadays, we know that it is not the copper but iron ions that form black complexes with tannins during the production of iron-gall inks. Although both Pliny, who describes different possible variations of colour with chalcanthum, and Dioscorides, who mentions three different varieties, know of the existence of various kinds of vitriolic substances, they do not seem to understand that they are dealing with different metals. Furthermore, it is likely that even blue vitriol (chalcanthite) collected by the ancients would contain, as an impurity, the iron essential to the reaction. It seems that until a first classification of the different vitriolic substances was made by Muhammad ibn Zakkaríja ar-Rází around 900 CE, the distinction between green vitriol (melanterite) and blue vitriol (chalcanthite) was not clear, possibly hindering the development of iron-gall ink (Karpenko and Norris 2002).

It is tempting to associate the inks from P 13500 and P 13501 with Philo's recipes. Indeed, as stated in the results, the halo observed and the behaviour of the ink under UV light (cf. Fig. 3a) suggest the presence of tannins, present in Philo's recipe in the form of crushed gallnuts dissolved in water, and the presence of copper as a major constituent could fit with the use of "χαλκοῦ ἄνθος" (or possibly more correctly "χάλκανθος"). However, there are several objections to linking the inks analysed in this paper with Philo's. First, Philo mentions only felt or skin as a possible support. This objection can be easily discarded, since this choice of support arises from the military context of Philo's recipe. His aim is to obtain a sympathetic ink to be used with a courier in the event of a besieged city. Writing a message on papyrus or parchment, even with sympathetic ink, could draw the attention of the enemy, while writing on the skin or inside the hat of the envoy would make it undetectable. Second, although the inks

Fig. 5 XRF scan of a portion of P 13501: the green rectangle indicates the scanned area (**a**) (© Staatliche Museen zu Berlin, Ägyptisches Museum und Papyrussammlung, scan: Berliner Papyrusdatenbank, P 13501 (https://berlpap.smb.museum/03735/)) and the corresponding distributions of copper (**b**) and iron (**c**). Scan parameters: measurement performed at 50 kV and 600 µA, acquisition time 5 ms/pixel, pixel size 100 µm



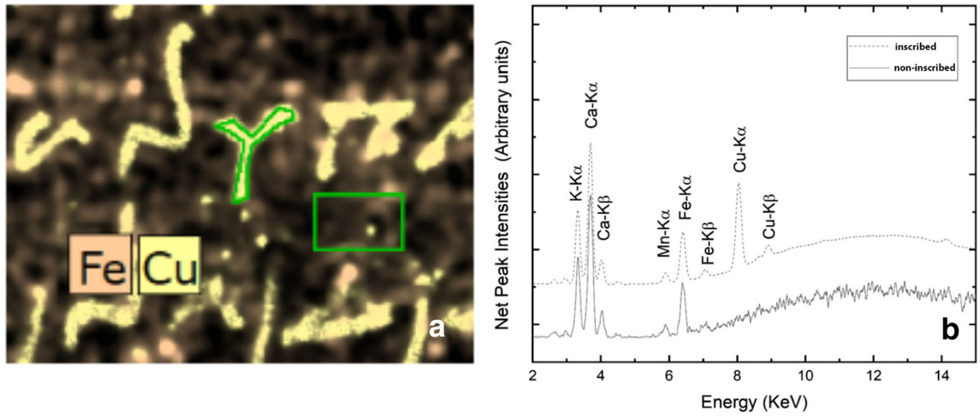


Fig. 6 XRF map of a detail of P 13501 showing contrast in Fe (in orange) and Cu (in yellow) and regions of interest: letter ϒ (green contour, top) and papyrus support (green square, bottom) (**a**). XRF spectra corresponding to chosen regions of interest: upper spectrum, inscribed; lower spectrum, non-inscribed (**b**). Scan parameters: measurement performed at 50 kV and 600 μA, acquisition time 5 ms/pixel, pixel size 100 μm

on papyri P 13500 and P 13501 do not appear plain black as a carbon ink does, they do contain carbon, as clearly demonstrated by the infrared images. Again, in the case of Philo's recipe, the aim of having an invisible ink would militate against using carbon together with the gallnut solution. Likewise, in the revealing stage, if flower of copper is enough to reveal the text, carbon is not needed. In the case of P 13500 and P 13501, it could have been used to make the text darker and more visible. The association of "χάλκανθος" is also not unlikely, since it is reported in the later recipe by Dioscorides (Dioscorides *De Materia Medica* V 162). Finally, although the halo and UV images suggest the presence of tannins, further analysis is needed to unequivocally prove it. For this purpose, it seems promising to apply Atmospheric Solids Analysis Probe (ASAP®) mass spectrometry, as suggested by Ghigo and co-authors (Ghigo et al. 2020).

Published data, together with the present examples P 13500 and P 13501, connect inks containing copper with the Hellenistic period. Moreover, since most of the evidence so far comes from Greek texts, we might even tentatively suggest that such an ink is a Greek invention. We should not forget, however, that the particular climate of Egypt and the Judean Desert contributed greatly to the preservation of papyrus rolls, and we cannot determine whether Egypt was indeed the birthplace of such inks or if we simply lack evidence from other regions. Until further evidence surfaces, we cannot determine whether the Greeks already knew of such an ink and brought it with them to Egypt during Alexander's conquests.

We can suggest two hypotheses why ancient producers of ink deemed it necessary to add chalcanthum to their ink. The first one is that it was used to stretch the ink, allowing the ink maker to use less soot. Soot might seem like a product that is easy to get. However, soot of good quality was apparently not so common. Among other sources for soot, Pliny mentions atramentum indicum (Pliny *Naturalis Historia* 35, 25), which had to be imported from far away and was certainly expensive, while the best varieties of chalcanthum were readily available in Hispania (Spain) and Cyprus (Pliny *Naturalis Historia* 34, 32). It is possible that the large Diadochi kingdoms resulting from Alexander's conquests needed much ink, be it only for their administration, which could explain why we observe the first occurrences of copper presence in inks from Hellenistic times. The second hypothesis is the need to make inks more durable. Several Latin authors mention the common use of sponges to erase ink. According to Suetonius, ink could even be erased with the tongue, which seems to have been a form of punishment (Suetonius, Caligula 20). Indeed, unlike pure carbon inks, which stay on the surface of the writing support, tannins and metallic ions penetrate the substrate, making inks containing metals harder to erase.

Conclusions

The corrosive brown inks of both studied documents, P 13500 and P 13501, contain copper. Using 2D scanning micro-XRF in combination with infrared reflectography, we identified elemental carbon and copper as components and therefore attributed this ink to the mixed type. In addition, the micrographs recorded under UV light suggest the presence of tannins. These observations make P 13500 the oldest known document written with an ink containing a metallic compound. Combining extant records and analysis of archaeological artefacts, we tentatively suggest that ink containing metal appears in Hellenistic times. We suggest that until the recipe for iron-gall inks was fully established and the difference between the various types of vitriol was understood, the substance called chalcanthum was added to tannins instead of iron sulphate. Although the discovery of such ink marks another milestone in our knowledge of the history of writing materials, it also exemplifies the need to collect more evidence. Without a doubt, a more accurate and comprehensive analytical approach would be desirable. However, given the nature of the objects analysed, destructive analysis is not an option. Nevertheless, we hope that micro-sampling for ASAP-MS analysis will be allowed in the future, in order to investigate organic ink components.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s12520-021-01320-5 .

Acknowledgements We gratefully thank Ivan Shevchuk, who assisted us while performing the IR imaging, for all his help in this project.

Availability of data and material All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information file. Additional data related to this paper may be requested from the authors.

Code availability Not applicable.

Authors' contributions G.N. performed the reflectography and XRF investigation of the two papyri under the supervision of IR and wrote the "Provenance of the documents", "Materials and methods", and "Results" parts, as well as the introduction and conclusion together with O.B. and I.R.

O.B. wrote the "Discussion" part, as well as the introduction and conclusion together with G.N. and I.R.

M.G. provided the historical background of the papyri and checked the validity of the historical conclusions and comments in the Greek texts.

M.K. wrote the "Detailed description of the documents" part.

I.R. supervised the whole work and structured the article.

Funding Open Access funding enabled and organized by Projekt DEAL. This research was partly funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) and within the scope of the Centre for the Study of Manuscript Cultures (CSMC) at the Universität Hamburg.

Declarations

Conflict of interest The authors declare no competing interests.

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