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Analyzing the Organic and Mineral Composition of Inkwell Residues as Preparation for Characterizing the Ink of the Dead Sea Scrolls

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This paper focuses on the study of the contents of inkwells dating to the Early Roman period, using an array of analytical techniques: portable X-ray fluorescence spectrometer (pXRF), Raman spectroscopy, powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS). Our goal was to shed light on the chemical composition of the inks used for writing in the late Second Temple period in Israel, particularly those which may have been similar to that used in the Dead Sea Scrolls (DSS). An understanding of the ancient ink's chemistry has important implications for conservation and preservation purposes, and may reveal important information about ancient scribal practices and writing schools. Although most of the analyzed inkwells revealed no ink residues, molecular traces of bone-derived carbon were detected in one sample, plausibly originating from bone black pigment used in ancient ink. Organic residues from three other inkwells may be the remains of ink binders.

Keywords: Early Roman period, inkwells, Dead Sea Scrolls, Carbon ink, Ink binders

Introduction

Ancient artifacts bearing writing carry special significance in archaeological research, as they often reveal a unique, first-hand account of the deeds and beliefs of past societies and individuals. Beyond the content of the written word, valuable information may be gleaned from the materials used in the writing process, among them the ink. The identification of the ink ingredients and recipes may aid in preserving ancient ink-written texts, as well as the medium to which they were applied. Such information may further prove significant for the

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understanding of scribal practices in antiquity and aid scientists in classifying ancient texts according to specific scribes and writing traditions, also potentially providing additional chronological and geographical information regarding the artifacts uncovered.

The manufacture of ink for writing is known from ancient Egypt (Christiansen et al. 2017) and China (Winter 1989), both traditions dating back to as early as the late fourth millennium BCE. Already at that time, the two most popular colors were black and red; the bulk of the writing was done in black inks, with red usually used for highlights and comments (Christiansen et al. 2017:208–219; 2020:27825–27835). Black and red inks remained one of the principal means of writing well into the Hellenistic and Roman periods, when the use of red ink for highlighting was especially common in regions such as Egypt (Eckardt 2017:57–67).

Generally, ink consists of two main components: pigment and binder. Ancient pigments consisted of mostly inorganic material, such as soot, charcoal or metal (primarily iron), with black pigment comprising carbon-based constituents, while the binder is made of organic materials that act as a glue (Christiansen 2017:167–195). The earliest written description of ink composition is found in Vitruvius (*De architectura* 7:10), where black pigment is described as originating from soot that was collected from vaulted furnaces. This description was later echoed in other sources, including Dioscorides (*De materia medica* 5:162) and Pliny the Elder (*Naturalis historia* 36:41). The binding was described in these sources as organic material (Pliny, *Naturalis historia* 36:41) such as gum Arabic, a sticky exudate from the stem and branches of Acacia trees under stressed conditions (Musa, Ahmed and Musa 2017:1–18), as well as egg whites, oil, bee honey and animal-produced glue (Murphy et al. 2010:77–98; Christiansen 2017:167–195). Ink made from soot and gum Arabic was produced by mixing the two ingredients (Vitruvius, *De architectura* 7:10), grinding the mixture and molding it into dry 'cakes' that the scribe could dissolve with water once needed to be used (Forbes 1993:236–239). Analyses of residue in inkwells from the Early Roman period in Italy demonstrated that it contained soot as the pigment and gum Arabic as the binder, corroborating accounts in the ancient sources (Rice 1987; Sibilia et al. 2021:7231).

Some evidence of metals used as ink components in carbon-based inks, referred to as "mixed inks," was preserved from the time of Ancient Egypt (Christiansen 2017:167–195). Iron gall ink, in which the pigment is iron-based, was introduced during the fourth or fifth century CE and became the dominant ink by the Middle Ages (Christiansen 2017:167–195).

This study was undertaken to help identify the composition of the ink used in the Dead Sea Scrolls, both the pigments and binders. The use of analytical, non-destructive techniques has been a priority in this field, given the immense importance of the scrolls to scholarship and world heritage. Our approach in this study was to analyze inkwells found in archaeological excavations in the Judean Desert, the region where the scrolls were found and may have been written, as a surrogate to direct analysis of scroll samples.

The Ink of the Dead Sea Scrolls

A thorough analysis of ink recipes and the origin of the ink components in the the Dead Sea Scrolls (hereafter, DSS) has yet to be achieved. First discovered some 75 years ago in the Judean Desert, this large group of documents was written on parchment and papyrus, preserved due to the arid desert climate. The scrolls originated from numerous sites in the Judean Desert, and their production spans a long period of time, from the late Iron Age to the time of the Crusaders; however, the largest and most expansive group of texts originated from 11 caves surrounding the site of Qumran, mostly dating between the second century BCE and the first century CE. These texts include the earliest known copies of the books of the Hebrew Bible, as well as parabiblical literature, poetical and liturgical compositions and sectarian works of the Yaḥad group and related communities. The scrolls significantly enriched our understanding of the cultural and religious background of rabbinic Judaism and early Christianity (Lim and Collins 2010:2–18).

Most of the scrolls, whether of parchment or papyrus, were written with black ink. Examination of several scroll samples from the Qumran caves found that the black ink was based on charcoal or soot (Nir-El and Broshi 1996a:157–167), whereas cinnabar (HgS) was identified in the red ink (Nir-El and Broshi 1996b:97–102). The use of gum Arabic as binder was recently demonstrated in a preliminary study of the ink composition of one fragment from Qumran Cave 11 (Zilberstein et al. 2021:249). Although black ink of the Hellenistic and Roman periods is known to have mostly incorporated soot as the ink's pigment and gum Arabic as binder (Christiansen 2017:167–195; Eckardt 2017:57–67; Sibilia et al. 2021:7231), the exact ink recipes and the origin of the ink components in the DSS remained unclear. This information has much potential for unraveling further insights regarding the production context of the scrolls. Furthermore, identifying the different components, and fine-tuned examination of the interaction of the ink with the parchment or papyrus, will contribute to our ability to preserve them for the benefit of future generations.

The Roman-Period Inkwells

These inkwells are made of ceramic, metal, stone or glass, occurring in a wide variety of shapes (Eckardt 2017:57–67). Prestige inkwells were made of metals, such as silver, while those of cheaper manufacture were made from copper-alloy and clay (Eckardt 2017:57–67). Most inkwells found in excavations in Israel are ceramic and similar in form, comprising a wheel-thrown clay cylinder, slightly curving out at the top and bottom, sometimes with a circular handle attached near the top. In most inkwells, there is a slight ridge at the top perimeter, which inverts close to the hole in the center, probably to allow the scribe to wipe off excess ink (Fig. 1). Inkwells of this type, made of clay or metal, are known throughout the Roman world (Eckardt 2017:57–67), with bronze parallels found at Pompeii (Sibilia et al. 2021:7231).

A relatively small number of Early Roman-period inkwells was uncovered in Israel, and several others were retrieved from the antiquities market. In this study, 18 inkwells from

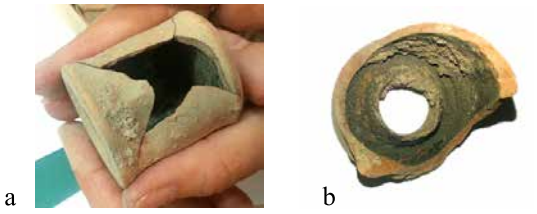


Fig. 1. Restored inkwell No. 5 (a) and its upper interior part (b), from which a sample was obtained.

excavated contexts within Judea were analyzed (Table 1): 3 from Qumran (Nos. 2–4); 1 from ‘En Feshkha (No. 1), on the northern shore of the Dead Sea; 10 from the Old City of Jerusalem (Nos. 5–15 and 18); and 2 from Herodium (Nos. 16, 17). Two of the inkwells were unique in form and material: one made of limestone, from Jerusalem (No. 10), an the other, of wood, was recovered from Qumran (No. 4).

As ceramic inkwells may absorb a considerable amount of ink (Eckardt 2017:57–67), we set out to analyze the residue absorbed in the clay to characterize its chemical composition. The working assumption was that the ink generally used in Early Roman Judea would resemble in its composition the ink used to write the DSS. We focused on non-destructive and minimally destructive methods for an initial characterization, the insights from which could be implemented in directly analyzing the ink of the scrolls.

Methods

Macroscopic identification of residual ink in ceramic inkwells is unlikely in most cases, as they are often washed during excavations, a treatment likely to destroy any surviving traces of ink. It is possible that some chemical components of the ink were absorbed within the pottery due to its porous structure and hence, it was decided to carry out a series of chemical analyses of residue scraped from the interior and exterior surfaces of the inkwells, as well as from the handle in cases where it existed.[2] This approach would allow us to separate between the components that made up the ink from those that comprised the inkwell; however, this separation was not altogether clear. The identification of the ink components was undertaken using a number of non-destructive methods, Raman spectroscopy and X-ray fluorescence spectrometry (pXRF)—employing a portable device and scanning electron microscopy with energy dispersive X-Ray spectroscopy (SEM-EDS). Powder X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) are minimally destructive techniques

[2] As several different types of analyses were conducted, the limited amount of material scraped did not always suffice for providing definitive results from all techniques.

Table 1. List of the Sampled Inkwells and Summary of Results of the Various Analyses

No.	IAA No.	Provenance	Material	Portable XRF (pXRF) (descriptions refer to sampling prior to scraping)	Raman	Powder XRD	FTIR	SEM-EDS
1	451648	'En Feshkha (6229/0)	Pottery	Nearly identical elemental composition in different parts of the vessel	The same chemical composition for measurements taken inside the inkwell, before and after scraping: amorphous carbon, dolomite, calcite and aragonite	Quartz, calcite, dolomite, aragonite, halite and traces of albite	Sample 1: quartz, calcite and clay; Sample 2: quartz, calcite and clay	Samples demonstrate a nearly identical elemental composition and concentration
2	463335 (Q473)	Qumran (3412/0)	Pottery	A sample from the handle had a different elemental composition than the rest of the vessel; it may indicate a use of different clays	The same chemical composition of samples from the interior and exterior: amorphous carbon, gypsum, calcite and possibly aragonite	Interior: gypsum, calcite, quartz microcline	Exterior: clay and calcite; interior: gypsum, calcite, fired clay	Interior with higher amounts of calcite and sulphur than the exterior
3	622933 (Q581)	Qumran (3412/0)	Pottery	A small amount of sulphur (S) in a sample from the top part	Not enough material for analysis	Not enough material for analysis	Not enough material for analysis	Not enough material for analysis
4	844956	Qumran (52-42)	Wood	Nearly identical elemental composition in different parts of the vessel	Not enough material for analysis	Not enough material for analysis	Not enough material for analysis	Not enough material for analysis
5	L116-2232	Jerusalem, the Palatial Mansion	Pottery	A somewhat elevated amount of silicon (Si) in a sample from the exterior; no apparent difference between the black and shiny surface and the other samples	Amorphous carbon (Maor 2020)	Calcite, quartz, diopside(?) and hydroxyapatite (Maor 2020)	calcite, bone black and organics (Maor 2020)	
6	401354	Jerusalem, City of David (A7634)	Pottery		The same chemical composition of a sample from the interior of the vessel and from loose soil found with it: mostly fluorescents, with a small amount of amorphous carbon	Not enough material for analysis	Not enough material for analysis	Not enough material for analysis

Table 1. (cont.)

No.	IAA No.	Provenance	Material	Portable XRF (pXRF) (descriptions refer to sampling prior to scraping)	Raman	Powder XRD	FTIR	SEM-EDS
7	1982-324	Jerusalem, Jewish Quarter (2921/196)	Pottery	Nearly identical elemental composition in different parts of the vessel	An abundant presence of fluorescents could have masked to the identification of some of the minerals, although the presence of a small amount of amorphous carbon was detected	Calcite, quartz and microcline	Not enough material for analysis	Not enough material for analysis
8	1992-1521	Jerusalem, Jewish Quarter (2921/196)	Pottery	A somewhat elevated amount of sulphur in a sample from a black-colored part of the vessel	A sample from a black-colored part of the exterior: amorphous carbon, sulphate minerals and magnetite; a sample from the exterior: magnetite, a small amount of amorphous carbon and sulphate minerals; a sample from the interior: gypsum, calcite, a small amount of amorphous carbon and hematite	Exterior 1: quartz and calcite; exterior 2: microcline, clinopyroxene, quartz, calcite and gypsum; interior: gypsum, calcite, quartz and clinopyroxene	Exterior: calcite, quartz, dolomite, clay (fired to 500–700oC); interior: gypsum, calcite, quartz/ clay and a small amount of organics	Interior with a higher amount of sulphur than exterior
9	2012-105	Jerusalem, Jewish Quarter, Israeli Tower and Hellenistic Tower (2921/190)	Pottery	Nearly identical elemental composition in different parts of the vessel	The same chemical composition for samples from the interior and exterior: mostly fluorescents, with a small amount of amorphous carbon and calcite	Exterior: calcite, quartz and dolomite; interior: calcite, quartz, dolomite, microcline and albite	Exterior: calcite, quartz and clay; interior: calcite, quartz and clay	Calcium levels higher in exterior sample
10	2012-1411	Jerusalem, City of David (2922/0)	Limestone	A somewhat elevated amount of sulphur in a sample from a black-colored part of the vessel	Interior: calcite and some amorphous carbon	Interior: calcite and quartz	Not enough material for analysis	Not enough material for analysis

Table 1. (cont.)

No.	IAA No.	Provenance	Material	Portable XRF (pXRF) (descriptions refer to sampling prior to scraping)	Raman	Powder XRD	FTIR	SEM-EDS
11	1982-1784	Jerusalem, Jewish Quarter (2921/196)	Pottery	Nearly identical elemental composition in different parts of the vessel	Exterior: mostly fluorescents, with a small amount of amorphous carbon, calcite and gypsum; interior: as for the exterior sample, but also containing magnetite	Not enough material for analysis	Not enough material for analysis	Not enough material for analysis
12	1982-312	Jerusalem, Jewish Quarter (2921/196)	Pottery	A somewhat elevated amount of sulphur in one of the samples	Mostly fluorescents, with a small amount of amorphous carbon	Not enough material for analysis	Not enough material for analysis	Not enough material for analysis
13	1982-1811	Jerusalem, Jewish Quarter (2921/196)	Limestone	Aluminium (Al) was detected in a sample from the bottom of the vessel	Fluorescents with calcite and a small amount of amorphous carbon	Calcite, quartz and dolomite	Not enough material for analysis	Not enough material for analysis
14	I-2179	Jerusalem, 'Ofel (9721/0)	Pottery	Nearly identical elemental composition in different parts of the vessel, besides a somewhat elevated amount of phosphorus (P)	Amorphous carbon and some calcite	Calcite, quartz, dolomite, albite and microcline	Calcite, clay minerals	Not enough material for analysis
15	1690 7	Jerusalem, Jewish Quarter (2921/196)	Pottery	A somewhat elevated amount of phosphorus (P) in a sample from a black-colored part of the vessel	Exterior: mostly fluorescents, with a small amount of amorphous carbon; interior top: fluorescents with mostly amorphous carbon	Interior at top: calcite, quartz, cristobalite; the possible presence of the mineral potassium tin phosphate was detected from the small amount of sampled material	Exterior: calcite, quartz, fired clay and small amounts of organics; interior at top: calcite, fired clay, apatite or another phosphate material and high amounts of organics	In both, few areas in what looks like a black organic area that was 100% carbon. Interior at top: higher levels of calcium than in exterior sample; exterior: a slightly higher amount of phosphorus than in interior sample

Table 1. (cont.)

No.	IAA No.	Provenance	Material	Portable XRF (pXRF) (descriptions refer to sampling prior to scraping)	Raman	Powder XRD	FTIR	SEM-EDS
16	HR L3505	Herodium	Pottery	Calcite detected in higher amount in a sample from the top of the vessel and from black residue over its surface	Black residue: amorphous carbon, calcite and quartz	Black residue: calcite and quartz	Black residue: calcite, quartz, clay (fired over 700°C), nitrates and organics	Calcium and oxygen
17	HR N.2332	Herodium	Pottery	Nearly identical elemental composition in different parts of the vessel	Sample from bottom of vessel: amorphous carbon and calcite	Not enough material for analysis	Not enough material for analysis	Not enough material for analysis
18	RA 6827	Jerusalem, Robinson's Arch	Pottery	Higher amount of calcite in a part of the vessel bearing brownish black residue	Black residue: amorphous carbon, calcite and traces of unidentified organic material	Not enough material for analysis	Black residue: calcite, quartz, clay (fired over 500°C) and minute traces of organics; inkwell: calcite, quartz and clay (fired over 500°C)	Samples with high amounts of calcite and Silica

used to gain additional information in preliminary analysis of the inkwells, although they will not be used in further research with the DSS themselves. Raman, FTIR and XRD provide data on the molecular level of the composition of minerals and organic matter in the samples, while pXRF and SEM-EDS are used to reveal the various elements which make up the molecules—all techniques offering measurements of the relative amounts of the minerals and their components. SEM was used to obtain high magnification images of the analyzed material.

Eighteen inkwells were sampled. Analysis by pXRF was carried out prior to scraping the ceramic inkwells (e.g., Figs. 1, 3), and powder was then scraped from the parts of each inkwell from where the pXRF readings were obtained, except for the intact inkwells in which case the interior could not be measured. The likelihood of detecting the presence of ink in the limestone and wooden inkwells was expected to be lower than with the clay inkwells, due to the low absorbance properties of these materials. Additionally, analysis was conducted on three of the inkwells that had visible traces of black material covering their interior and suspected to be ink (Nos. 5, 16, 18), and another inkwell that exhibited black and shiny surfaces (No. 15). The analyses were carried out at the IAA Analytical Laboratory, unless specified otherwise. As the preparation of the samples varies from one analysis to the other, detailed descriptions of the preparation procedures are provided below.

X-Ray Fluorescence (pXRF).— This analysis was carried out on all samples. The inkwell was placed on the instrument and measurements were carried out using a handheld Bruker 5i Tracer energy dispersive XRF spectrometer with internal elemental calibration (see Rowe, Hughes and Robinson 2012:122–131). The instrument is equipped with a Rh-anode, miniaturized X-ray tube operating at a maximum voltage of 50 kV and a Peltier-cooled high-resolution silicon drift detector. The diameter of the X-ray spot on the sample was 7–8 mm, and accurate positioning was achieved by means of an integrated camera. The measurements were obtained by a 75-second spot analysis.

Raman Spectroscopy.— The inkwell powder was placed on a microscope glass slide, and 10 dark and bright areas in each of the samples (e.g., Fig. 7) were photographed and measured. The measurements were made on a Horiba Jobin Yvon (LabRAM HR Evolution®) micro-Raman device using two lasers, an infrared laser (785 nm) and a red laser (633 nm). The sampled areas were examined at ×10, ×50 and ×100 magnifications, using a 600 g/mm grid. The measurements were taken in the Space Spectroscopic Laboratory in the Chemical Research Infrastructure Unit, Weizmann Institute of Science, Rehovot.

X-Ray Diffraction (XRD).— The powder was placed on a dedicated surface and measured on a Bruker AXS D8 Advance device. The measurement was performed with a goniometer radius of 217.5 mm, secondary Graphite monochromator, 2-degree Sollers slits and 0.2 mm receiving slit. XRD patterns within the range 2θ=5–55 degrees were recorded at room temperature, using CuKα radiation (λ=1.5418 Å), with the following measurement

conditions: tube voltage of 40 kV, tube current of 40 mA, step-scan mode with a step size of 2θ=0.02 degrees and counting time of 1 second/step. The phase detection and semiconductor analysis were done in EVA (Bruker ASX) software, and a PDF 4+ database was used. The analysis was performed at the Nanotechnology Center at The Hebrew University, Jerusalem.

Fourier Transform Infrared Spectroscopy (FTIR).— One gram of each sample of the inkwell powder was homogenized by crushing with an agate mortar and pestle. After crushing, approximately 0.2 mg of each sample was mixed with potassium bromide salt (FTIR-grade KBr)—a material which does not respond to the infrared rays, the mixture was then pressed into a dedicated die to create a homogeneous slide and measured. Samples were pressed into a 13 mm pellet using a manual hydraulic press at 7 tons (Specac). Infrared spectra were collected at 32 scans per measurement with a 4 cm^{-1} resolution.

Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy (SEM-EDS).— The sample powder was placed on a carbon tape sited on a stub and sprayed with compressed air to prevent the sample from being detached into the device. The stub was placed on a dedicated surface inserted into the vacuum chamber. Different areas of the sample were photographed, and the chemical elements were mapped by means of the EDS function in a 15KV accelerating voltage. The measurements were carried out with a Thermo Scientific TM Phenom XL instrument.

Results

A previous preliminary analysis of one of the inkwells (Table 1: No. 5) with visible remains of suspected ink indicated the presence of a carbon-based pigment produced from bones—bone black, based on the identification of both hydroxyapatite and calcite in the sample by FTIR and XRD analyses (Figs. 1, 2; Maor 2019).[3] Bone black was a high-quality pigment produced by the pyrolysis of bone, forming a coke from the mixture of collagen and hydroxyapatite (Winter 1983:49–66; see also Daveri Malagodi and Vagnini 2018). This study aimed to investigate whether such ink-derived material was commonly present in inkwells from the period under consideration.

Measurements taken by pXRF from the interior and exterior surfaces of the inkwells (Fig. 3) found no significant differences in elemental composition, as shown for example for No. 7 (Fig. 4). Hence, the possibility that heavy elements originating from the inorganic materials in the ink were absorbed within the vessel interior was not confirmed, as such absorption would have resulted in a noticeable difference between the vessels' interior and exterior. Additionally, no significant differences in elemental composition were identified

[3] Maor (2019) conducted the Raman spectroscopy, powder XRD and FTIR analyses, while the pXRF and SEM-EDS analyses of this item were carried out in the present study.

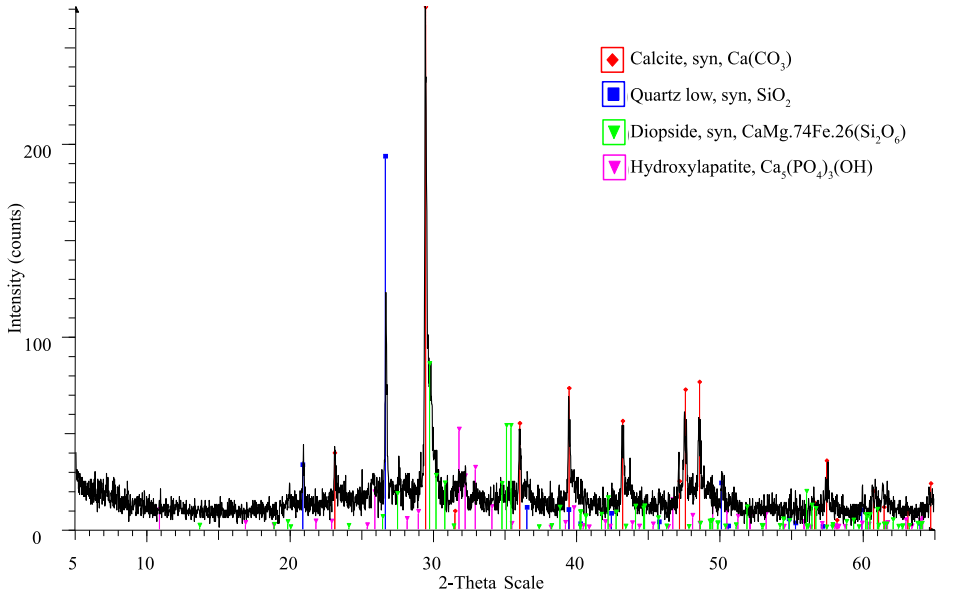


Fig. 2. XRD reading of inkwell No. 5, showing its elemental composition and concertation measurements (from Maor 2020).

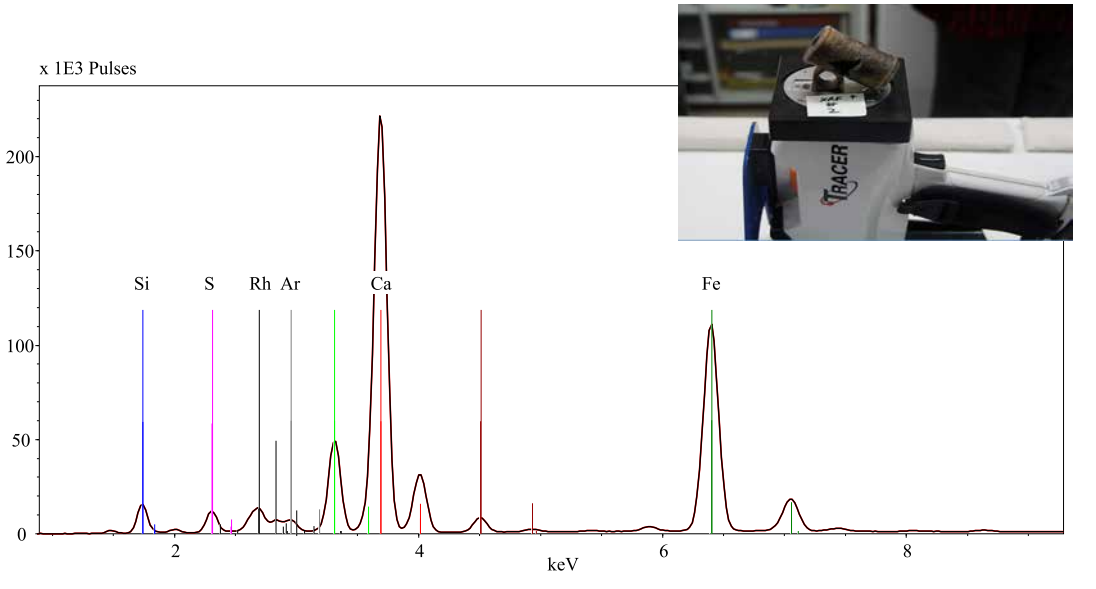


Fig. 3. Inkwell No. 2, mounted on the pXRF instrument (inset) and its XRF spectrum and measurements.

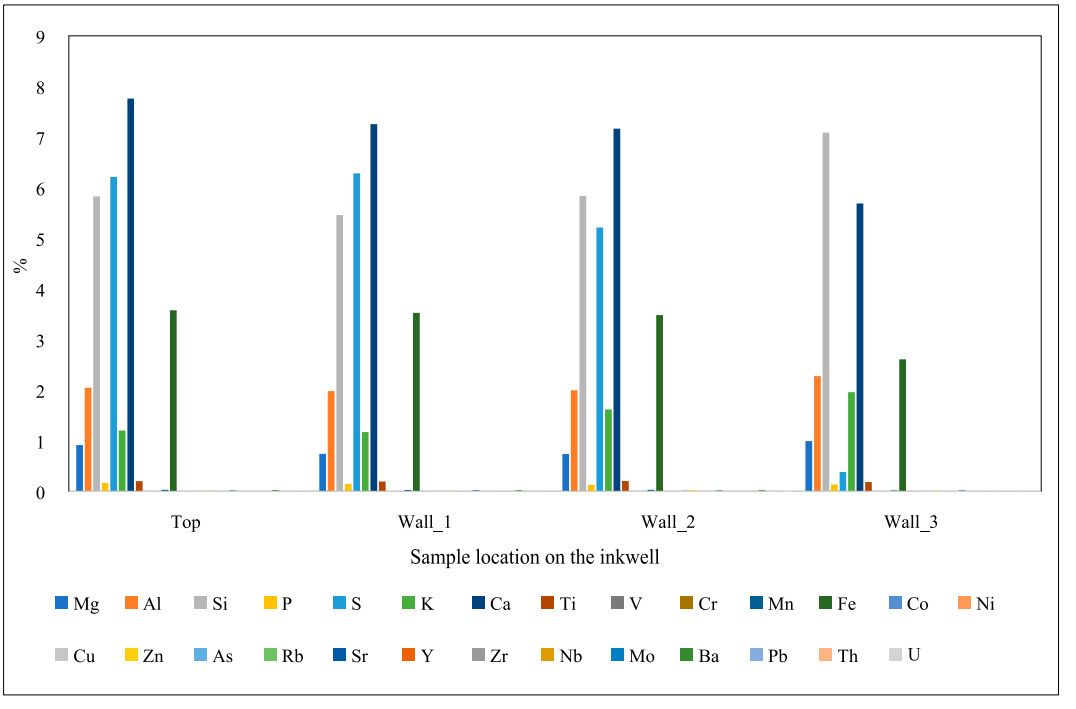


Fig. 4. Summary graph of the pXRF-measured elemental concentrations in all samples taken from inkwell No. 7.

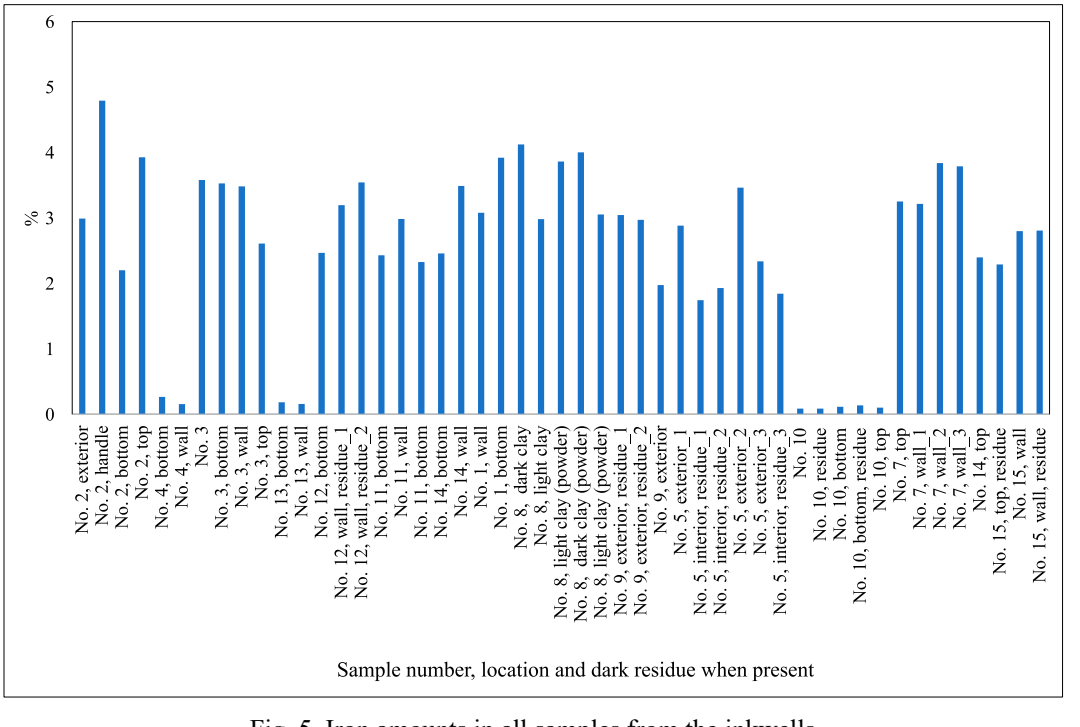


Fig. 5. Iron amounts in all samples from the inkwells.

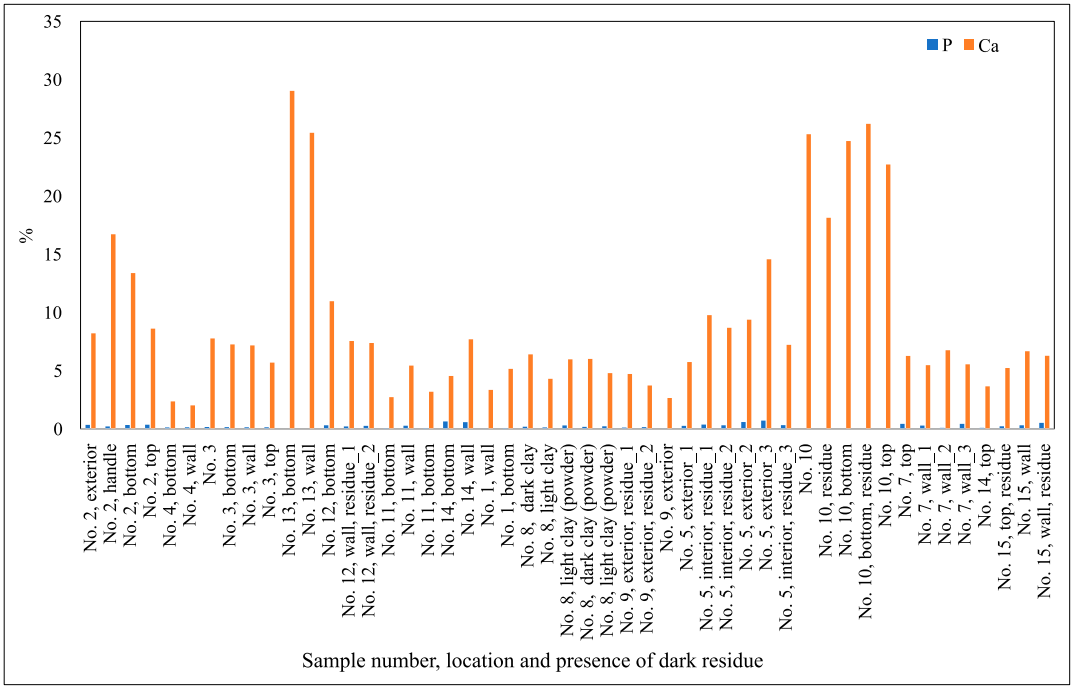


Fig. 6. The amounts of phosphate (P) and calcium (Ca) in all samples from the inkwells.

among the inkwells for most of the elements, as shown for the iron content (Fig. 5); while some of the iron readings were rather low (<1%), they represent variability among different readings of the same inkwell rather than among different inkwells. Nevertheless, in addition to inkwell No. 5, in two of the inkwells, Nos. 14 and 15, the analysis detected relatively high amounts of phosphorus (P; Fig. 6), possibly due to hydroxyapatite, whose chemical formula is $Ca_5(PO_4)_3(OH)$, or other while another phosphate minerals. Calcite ($CaCO_3$) was also common but showed less variation among the inkwells. It is noteworthy, however, that the calcite in this case could have originated either from ink or from the inkwell.

Raman spectroscopy revealed the presence of amorphous carbon (i.e., a non-crystalline structure) in all the inkwells, except for Nos. 3 and 4, where not enough scrapped material was available for this analysis. Amorphous carbon makes up the molecular structure of both soot and charcoal, the main ingredients from which pigment in Early Roman-period ink was made. This component was found in relatively high amounts in two of the inkwells (Nos. 14 and 15). The typical peak indicating the presence of amorphous carbon is found around 1390 cm^{-1} in the Raman spectra, the D peak characteristic of coal disarray (e.g., No. 14; Fig. 7; see also Fig. 8). Another peak, around 1590 cm^{-1}, called the G peak, is typical of the molecular structure of graphite (Fig. 7). An inkwell from the excavations at Robinson's Arch (No. 18), with traces of black material on the interior and exterior, revealed the presence of amorphous carbon in a sample from the black residue, as well as high amounts of calcite.

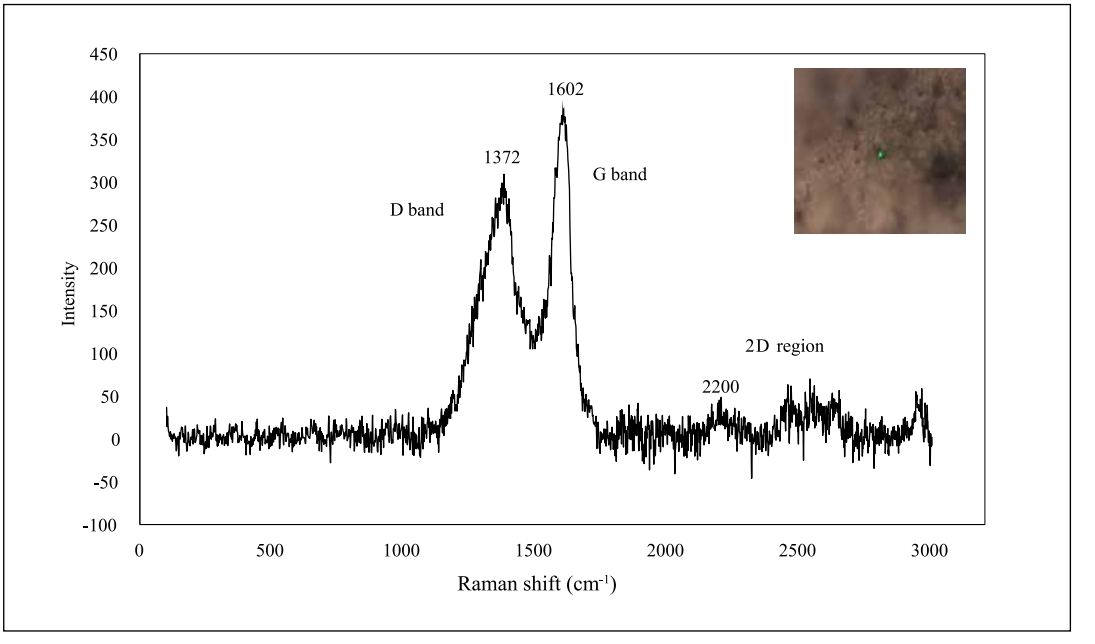


Fig. 7. Raman spectrum of a sample from the interior of inkwell No. 14, indicating the presence of amorphous carbon based on observed measurement peaks, and an image of the area sampled with the laser spot (inset).

Raman spectroscopy identified calcite minerals in 11 of the inkwells (e.g., No. 16; Fig. 8), with its characteristic peaks at 1085 cm^{-1}, corresponding to the v1 symmetric stretching mode of the carbonate ion; a v4, in-plane bending mode of the carbonate found at 712 cm^{-1}; and additional peaks at 280 and 153 cm^{-1}, which correspond to the translational and rotational lattice modes. Calcite was more dominant than carbon in all samples. The presence of organic compounds can be detected by peaks at 2200 cm^{-1}, attributed to C=C and C=N vibrations (see Fig. 7). Peaks attributed to organic compounds were also detected between 600 and 1300 cm^{-1}, the C-C aliphatic vibration, while a well-defined peak around 1110 cm^{-1} can be attributed to aromatic C-S vibrations (No. 18; Fig. 9).

The minerals and carbon concentrations examined in different parts of the inkwells were mostly similar (see Table 1). Item No. 15 was an exception in that a sample from the exterior top of the vessel had a low amount of amorphous carbon, while the interior sample had a high amount of this component, possibly indicating the presence of ink (see also FTIR analysis of this item below). In item No. 8, a high amount of sulfur was detected, with

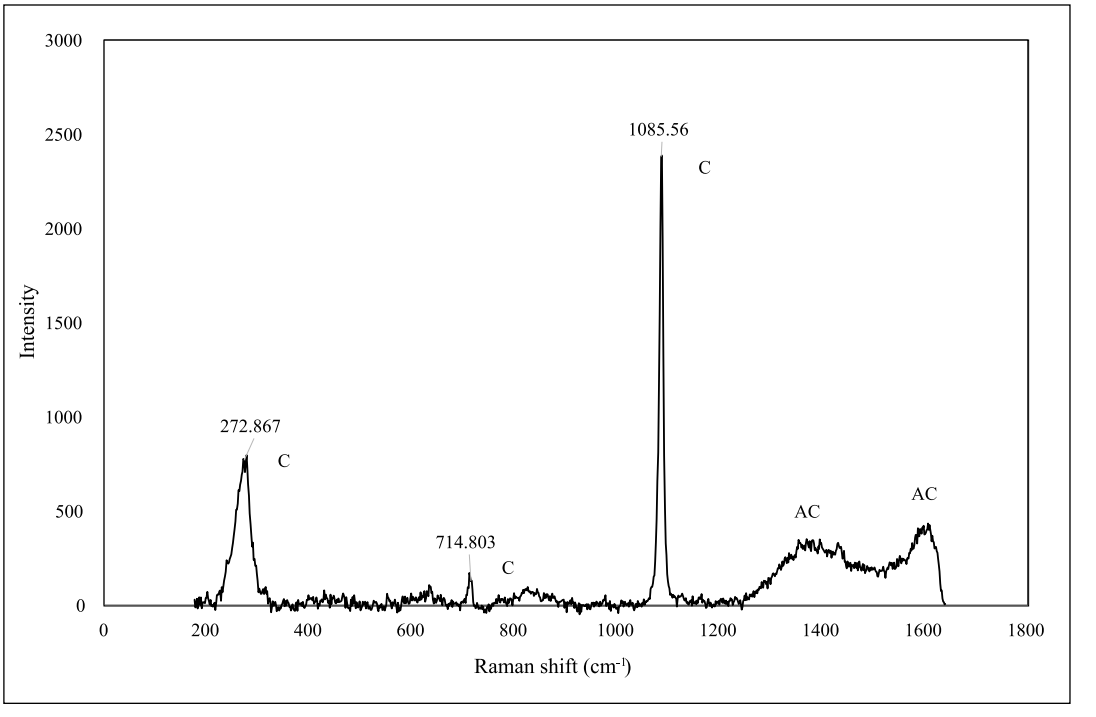


Fig. 8. Raman spectrum of black residue adhering to inkwell No. 16, indicating the presence of calcite and organic compounds based on observed measurement peaks.
Legend: C = calcite; AC = amorphous carbon.

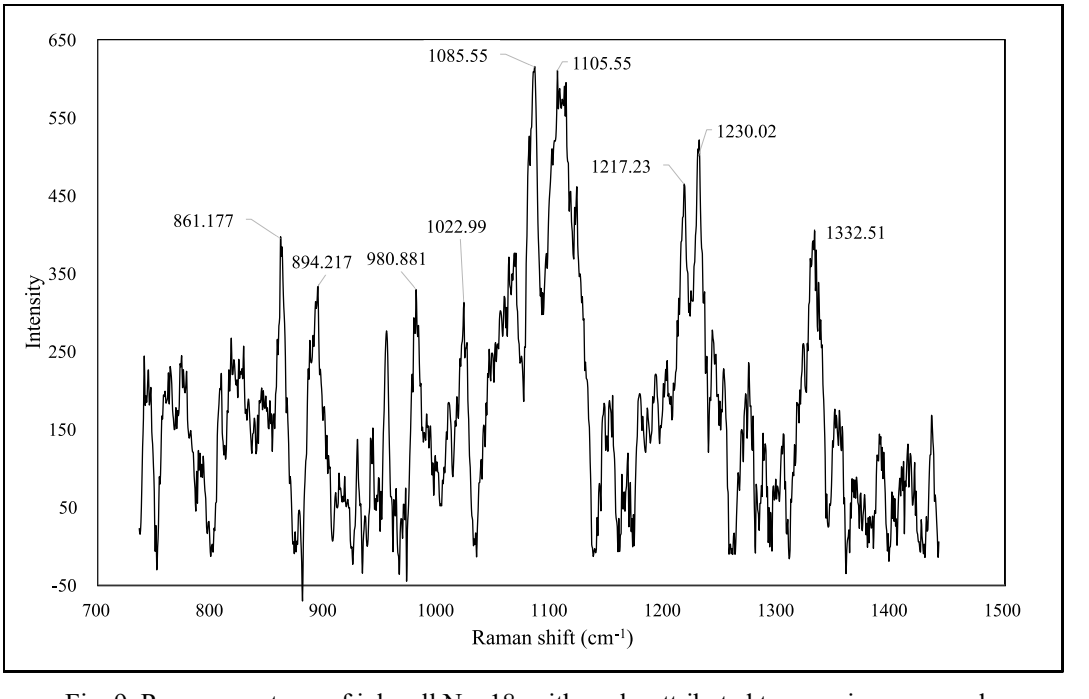


Fig. 9. Raman spectrum of inkwell No. 18, with peaks attributed to organic compounds.

the source of the sulfate revealed to be gypsum mineral ($CaSO_4 \cdot 2H_2O$). The gypsum was detected in a higher concentration in a sample from the interior of the inkwell than in a sample from its exterior. Raman analysis of this item also revealed the presence of a number of iron minerals, which were not detected by XRD analysis (see below).

The XRD analysis of the inkwells mainly found calcite and minerals that were clearly clay-derived. Dolomite was identified in four of the inkwells (Nos. 1, 9 13, 14), and gypsum was identified in two (Nos. 2, 8), including one from Qumran. No clear traces of either potassium, tin or phosphate, which could account for the presence of phosphorus in the high concentration shown in pXRF, were detected in the samples from the interior or exterior of No. 15, due to the small amounts of powder available for XRD analysis.

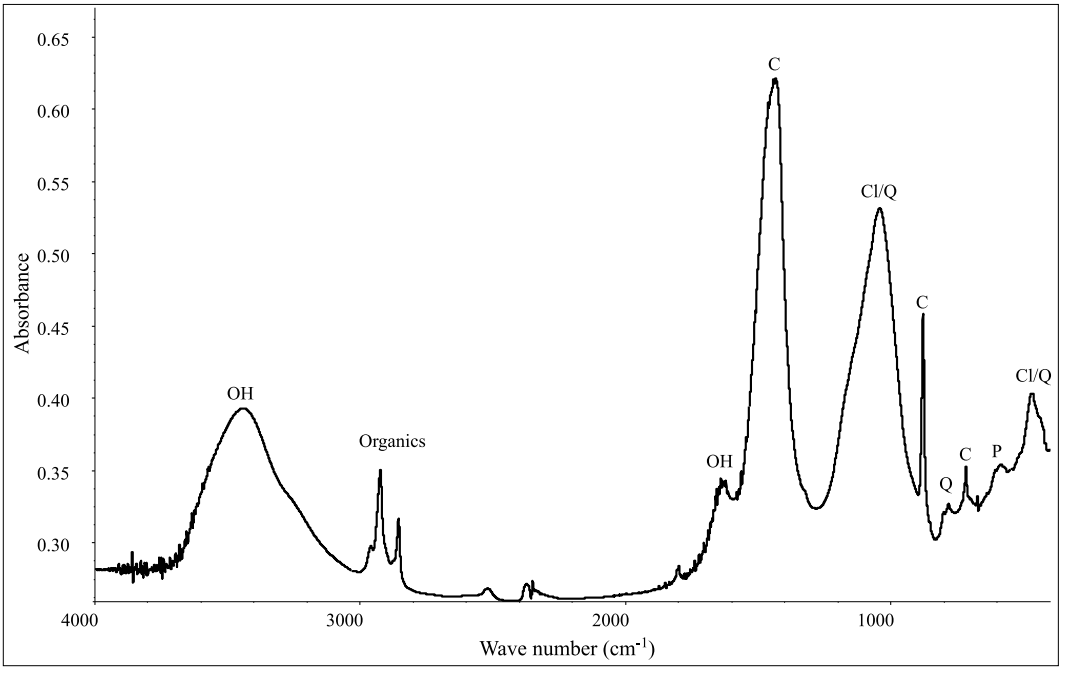
Similar to the XRD results, FTIR analysis revealed the presence of calcite, also showing that this was the dominant mineral in most inkwells (peaks around 1425, 875 and 713 cm^{-1}; Fig. 10). Additional components were quartz (shoulder at 1085 and peaks around 797, 779, 695 and 510 cm^{-1}) and clay (3630, 1035, 530 and 915 cm^{-1}). Gypsum was identified in the same two inkwells in which its presence was revealed by XRD, based on peaks around 3546, 3405, 1685, 1621, 669 and 602 cm^{-1}.

Inkwell No. 15 (Fig. 10) exhibits absorbance bands attributed to calcite, quartz, clay and organic molecules of unclear nature, identified as the CH stretching, at 2850 and 2919 cm^{-1}. A sample from the interior top part of No. 15 had an large amount of such organic material compared to a sample from its exterior top part, with the presence of a peak at 1464 cm^{-1} attributed to CH_2 deformation vibrations.[4] Traces of the phosphorus group (PO_4) were identified in the interior sample by the presence of the 604 and 567 cm^{-1} peaks, possibly an indication of apatite or other phosphoric minerals. A peak at 1624 cm^{-1} may be identified as part of the peak of calcium oxalate, wherein the carbonyl stretching band at 1318 cm^{-1} is a shoulder in the calcite peak of 1425 cm^{-1}. However, it is also possible that this peak represents the water O-H bending and the addition of a peak at 1460 cm^{-1}, which is the CO_3 asymmetry vibration.

Inkwell No. 8 contained gypsum, calcite, clay and quartz, as well as some organic residue of unclear nature, identified by CH stretching at 2850 and 2919 cm^{-1}. The low amount of organic matter from the inkwell interior (Fig. 11), not detected in a sample from its exterior, indicates that the organic materials may have originated from ink binders of an unidentified source.

The scraped residue suspected as ink from No. 16 contained clay, which seemed to be fired at temperatures over 700°C (a shift of the 1032 peak to 1082 cm^{-1}), and quartz, both of which probably originated from the inkwell. Calcite, also identified in No. 16, could originate from the inkwell or the ink. Peaks at 2852 and 2923 cm^{-1} reveal the presence of an unidentified organic compound (Fig. 12), and a peak at 1380 cm^{-1} reveals the presence of

[4] A shift observed in the clay peak of the exterior sample, from 1035 to 1037 cm^{-1}, indicates that the clay of this inkwell was fired at a low temperature (up to 500°C; see Berna et al. 2007:358–373).



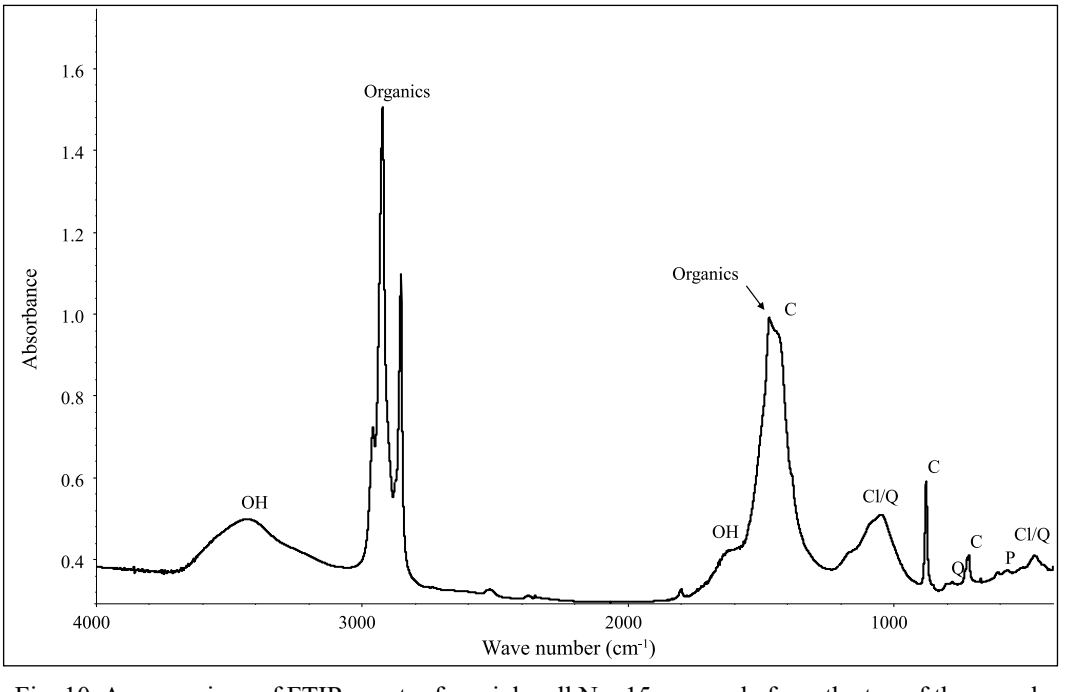


Fig. 10. A comparison of FTIR spectra from inkwell No. 15: a sample from the top of the vessel, with measurement peaks at 2918 cm^{-1} indicating the presence of a small amount of organic material (top); a sample from the interior of the inkwell containing a high amount of organic matter (bottom). Legend: C = calcite; Cl = clay; Q = quartz; P = phosphates; OH = hydroxide (oxygen and hydrogen).

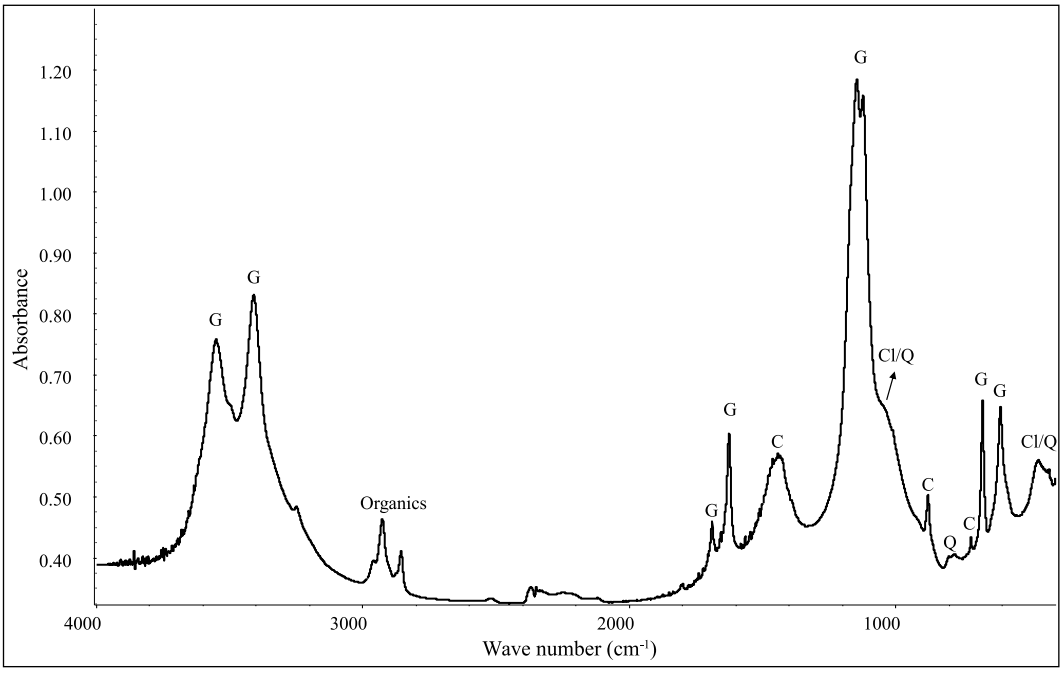


Fig. 11. FTIR spectrum of inkwell No. 8, with measurement peaks indicating the presence of minerals and organic components. Legend: C = calcite; Cl = clay; Q = quartz; G = gypsum.

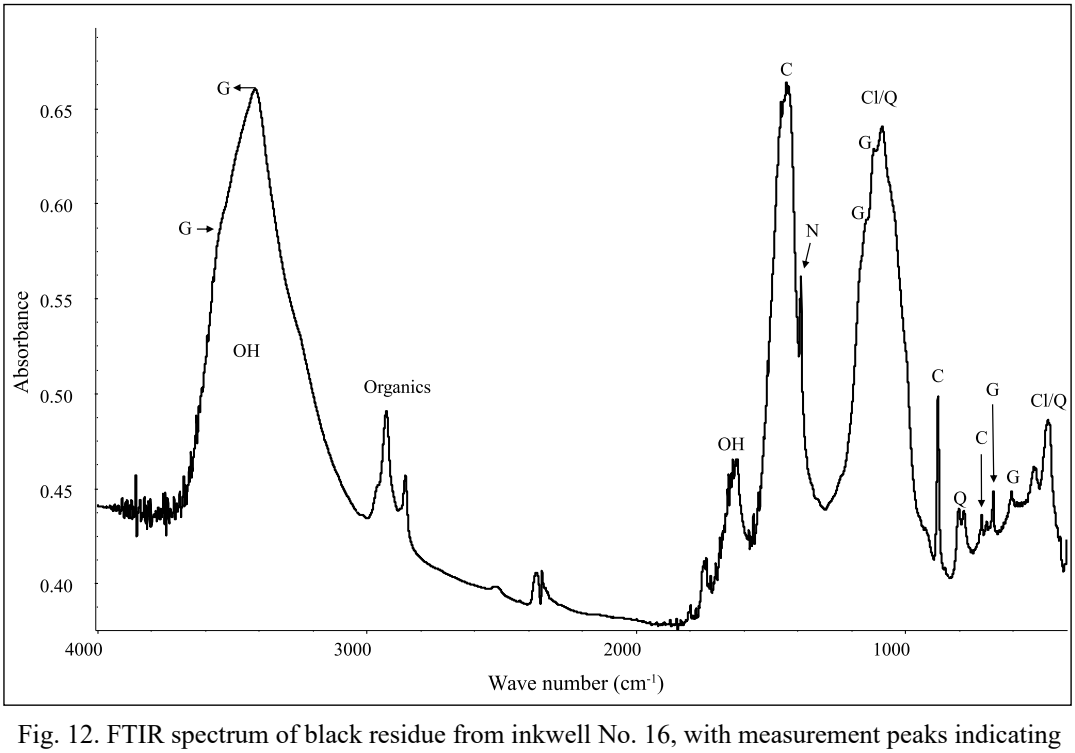


Fig. 12. FTIR spectrum of black residue from inkwell No. 16, with measurement peaks indicating the presence of minerals and organic components. Legend: C = calcite; Cl = clay; Q = quartz; G = gypsum; N = nitrates; OH = hydroxide (oxygen and hydrogen).

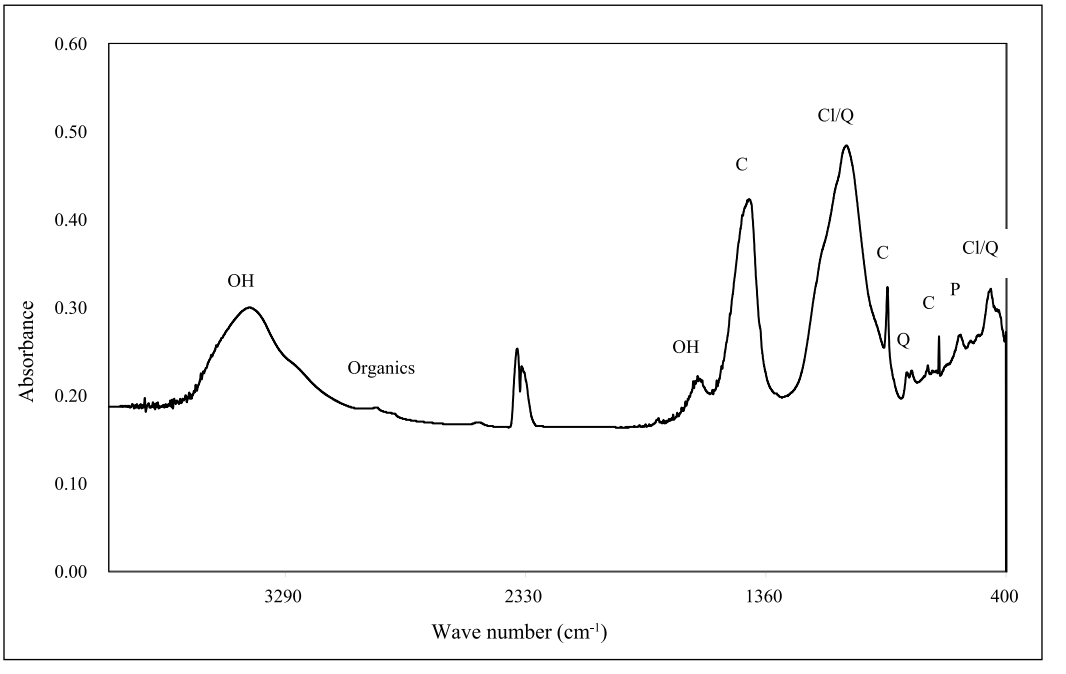


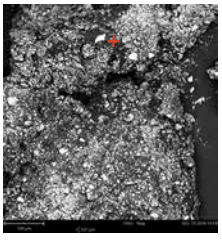
Fig. 13. FTIR spectrum revealing a minute amount of organic material in part of inkwell No. 18 that did not bear black residue. Legend: C = calcite; Cl = clay; Q = quartz; OH = hydroxide (oxygen and hydrogen); P = phosphates.

nitrates. A possible indication of protein in No. 16 may be observed in a peak at 1618 cm^{-1}. The presence of unidentified organic matter was also detected in No. 17.

Inkwell No. 18, from Robinson's Arch, revealed that the main component in the blackish material on the exterior and interior surfaces of this item is calcite, with some presence of mineral clay.[5] A minute amount of organic material was also detected in the clay itself, in a part of the inkwell that did not bear the black residue (Fig. 13).

SEM-EDS analysis yielded much the same results as other analyses for both the inkwells and the suspected ink, showing that they contained high amounts of calcium (Ca), oxygen (O), silicon (Si) and different metallic elements, such as iron (Fe), magnesium (Mg), sodium (Na), sulfur (S), phosphorus (P) and in some cases bromine (Br), usually in higher concentrations in samples from exterior surfaces of the inkwells. This analysis also revealed that the black and shiny surfaces of No. 15 contained higher than usual amounts of carbon (Fig. 14). The well-defined shape of these surfaces observed at high magnification suggested they may be the residue of bitumen, and this was reinforced by comparing the FTIR spectrum of the sample to that of bitumen (Fig. 15), demonstrating the presence of peaks in similar wavenumbers. However, the sulfur concentration in the sample (Fig. 14) was appreciably lower than that of the bitumen source nearest to Jerusalem, found in the

[5] The clay mineral seemed to be fired at around 500°C (see Berna et al. 2007:358–373).



Element			Concentration	
No.	Symbol	Name	Atomic	Weight
6	C	Carbon	90.01	85.27
8	O	Oxygen	8.84	11.15
20	Ca	Calcium	0.95	3.01
26	Fe	Iron	0.05	0.24
15	P	Phosphorus	0.06	0.14
12	Mg	Magnesium	0.05	0.1
16	S	Sulphur	0.04	0.09

Fig. 14. SEM image of tar-like blackened surface of inkwell No. 15, with the measurement point marked by a red plus (left), and the results of the EDS analysis of its elemental composition (right).

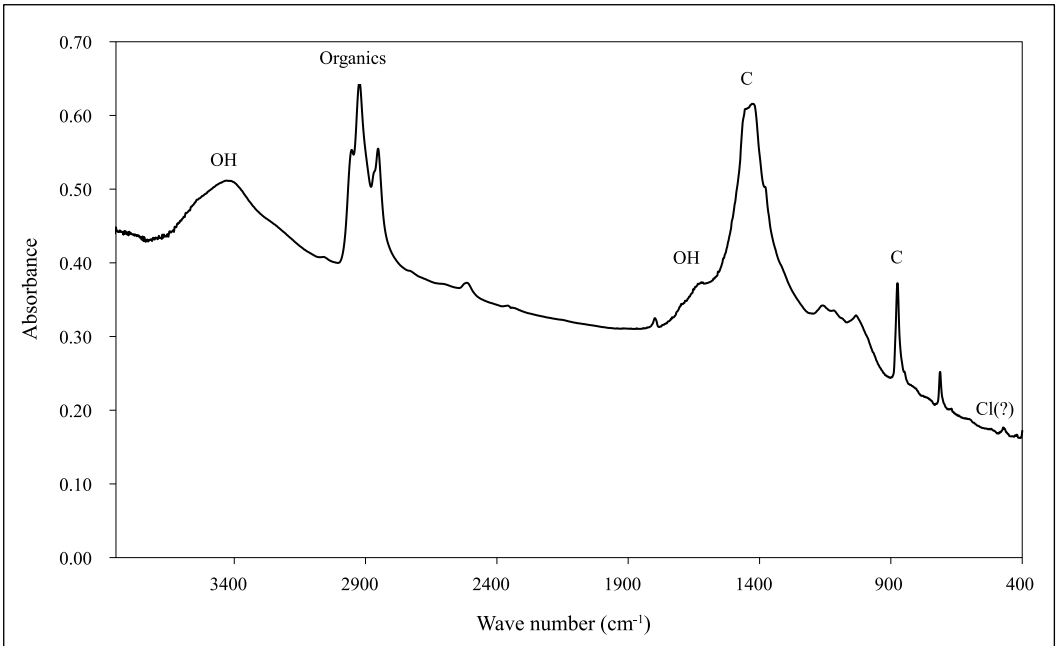


Fig. 15. Bitumen standard taken from the online database of the FTIR Library of the Kimmel Centre for Archaeology, Weizmann Institute (https://www.weizmann.ac.il/kimmel-arch/infrared-spectra-library). Legend: C = calcite; Cl = clay; OH = hydroxide (oxygen and hydrogen).

Dead Sea area (9.4%; Nissenbaum 1978:837–844; Nissenbaum, Aizenshtat and Goldberg 1980:157–161) and hence, it is unlikely to have been bitumen-derived. Bitumen, which is known to have been used as a black pigment in antiquity (Winter 1983:49–66; Tomasini, Siracusano and Maier 2012:28–37), is mainly composed of amorphous carbon (88%; Nissenbaum, Aizenshtat and Goldberg 1980:157–161), and could not be differentiated from ink-derived soot in a Raman spectrum. Another possibility is that the dark and shiny material originated from hydrated ink extract, formed after the water evaporated and the organic binder degraded. This process could result in overlap of the mineral peaks

within the FTIR spectra, making material identification ambiguous. According to Winter (1983:49–66) a tarry organic substance was an unwanted byproduct in the production of carbon pigment, which could be collected and added to soot in the formation of ink. The degradation of such material could account for the residue observed on the wall of item No. 15.

Discussion

This study was undertaken to examine the composition of the ink used in Judea during the Early Roman period, the time when most Dead Sea Scrolls were written. The identification of the ink recipes of that period would enable us to compare the composition of these inks with those known to have been used in ancient Rome, based on written sources (Vitruvius, *De architectura* 7:10; Dioscorides, *De materia medica* 5:162; Pliny the Elder, *Naturalis historia* 36:41) and analyses of inkwell residue from Italy (Rice 1987; Sibilia et al. 2021:7231). Minerals were the predominant component identified in most of our samples. As the same mineral composition was identified over different parts of the sampled inkwells (interior, exterior and the handle or upper rim), we can generally conclude that the sampled material mostly, although not exclusively, originated from the clay and temper used to produce the inkwells. There is a large amount of calcite in most of the samples, as well as quartz and other clay minerals like dolomite and gypsum. Some minor differences observed among the samples in the mineral composition is likely due to different sources of clay and different techniques of pottery production (i.e., different tempers and heating temperatures). One possibility is that the large amounts of calcite present in all the sampled inkwells originated from the ink; however, it is also possible that the calcite originated from the clay from which some of the items were made, or was the result of post-depositional processes. Canavali et al. (2011:1801–1814) identified calcite in ink powder found in vessels from Pompeii, and postulated that it may have originated from an ink-making procedure in which hard water was used to dissolve the soot and the gum Arabic. Presumably, the presence of calcite in the ink could also be due to the ancient practice of collecting soot for producing the ink from walls containing calcium, as described by Pliny the elder (*Naturalis historia* 36:41).

The different tempers used in pottery production throughout antiquity, such as bone, limestone or shell (Rice 1987), are another possible source of the abundant calcite detected in the inkwells. Some tempers, including bone, charcoal, soot and plant fiber (Rice 1987), could also be the source of amorphous carbon derived from the clay of the inkwells. Given the high presence of both calcite and amorphous carbon in the sampled inkwells, the use of these components as ink indicators is problematic.

Some indication of the presence of ink in the clay could be detected in Nos. 8 and 15. Analysis by pXRF suggested that No. 15 contained a high amount of phosphorus, while its FTIR spectrum and XRD analysis indicated the presence of a phosphate material of unidentified nature, perhaps hydroxyapatite; the XRD results showed that this material was present in the sample in a small amount. FTIR also detected the presence of unidentified

organic material, occurring at an appreciably higher amount in a sample from the interior of this inkwell compared to its exterior. No clear indication was obtained whether the organic molecules belonged to specific binders, such as gum Arabic or other materials (Daoub et al. 2016). SEM-EDS analysis of a sample taken from the vessel's black and shiny surfaces identified the presence of a high amount of carbon, possibly originating from a bitumen-like byproduct of ink degradation.

Another possible indication of ink was detected in item No. 8. A small amount of organic matter was found in a sample from the inkwell interior, but was not detected in a sample from its exterior, implying that the source may have been ink binders of an unidentified nature, as suggested above for inkwell No. 15.

Among the three inkwells with apparent ink residue (Nos. 5, 16, 18), Nos. 5 and 16 yielded calcite, of a rather high amount (56%, based on XRD measurements); amorphous carbon—according to Raman analysis; and organic matter of an unidentified nature. As with No. 15, FTIR of these two inkwells could not determine the presence of organic binders, either gum Arabic or other kinds, due to the overlap of mineral peaks or the degradation of the binders. Unlike inkwell Nos. 5 and 16, No. 18 yielded only a neglectable amount of organic material as shown by FTIR. Traces of organic remains that were identified by Raman analysis indicated a high state of degradation, possibly due to the presence of this particular inkwell in a drainage channel.

Unlike Maor's (2019 study that demonstrated the presence of hydroxyapatite in ink residue from item No. 5, the same study preformed on other inkwells did not unambiguously identify the presence of bone-derived carbon, which could originate from ink. No clear indication of such bone-derived carbon was found in samples of plausible ink residue from inkwell Nos. 16–18, nor in samples from the other inkwells. The pXRF analysis of item Nos. 14 and 15 detected relatively high amounts of phosphorus, possibly indicating the presence of hydroxyapatite, while FTIR and XRD analyses of samples from No. 15 indicated the presence of a phosphate material of unidentified nature, perhaps hydroxyapatite. The latter two specimens also yielded relatively high concentrations of amorphous carbon, compared to all other samples, possibly indicating the origin of the carbon in ink pigment. No such indications were found for any of the other inkwells. It is possible that such ink components were originally present in the other inkwells, although they may have degraded due to post-depositional processes and the impact of washing the inkwells during excavation.

To conclude, it seems that due to the highly degraded nature of organic compounds in the analyzed samples they could not be identified using spectroscopic methods, while the possible presence of organic substances used as binders for the pigment were detected using FTIR. It is possible that the detected organic substances included gum Arabic, as discovered in a recent study of a DSS fragment (Zilberstein et al. 2021:249), although this possibility could not be verified. Future research of ink composition in relation to the DSS will shed further light on the important issues raised in the present study, with implications for understanding the cultural transmission of ink recipes over time, the ability of scholars to distinguish between different scribal schools based on ink analysis, commodities

trade and questions of provenance of different types of ancient inks. Despite the limited conclusions emanating from the present study, it is an important step toward the creation of a methodology for ancient ink analysis.

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