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Fourteenth-century documents of the Knights of St. John of Jerusalem: analysis of inks, parchment and seals

The National Library of Malta located in Valetta, capital of Malta, comprises a unique collection of the documents of the Order of St. John of Jerusalem, known also as the Knights of Malta. The collection is the only repository of the Order's earliest documents, dating from the beginning of the eleventh century.

The Order originated in the Holy Land, in Jerusalem, as the hospice for the Christian pilgrims. Its initial mission was to provide care for pilgrims and this mission remained the predominant function of the Order through the centuries, and inspired the name of the Knights Hospitallers. Not until later, due to the political circumstances, did the Order expand its function as a military order.

In 1113 Pope Paschal II recognized the Knights Hospitallers as a Religious Order, bestowing ecclesiastical privileges on the knights, such as exemption from Episcopal jurisdiction and direct responsibility to the Pope, freedom from paying tithes, the right to have its priests and chaplains, and its own churches and cemeteries.

The Knights of St. John remained in the Kingdom of Jerusalem during the thirteenth century, until the Mamluks of Egypt finally conquered the remaining Christian territories, with the capital Acre the last to fall in 1291.

In 1291 the Knights were invited by the King of Cyprus to reside on the Island. The Order remained on Cyprus for 15 years. In 1308 the Knights conquered the island of Rhodes, off the south-western coast of Asia Minor, re-establishing its strategic and political importance. The island was used by the Knights as a base for crusading attacks on the Muslim powers. The revenues generously flowing from the Order's estates in Europe enabled the Knights to make Rhodes one of the most fortified places in the world.

Rhodes was not only an important outpost for the defence of the crusading movement. It was a highly organized and efficiently administered sovereign state, with a strongly developed class of merchants, bankers, shipbuilders, architects and lawyers. One of the industries in Rhodes was piracy, which the Order sheltered and encouraged. It was a threat to maritime security and one of the reasons which led the Turkish Sultan Mehmed II to undertake the siege of Rhodes in 1480. Not until 1522 did the Turks succeed in taking the island, after the second major siege, led by Sultan Süleyman. The Knights surrendered Rhodes on terms which included evacuation of the island and relocation of the Order. The Knights sailed away, to stay for a short period on the island of Crete from 1523 to 1530. The Emperor Charles V offered the islands of Malta and Gozo to the Knights in order to create a base against the growing power of the Turks. The Knights accepted the offer and relocated to Malta in 1530. At that time the Archive of the Order was moved to the Maltese Islands and in the seventeenth century it found its permanent home in the Bibliotheca which was designed and built by the Knights for that purpose. There the collection of the documents was well taken care of by the Knights, who appointed a man whose sole responsibility was to clean the books. Their care was not so well organized in the turbulent later times.

The contents of the Archives have never been systematically studied, though a few documents have been included in historical publications. In 1988 the first conservation survey of the Archives was conducted. In 1989-90 a conservation pilot project was carried out on a selected group of documents in order to develop a guide for care and treatment of the collection. At the same time

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samples were taken for materials analysis. The conservation pilot project involved disbinding the volume, conserving the parchment documents, seals and metal skippets, and preparing the volume for storage and display. The challenge of the conservation of parchment was due to the presence of pendant seals and was a subject of an earlier publication.²

Among 400 volumes of the earliest documents – papal bulls, charters, correspondence or other documents issued by the Order from the twelfth to sixteenth centuries – 36 contain pendant seals within their bindings (Fig. 1). One of the volumes, Volume 21, which was representative of the structural characteristics and conservation problems of this group of documents as a whole, was selected as the pilot project. The fourteenth-century documents in this volume have undergone conservation and the analysis of seals, inks, and parchment grounds.

Documents in Volume 21
Volume 21 comprises 10 original bulls on parchment issued during the reign of the Grand Master Pinibus by the dignitaries of the Order of St. John of Jerusalem and other important figures in the fourteenth century. The title of the volume is: 'Bullae originales per titulos et materias cliuisae quae in libris bullarum non sunt registratae sub Em: et Reu Domino Magro Fre Rugerio de Pinibus expeditae de annis 1336: 1356: 1358: 1362: 1373' (Original edicts, titles, and materials not

Fig. 1 Collection of the earliest documents of the Knights of St John of Jerusalem, probably bound at the time the Knights moved to Malta in the sixteenth century.

registered in the books of edicts, and organized for the years 1336, 1356, 1358, 1362, and 1373 by the revered Grand Master Roger de Pinibus.) (Fig. 2). Two documents (2 and 8) were translated for this research. We are not aware of translations of any of the others, however, the titles indicate that most of the documents are related to the financial matters of the Order during its stay in Rhodes.

Considering the disparity of dates, it seems evident that the documents were bound together to prevent their misplacement during relocation of the Archives from Rhodes to Malta. The structure of the binding, simple full-limp parchment, would be characteristic for the period of the Knights' departure from Rhodes.

In addition to the study of the art-historical context of the documents analyses of the materials used in their construction was carried out. Microscopic samples of inks, grounds and seals were taken and forwarded for testing to the Smithsonian Center for Materials Research and Education (at that time the Conservation Analytical Laboratory).

Analysis of Samples
Three analytical methods were used (see Appendix for details). X-ray diffraction (XRD) was used to determine the mineral or compound present, for example that the red pigment cinnabar was used to color a wax seal. Scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDS) was used to determine the major and minor elements present. This information could support the presence of a compound identified by x-ray diffraction, suggest the possible presence of other compounds, or give indication of impurities present. Fourier transform infrared spectroscopy (FTIR) was useful in particular for the identification of organic compounds such as the beeswax of the seals, and gave some indication of the medium of the inks and grounds.

1. Parchment and grounds
All the documents in volume 21 were written on what appeared to be goat skin parchment, with exception of document 1, which was probably calf skin. The assessment of the parchment origin was made based on comparative examination of the hair follicle pattern with that of a reference source. The surface examination was carried out using a monocular under x10 magnification.

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Historically, parchment was prepared as a writing material by a process which included extended soaking of the skin in lime solutions. The final finishing layer of chalk (calcium carbonate) was applied as a ground to increase opacity, to provide a good contrast for writing, and to promote better absorption of inks. Therefore it came as no surprise to find a significant quantity of calcium carbonate in the samples of grounds. Some gypsum was found with the ink samples, which may also indicate traces of ground material (see Section 2).

The calcium carbonate in the samples of ground was identified by XRD as calcite ($\text{CaCO}_3$) alone or mixed with vaterite ($\text{CaCO}_3$), a form of calcium carbonate that rarely occurs in nature. It forms in admixture with artificial calcite under certain circumstances and its presence might indicate that the calcite used for the grounds was of artificial origin. Samples from the verso and recto of document 5 and the recto of two other documents (2 and 7) were calcite alone. Samples from each side of document 4 were a mixture of calcite and vaterite. Analysis of these grounds by SEM–EDS showed calcium to be the major element present, as would be expected, and other elements to be present in minor and trace quantities as impurities, except for chlorine as a major element in one case (document 7). FTIR analysis showed the presence of a proteinaceous material, possibly animal glue, or more likely from the parchment itself.

2. Inks

The text on all the documents was written in dark and light brown inks in the script characteristic for the fourteenth century scriptoria in Europe. Although four of the documents originated in Rhodes, which was at that time under an influence of Greek cultural elements, there was no evidence in the penmanship or preparation of parchment, of other writing schools such as those of Byzantium or Islam. All characteristic of the inks indicate similarities to the contemporary scriptoria in Europe. Over the centuries many inscriptions were added to the verso of the documents, in various brown inks.

Several ink samples from volume 21 were analysed. Interestingly, five samples showed the presence of gypsum (calcium sulphate, $\text{CaSO}_4\cdot\text{H}_2\text{O}$) and lepidocrocite (ferrous oxide, $\text{FeO(OH)}$), by XRD. The occurrence of lepidocrocite is difficult to explain and can only be accounted for by conjecture. The ink on manuscripts of this date is generally accepted to be an iron gall ink. Lepidocrocite is a ferrous oxide, red to reddish brown in color, that can result from the oxidation of iron. It might be that its presence is the result of the alteration of the ink.

The gypsum in the ink may well have originated from a ground. It occurs alone in one other ink sample, and in another cinnabar (red mercuric sulfide, $\text{HgS}$) was identified with it; in yet another sample cinnabar was found alone. The cinnabar might be an intentionally added colorant; it was known in the production of early coloured inks.6

The proteinaceous material in four ink samples, determined by FTIR analysis, may have come from the parchment. A carbohydrate gum identified in five ink samples may be gum arabic, the medium known to have been used in iron gall ink.7

3. Seals

A unique collection of seals, exclusively designed in the twelfth and thirteenth centuries for the Knights of the Order of St. John of Jerusalem, served the organization for five centuries. The Knights used seals which reflect in their iconography the complexity of the Order’s multiple functions, social origin and importance in Europe. The symbolism of the images and design also reflect the order’s interaction with its surrounding cultures.

There are 18 types of seal described in the thirteenth-century Statutes of the Order, which represent functions of highly organized offices. The Marshal had a seal depicting a knight fully armed with a banner in his hand. The Commander of Cyprus used a seal with an image of a vessel. The Commander on this Side of the Sea used a griffin in his seal.


7 Levey, 7.
The best illustration, however, of the complexity of the designs, as well as the origins of the symbols, combining elements of the East and the West, is the lead Master’s bulla, the most important seal of the Order, on document 5. It incorporates ecclesiastical images and allegoric, monastic scenes with symbols of the Order’s function. The image on one side depicts the Master of the Hospital kneeling in prayer before the patriarchal cross, and on the reverse, the man lying before the tabernacle.

Four documents in volume 21 were secured with pendant seals attached on strings and parchment ribbon (documents 2, 5, 7 and 8). One of them, attached to the document 7, was found to be in fragments which clustered around the string. The seal on document 2 was contained in a metal skippet. The seals on other documents in the volume have been cut, and their presence is only indicated by the openings for the string attachments.

The four seals in volume 21 were:
1. Lead bulla of the Grand Master Roger de Pinibus, document 5, dated 1358. (Figs. 3, 4)
2. Green and yellow seal of the Grand Commander on this Side of the Sea, Raimondo Berengario, document 8, dated 1362. (Fig. 5)
4. Red seal of the Archbishop of Nicosia, document 2, dated 1336. (Fig. 6)

Only one seal in the volume was not issued by a member of the Order. Document 2 was issued by the Archbishop of Nicosia, Cardinal Elie de Nabinaux, and sealed with his ecclesiastical seal. The pointed oval shape and iconography of the image showing the transfiguration of Christ are characteristic for this category of seal, in use between the twelfth and fifteenth centuries.

In addition to a study of the historical context of the seals attached to the documents in volume 21, analysis of the materials was undertaken in order to obtain a better understanding of their composition. This was an essential step in the process of choosing the most appropriate conservation treatment and materials.

No previous analytical studies of wax seals from the documents of the Knights of Malta are known to have been carried out, but comparative material is available from England and Spain from the same period and some historical information is known about the materials used to make non-metal seals.

English royal and great seals from the medieval (thirteenth to mid sixteenth centuries) to the early modern period (early eighteenth to late nineteenth centuries) have been analysed by C-13 Fourier transform nuclear magnetic resonance. It was shown that beeswax was the single material used until the time of George III (1760–1820) when it was supplanted by mineral wax. After that period seals were made of a mixture of wax and colophony (pine resin).

Analysis of almost 80 royal seals from five Spanish state archives by FTIR showed that beeswax alone was the common material in Spain until the reign of Alfonso IV, King of Aragón (1327–38), when colophony first appeared mixed with it, at an earlier date than when it was added in England.
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The three wax seals from volume 21 were found by infrared spectroscopy to be made of beeswax. There was no evidence of the presence of colophony. Figure 7 shows the infrared spectra from these three seals compared with that of a beeswax standard.

The colouring materials of the seals are also of interest. Among the colours of medieval wax seals are red, dark green, dark brown and black. King, writing about the seals of the Order of St. John of Jerusalem, quotes a document, probably drawn up in the mid thirteenth century, that reported the use of green and black wax. The natural yellow to brown color of beeswax also is known. Parra et al. suggest that the brown and yellow colours might be from a dyestuff or that brown may represent the decomposition of a green product, since trace amounts of copper were found. Cinnabar and verdigris have been mentioned as colorants in the historical literature. Fillers in wax seals were chalk (calcite, CaCO₃), flour, and other materials. A brown varnish coating was said to be common although from visual examination there was no evidence of its presence on these seals.

Some identification of the coloring materials was carried out on the Spanish seals cited above. Parra and his co-workers found the elements mercury and sulphur by x-ray fluorescence in red seals dating between 1258 and 1665, thus indicating the presence of cinnabar (vermilion). Similarly the presence of lead in red seals suggested the presence of red lead, which was found alone and mixed with cinnabar, from 1324 to 1420. Royal seals were generally coloured with vermilion, while others were more likely to have a mixture of vermilion and red lead. It has been suggested that traces of copper in a green seal indicated the use of the green copper resinate; this seal, dated 1512 and used by Henry VIII, is the one non-Spanish seal in their series. The possible green colorant in wax seals is discussed overleaf.

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The three wax seals from document 21 were analysed. The red colorant of the seal on document 2 was identified by XRD as cinnabar (mercuric sulphide, HgS), a mineral which is identical to dry-process vermilion, the manufactured pigment (Table 1). Artificial dry-process vermilion was manufactured as early as the eighth century and was common by the fourteenth century. The red could be either mineral cinnabar or dry-process vermilion. The presence of the elements mercury and sulphur, determined by SEM-EDS, was consistent with the presence of cinnabar. Minor elements present were calcium, possibly due to chalk filler, and silicon, an impurity; other elements present in trace amounts were tin and iron, possibly from the mount used in the analysis, or from the tools used to retrieve the samples.

The red colorant of the seal on document 7 was identified by XRD as minium (lead dioxide, PbO₂) (Table 1). Red lead was used as early as classical times; it is a manufactured pigment, crystallographically identical to the naturally

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<th>Cinnabar JCPDS 6-256</th>
<th>Seal from document 7</th>
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9 Dry-process vermilion is prepared by heating together sulphur and mercury which sublime to form mercuric sulphide. The ground dry-process material is indistinguishable microscopically from ground mineral cinnabar. Wet-process vermilion, the other kind of artificial vermilion, is prepared by precipitation from solution, and has a different appearance microscopically.

occurring mineral minium. The mineral was probably never used as a pigment, although the term minium has often been applied to the artificial pigment.\(^\text{21}\) The presence of lead was determined by SEM-EDS. A minor element present was calcium, probably from a chalk filler. Trace elements present were sodium and silicon, probably impurities. Metal salts of carboxylic acids detected by FTIR analysis probably resulted from the reaction of the red lead with the beeswax.

The analysis of the inorganic components of the green seal on a yellow base on document 8 suggests a possible colorant. The only inorganic compound determined to be present by XRD was calcite (calcium carbonate, CaCO\(_3\)) in both green and yellow areas: this is undoubtedly a chalk filler. The analysis of both the green and the yellow wax showed calcium to be a major element, consistent with the presence of calcite. Silicon was also present in one sample as a major element, either from some filler or as an impurity. Silicon was chiefly present as a minor element; trace elements, probably impurities, were sulphur, chloride and aluminium. Iron was present in the yellow wax, probably from the sample holder. Copper was present in minor amounts in the green wax, but not in the yellow.

As noted above verdigris was known to have been used as a green colorant in wax seals. Verdigris is a collective term for copper acetate pigments of varying composition, ranging from green to blue in color. It can react with oils, resins, and proteins to form copper oleates, resinate, and proteinates.\(^\text{22}\) It seems reasonable to conclude that the green color in this seal is due to the presence of a copper containing compound, possibly introduced as verdigris. As with the seal colored with red lead, metal salts of carboxylic acids were detected in this seal, possibly an indication of the presence of copper.

In the twelfth and thirteenth centuries seals were often impressed on and surrounded by a thick cake of wax, the edges of which rose above the margin of the seal to form a protective fender.\(^\text{23}\) An arrangement such as this may explain the two-color appearance of the green and yellow seal. Sometimes a twisted shred of parchment was embedded in the wax around the seal impression for the same purpose.

Medieval seals are often protected by boxes of wood, metal, or ivory known as skippets.\(^\text{24}\) The metal skippet containing the seal on document 2 consists of two parts which fit into each other to form a box-like container. The skippet was determined by spot tests to consist chiefly of iron, with a tin surface. One side was made of zinc and there is evidence of a lead-zinc solder at the joins. The surface material from the skippet was found by XRD to consist of two mineral compounds, lepidocrocite and cassiterite (tin oxide, SnO\(_2\)), with some unidentified lines; the determination of Fe and Sn by SEM-EDS is consistent with these compounds. Lepidocrocite and cassiterite are corrosion products which would be expected on a metal object of iron and tin.

It is of interest to note that beeswax has long term chemical and microbial stability. No chemical deterioration of medieval beeswax has been noted. It has been suggested that the presence of copper and mercury contributes to its microbial stability and this has been confirmed.\(^\text{25, 26}\) Some surface alteration in the form of bloom is probably due to physical change through loss of small amounts of volatile material; indication by infrared analysis of some unsaturation of the beeswax, owing to oxidation, supports this.\(^\text{27}\)

**Conclusions**

Analysis of materials in Volume 21 positively confirms the usage of minium and cinnabar as colorants in wax seals, although the use of these materials has been mentioned in medieval sources, and elemental analysis has previously indicated their presence. It is also of interest to learn that the use of beeswax is consistent with the known medieval tradition. The work reported here makes a particularly important contribution to the history of the Archives of the Order of St. John, being the first scientific examination undertaken of the materials from their repository.

23 Enc. Brit. (1911), 541.
26 Cassat et al., 239.
27 Robbins et al., 90.
Appendix

Experimental details

Samples from the documents were analysed at the Smithsonian Center for Materials Research and Education (SCMRE), formerly the Conservation Analytical Laboratory (CAL), Smithsonian Institution. Melanie Feather carried out the X-ray diffraction and the scanning electron microscopy with energy dispersive x-ray analysis. Fourier transform infrared spectroscopy was done by Walter Hopwood.

X-ray Diffraction (XRD) was carried out using a Gandolfi camera on a Philips PW-1720 x-ray generator with Ni-filtered CuKa radiation, 45 mA for 12–30 hours. Kodak DEF-392 Direct Exposure Film was used to record the patterns. Representative film patterns were then indexed for d-values and relative intensities of the lines and a search was conducted using the MDI 'MicroID' computer program to find known compounds of matching values.

Scanning Electron Microscopy with Energy Dispersive Analysis (SEM–EDS) was carried out with a JEOL JXA-840A Scanning Electron Microscope with a Tracer Northern TN-5502 energy dispersive x-ray analysis system. Small pieces of the samples were placed on graphite stubs attached with conductive carbon adhesive. The sample stubs were then coated with a thin layer of evaporated carbon to increase conductivity under the electron beam. Multiple samples (2 or 3) were run. Elemental spectra were obtained at 20kV (in one case 15kV) for a 60 second live-time acquisition. Qualitative EDA was done on random areas of the samples to determine the major and minor elements present (with atomic number greater than 10). No correction factors were applied.

Fourier transform infrared analysis (FTIR) was carried out with a Mattson Cygnus 100 Fourier transform infrared spectrophotometer with Spectra Tech IR Plan microscope. A particle of the sample was compressed in a diamond-anvil cell. Only a portion of the flattened particle was used to collect each spectrum. By repetition of this operation each sample was prepared for infrared spectrometric analysis. Infrared spectra were obtained at 8 wavenumbers resolution in five-minute scanning times.

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Summary

The national Library of Malta in Valetta comprises a unique collection of the documents of the Order of St. John of Jerusalem (the Knights of Malta). In 1988 the first conservation survey was initiated and funded by the Fulbright Council of International Exchange of Scholars followed by a conservation pilot project supported by the Samuel Kress Foundation in 1989. Selected volumes documenting the earliest history of the Knights were examined from a conservation and analytical point of view. The conservation needs of the collection were addressed in a 1992 publication. The focus of this paper is analysis of the grounds, inks and seals from volume 21 which dates between 1336 and 1373. All the documents were written on parchment in iron-gall ink. Four documents retained their original seals, one of lead and three of wax. Analysis was carried out using x-ray diffraction, scanning electron microscopy with energy dispersive analysis, and Fourier transform infrared analysis, at the Smithsonian Center for Materials Research and Education. The usage of minium and cinnabar as colorants in wax seals, mentioned in medieval sources, was confirmed, and the use of beeswax for these seals is consistent with known medieval tradition.

Résumé

Fourteenth-century documents of the Knights of St. John of Jerusalem

(FTIR), au Smithsonian Center for Materials Research and Education. L'utilisation de minium et de cinnabar (vermilion) comme colorants dans les sceaux en cire, mentionnée dans des sources médiévales, a été confirmée et l'utilisation de cire d'abeille pour ces sceaux est en accord avec la tradition médiévale connue.

Zusammenfassung

Biographies
Hanna Maria Szczepanowska is a certified conservator of art on paper and parchment. In 1978 she received her Master Degree from the University of Nicholas Copernicus in Torun, Poland and in 1985 was certified by the American Institute of Conservation, USA. Her areas of specialty are medieval illuminated parchment manuscripts and damage to art works caused by fungi. Between 1990 and 1991 she worked as a conservator and consultant for the collection of the Knights of Malta at the National Library in Valetta and the collection of Prints and Old Master Drawings at the Cathedral Museum in Mdina, Malta. Currently she is working at the Maryland State Archives, Annapolis MD, holding a position of a Preservation Officer and Supervisory Conservator.

Elisabeth West FitzHugh has a BA in chemistry from Vassar College and a Diploma in the Archaeology of Western Asia from the University of London. She was a conservation scientist in the Department of Conservation and Scientific Research at the Freer Gallery of Art and the Arthur M. Sackler Gallery, Smithsonian Institution, until 1991 and she is now a research associate there. She has carried out investigations into the materials of art and archaeology of Asia, including Chinese jades and bronzes. Her main specialty in recent years has been the history and identification of pigments, and she edited Artists' Pigments; A Handbook of Their History and Characteristics, vol.3, for the National Gallery of Art, as well as contributing to other volumes in the series. She has been active in the American Institute for Conservation where she served as President (1984-6) and editor of the Journal of the AIC (1989-95).

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