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Pigment analysis: potentialities and problems

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ABSTRACT. — The field of pigment analysis is explored through a series of examples taken from the authors' work experience. Some analyses are easy to make, other may require the combination of various techniques, still others require the use of sophisticated equipment such a synchrotron or neutron diffraction analyses. Sometimes the results obtained do not agree with the accepted theories about the use of specific pigments (e.g. Egyptian Blue), or a new, unexpected substance is found to be used as a pigment (e.g. magnesium oxalate or lead sulfate). Investigations into illuminated manuscripts revealed the presence of a variety of verdigris, only matched by our laboratory synthesis of this variant. The discovery that the binders used were of size, resulted in the presence of copper-proteinates from reaction of the media with verdigris. The red pigment in a manuscript by Von Ems was found to be made from rhubarb, which is the first time this colorant has been detected from illuminated manuscripts. Examination of an Egyptian ushabti of the New Kingdom revealed a layer of tridymite white pigment overlying a calcite ground. This unusual discovery may signify that the Egyptian pigment palette is much more extensive than previously thought.

RIASSUNTO. — Lo studio dei pigmenti è affrontato attraverso una serie di esempi presi da esperienze di ricerca. Alcune analisi sono molto semplici da eseguire, altre richiedono la combinazione di più tecniche analitiche, altre ancora prevedono l'uso di strumenti sofisticati come il sincrotrone o analisi di diffrazione con neutroni.

A volte i risultati ottenuti non sono in accordo con le teorie già attestate sull'utilizzo di pigmenti specifici (es. il blu egizio), o si scopre l'utilizzo inaspettato di alcune sostanze per ottenere dei pigmenti (es. ossalato di magnesio o solfato di piombo). Gli studi di manoscritti miniati hanno rivelato la presenza di una varietà di "verdigris" che è stata preparata, in questa variante, solo dal nostro laboratorio di sintesi. La scoperta che i leganti erano nel giusto rapporto, è confermata dalla presenza di pitture con proteinati di rame, prodotti dalla reazione del supporto con il verdigris. In un manoscritto di Von Ems, si descrive la produzione del pigmento rosso a partire dalla pianta del rabarbaro, che è stato individuato per la prima volta in un manoscritto miniato.

Esaminando un ushabti egizio del Nuovo Regno è emerso un livello di pigmento bianco a tridymite posto su di un fondo di calcite. Questa scoperta inconsueta, può significare che la tavolozza dei colori Egizi è molto più ampia di quanto fin ora conosciuto. (tradotto dall'editor).

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INTRODUCTION

Practically all art employs pigments of one kind or another. This fascinating area of study frequently makes use of the latest scientific tests to establish their identity, yet the world of pigments is a comparatively well-known one, which has been the subject of several classic studies, such as the compilation by Gettens and Stout, originally published in 1942. As long ago as 1910, Laurie was able to write a useful account of Egyptian pigments, yet such is the increase in our knowledge that many discoveries since that time have resulted in the need for more recent review, such as that for Egyptian pigments by Lee and Quirke in 2001. Despite the recent date of that review, we have discovered the use in ancient Egypt of still more pigments, some of which will be discussed in this short paper. There are many historic accounts of how pigments were made, such as the compendium of principally Venetian manuscripts by Merrifield (1849) and «La fabbrica dei Colori» (1986), which contains information about use and manufacture.

For wall-paintings, we have a recent and useful review by Howard (2003), which concentrates on the Medieval period, and reveals the complexity of some of the colour schemes employed by Gothic and Mediaeval artists. Over the last fifteen years a series of volumes on pigment has been produced by the National Gallery of Art, Washington, which promise to remain standard works of reference for many years to come (Feller 1986; Roy 1993; Fitzhugh 1997), and which document preparation, identification, geographic location and period of use for many of the important pigments of ancient art.

The examination and characterization of pigments is an interesting task for the experienced conservation scientist, since some of them are relatively easy to identify, once their characteristics and the history of their use is known and understood. The task, therefore of analyzing these pigments should not be too difficult, since until recent times:

(a) Their number is limited to between 50-100 common types.

(b) The composition of most of them is well known and published.

(c) They can be categorized in a range of simple colours, so that the number of possible alternatives is further restricted (e.g.: a few blues, a few yellows or blacks etc).

Furthermore, one can make use of other information such as the time and geographic provenance of the work of art. In fact, it may have been retouched with pigments only available at a later date, in which case further information can be revealed.

All this is true when the pigments are pure and the colour can be easily studied and identified. In this case, simple observation, by use of the naked eye, or with the help of optical microscopy can help to solve the problem of identity. Microscopy can be carried out directly to observe the surface of the work of art, or more efficiently by means of a cross section, which allows for the understanding of the succession of layers of pigment which may be present. In case of doubt, a relatively simple X-ray fluorescence analysis (XRF) can help to solve the problem. For example, a red-orange pigment, for which XRF shows only mercury, allows for an almost certain identification: cinnabar. But it is not always that easy: in fact, X-rays penetrate beyond the surface, so that information from many layers may be mixed together, with the result that all elements heavier than sodium present in a multi-layered pigment or paint layer, would be detected. Therefore, when the analysis point selected is part of a white, pink, gray, yellow, orange, red or dark-purple colour, and XRF only reveals the presence of lead, the choice still remains among: lead white $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, used both as white pigment and as a substrate; massicot (yellow) PbO ; litharge (orange) PbO ; minium (red) Pb_3O_4 [$\text{PbO}_2 \cdot 2\text{PbO}$] or plattnerite (an alteration of lead white, which may be coloured dark purple or almost black) PbO_2 . In fact, oxygen, carbon and hydrogen are not visible by XRF.

In such a complex situation one may have to refer to some other analytical techniques, such

as X-ray diffraction or Raman spectroscopy, which can provide the extra information needed for an unambiguous identification of the compound rather than the elemental composition only, which is obtained using x-ray fluorescence analysis.

Another problem faced by the conservation scientist, is that the pigments which are present may be present in such low concentrations or amounts that they are not easily detected by the analytical techniques employed. When using micro-invasive techniques one tends to remove

samples of the order of the milligram, using a microscalpel or other small tool. This amount is usually sufficient to carry out an analysis, given the tremendous progress in analytical instrumentation provided by modern technology.

In the case of paintings, one must consider the fact that the painted layer, which is the ultimate goal of the analysis, is generally very thin ($\sim 50 \mu\text{m}$) and may represent only a small fraction of the sample removed. It is therefore not unusual for the pigment of interest to fall below the sensitivity threshold of the method employed. In this case, the experienced investigator may be able to work with small clues, determined from the context of the investigation.

For example, on the facade of the Casa Velasquez, in Santiago de Cuba, very small remnants of a turquoise blue were found. If this pigment proved to be Maya Blue, more evidence of the trade of the pigment from Mesoamerica to Cuba could be ascertained. X-ray diffraction showed quartz, calcite and gypsum only (See Fig. 1a). These minerals obviously did not justify the blue colour. After a simple acidic attack the pattern in Figure 1b was produced, in which palygorskite (the clay composing, together with indigo, Maya Blue, discussed later) is unambiguously present. The presence of this particular clay mineral in the context of this blue pigment is an important clue for the investigator that the pigment is, in fact, Maya blue.

If the pigments under investigation are known and properly described from previous studies the task of recognizing them is easier. Although very rarely, it is still possible to find «new pigments» or alterations such as bronze corrosion products, never studied before. Since the majority of the techniques work by comparison of the actual sample with standard references contained in databases, an unknown product may be very difficult to identify and to characterize.

As an example, let us consider the verdigris group of pigments, which are based on copper acetate. These can be simply made by exposing

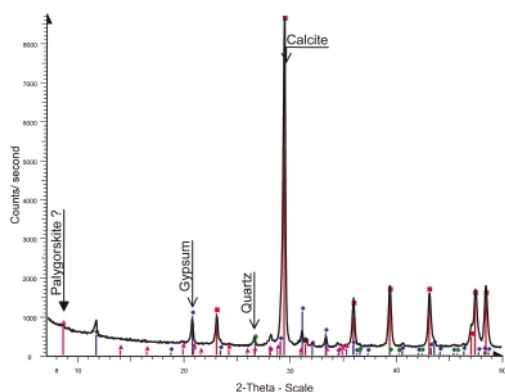


Fig. 1a – XRD pattern of a blue paint residue as sampled. There is no evidence of Maya Blue.

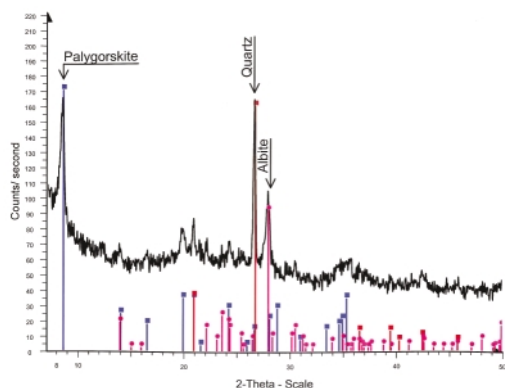


Fig. 1b – XRD of the same sample after acidic attack. Palygorskite was present.

copper sheets to stale wine or sour vinegar. The verdigris pigment group, consisting of various copper acetates, have been important as pale blue or turquoise pigments from antiquity, but especially in the late mediaeval and renaissance period, when numerous alchemical recipes were recorded for their manufacture.

Most of these recipes produce variations on the copper acetates, usually basic salts, such as $\text{Cu}(\text{CH}_3\text{COO})_2[\text{Cu}(\text{OH})_2]_2$, which is a light blue colour, often used as pigments for a variety of purposes (Scott 2002). These basic copper acetates could be recrystallized from vinegar solutions to form the neutral copper (II) acetate dihydrate, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, which is green in colour, and was preferable in oil painting, as being less susceptible to undesirable reactions or colour changes than the basic salts.

The identification of some later Medieval pigments based on the copper acetates can be a complex task, because the alchemical recipes for their preparation becomes increasingly subtle. For example, a fifteenth-century manuscript, MS 1243 in the Biblioteca Riccardiana, Padua, (Merrifield 1849), gives this recipe for a durable azure:

«Mix well one part of sal ammoniac and three parts of verdigris with oil of tartar until it is soft and paste-like....then place it in a glassed vessel under hot dung for a day; afterwards you will find that the green has turned to best blue.....»

«Oil of tartar» can be identified as potassium carbonate, and our synthesis in the laboratory to replicate this preparation, produced a mixture of blue and colourless phases, which gave a complex set of X-ray diffraction data partially matching potassium copper acetate $2\text{K}(\text{CH}_3\text{COO}) \cdot \text{Cu}(\text{CH}_3\text{COO})_2$ and ammonium copper acetate acetic acid $\text{C}_{14}\text{H}_{50}\text{CuN}_4\text{O}_{20}$. Thus, this recipe does indeed produce a durable blue colour, but identifying this particular blue concoction in an illuminated manuscript would be far from easy, especially since the pigment mixture may react with the media. The complete identification of some of these blue and green pigments in works of art continues to

be an interesting analytical challenge for the years ahead.

For other pigments of unknown composition it took years to unravel the mystery. An interesting example is that of Maya Blue. This beautiful pigment was made by the Maya by mixing the clay palygorskite with indigo and warming the mixture to around 100°C , which produced a blue pigment of exceptional stability and permanence. To try to discover some of the reasons for the remarkable properties of this pigment and its structure, not only the usual techniques of analysis have been employed, but also very advanced scientific tools from different disciplines, such as various types of spectroscopy, thermal analyses, electron microscopy, synchrotron radiation and neutron radiation for highly advanced diffraction studies. (See Chiari *et al.*, 2003; Giustetto & Chiari, 2003 and references therein). For Maya Blue, even a trial experiment for dating the pigment using ^{14}C AMS was performed, unfortunately with dubious results.

WHY DO WE ANALYZE PIGMENTS AT ALL?

To understand and reconstruct the painting technique (this has value on itself, just as in other branches of archaeometry).

To reconstruct the history of the use of a given pigment: this may be of great help in indirectly dating a painting or even more frequently, a retouch or repainting. A typical example is that of the «braghe» or censure panels used to cover some nudity in Michelangelo's Last Judgment. (Chiari, 1996).

To aid in the conservation of the work of art or to suggest possible problems or alterations of existing pigments.

Sometimes one can discover unexpected results: for example, Egyptian blue is one of the most widely utilized pigments of Egyptian and Western civilizations up to the fall of Roman Empire. It was widely used throughout the Ancient Middle East, starting from about 3600 BC, when it was first synthesized. It was

obtained by heating at 800-900°C a mixture of calcium carbonate, silica and copper compounds (possibly bronze scrapings). It is possible that the Egyptian Blue «secret» traveled along the Silk Road and reached China, where the manufacture was readapted to the local mineral sources. Han Blue, in fact, contains barium instead of calcium, and has more or less the same colour, while its homologous member containing strontium is Han Purple. It is universally accepted that the manufacture of Egyptian Blue, in spite of the recipe left by Pliny, was lost with the advent of the Middle Ages. Only in the second half of the 20th century was the recipe recovered thanks to modern analysis (Schippa and Torraca, 1957), which proved the formula to be $\text{CaCuSi}_4\text{O}_{10}$, identical to the rare mineral cuprorivaite (Pabst, 1959), although several 19th century scientists were beginning to unravel the truth, such as Sir Humphry Davy who wrote about the constitution of Egyptian blue in 1815, and was also able to synthesize the pigment. Pliny mentioned, as ingredients, sand and Cu compounds, without specifying if the sand was lime or silica based. Very likely, the sand that Pliny saw adding to the mix contained both silicon and calcium. The Renaissance trials to duplicate the process failed because the sand added was either silica- or lime-based. Therefore the unequivocal finding of Egyptian blue on a painting of the 12th century (Nicolaus Johannes Last Judgment in the Vatican Museums, unpublished result) may be puzzling. The pigment is not occasional or attributable to a few small retouches. On the contrary it constitutes the whole dark blue sky in the background. Do we have to, on the basis of one finding, change completely the theory regarding the history of Egyptian blue? Perhaps we should, if all other possible explanations of a well documented fact can be excluded. In this case there is a possibility that the pigment derives from an ancient small object made of sintered Egyptian blue, (of which there are many examples) and therefore the direct synthesis of the pigment is not the only possible interpretation. Nevertheless, there is a suggestion that in the

12th century somebody knew how to synthesize the prestigious pigment. For this reason it is important to analyze works of art and cumulate our knowledge, because only when several findings of this type will corroborate each other, an important chapter of art history may have to be re-written.

At least in one specific case a pigment (haematite) when used on mural paintings can give directly the date of a painting. This technique is recent and not completely developed (since it requires a non trivial calibration procedure). (Chiari & Lanza, 1997, 1999). It is based on the fact that the small grains of haematite are magnetized, and therefore can preferentially orient themselves toward the magnetic pole while suspended in the medium used to execute the mural paintings. When the paint dries, the grains are trapped in that position (Pictorial Remanent Magnetization, PiRM) and, provided that no change in orientation of the support took place between the moment of painting and the measure, one can retrieve the position of the magnetic pole by statistically interpreting the results of a number of samples (at least 7-8). The sensitivity of the method depends upon several factors, beside the measurement errors, such as the shape of the curve of the magnetic pole movements at the time to be dated. The Secular Variations of the magnetic pole position are not well known due to the lack of precise data, but at least from 1820 on (when precise measurements started to be carried out) they are large enough to guarantee a sufficient precision (10-50 years). The winding of the curve creates intersections and therefore multiple dating for the same magnetic values. For this reason, some ideas of the date may be required to discriminate amongst various possible dates. The application of the method is limited since it is rather destructive (multiple samples of about 1 cm² need to be retrieved for the measurement). In many situations though, given the extremely common use of haematite for mural paintings, both in fresco and tempera, it is possible to find borders or solid red backgrounds that can be reasonably sacrificed

in order to obtain a dating that cannot be otherwise achieved.

HOW DO WE ANALYZE PIGMENTS?

The number of techniques now available is large. The specialist can therefore pick and chose according to the type of object to be analyzed, its value, the importance of the information retrievable, the instruments which are available, the time and the budget for the work. In the last few years the technological advance in the instrumentation was such that the amount of sample needed for an analysis is often under a milligram, thus allowing one to classify most techniques as micro-invasive. Furthermore, the number of techniques which can be called non-invasive, since they do not require a sample to be taken at all, increases every day. Often the information retrievable using non-invasive techniques is not complete, but the use of more than one complementary technique normally produces the requested results. The most important thing for the analyst is to be result-oriented and not instrument bound (although one tends to be naturally attached to the technique that one uses more frequently and, knowing it better, to attribute to it a larger capability than it has).

Often the simple techniques of optical examination and micro chemical tests can provide excellent results with pigment identification problems. This is because of the limited number of them and the acquired experience of the optical microscopist, which renders polarized light microscopy such a useful tool for examination and identification.

A trained eye can recognize without fault several pigments. This may lead to the temptation of just «trusting your eyes». That can be dangerous because many times, together with the main pigment that one may be able to recognize at sight, there are smaller quantities of other pigments, which can be interesting. In other instances our eye may completely fail. It is the case of a curious finding, still not understood at all: in the small Church of San

Fiorenzo, in Bastia Mondoví (Piedmont, Italy) there is a 1474 fresco cycle: on the cupola a Christ figure is holding a white scroll. The eye immediately suggests «Bianco di San Giovanni», which is a form of good-quality calcite, but since it could have been lead white as well, a small sample was taken to be analyzed by XRD. Very surprisingly it turned out to be glushinskite, a magnesium oxalate. The most simple explanation was that the mortar contained magnesium and the oxalate was the result of a reaction similar to the one producing weddellite or whewellite (the two well studied calcium oxalates). Analysis of the mortar showed that it was made of pure calcite and glushinskite was limited exclusively to the white manuscript. Other white parts in the same painting only contained calcite (pointing to Bianco di San Giovanni as white pigment). These types of findings are intriguing, puzzling and many times are not published at all (it is hard to write even a short paper on a single analysis, quite simple *per se*, leading to a sporadic finding). On the other hand publishing sporadic result may be the only way to group them with those of other researcher and determine if they are indeed a simple curiosity after all, or the result of the application of a previously unknown technique, although rare. In the case of San Fiorenzo, the only explanation one can imagine for the result is that a painter in 15th century found some pure magnesium oxalate (or some alchemist prepared some for him) and used it as a pigment. But until at least some more examples can be found, the whole matter remains a simple curiosity. Another example of this type is the find of anglesite (lead sulfate) on a *lunetta* attributed to Antelami and located on the entrance of the Sant'Andrea church in Vercelli, Piedmont, Italy (Fig. 2a). The preparation layer for all faces and hands of the protagonists of the scene is made of lead white. The background, of a slightly warmer tonality, more similar to the stone used for the carving is instead anglesite, i.e. lead sulfate. On the top of the *lunetta* there is a frieze portraying flowers and an angel who takes to heaven San Andrea

soul. All faces and hands are made with anglesite. This substance is not known to be a pigment, to our knowledge. Was it brought back from England by the bishop who built the church? Was it commonly used but we do not know it because we trust our eyes too much?

Another interesting example where simple assumptions as to the nature of a white pigment were proved to be erroneous concerns the case of an Egyptian New Kingdom wooden painted Ushabti in the collections of the Department of Religion, University of Southern California. A micro scalpel was used to obtain a minute sample of pigment which was mounted for polarized light microscopy. This sample proved to have all of the optical characteristics of calcite, and since this is well-known to have been extensively employed by the Egyptians as a white ground and paint, this seemed perfectly reasonable and in accord with visual estimation. We decided to check on the identification of calcite by x-ray diffraction of another micro sample from the Ushabti, but



Fig. 2 – Sant'Andrea in Vercelli. Lunetta attributed to Antelami. The white pigment on the faces of the main scene is lead white, as expected. In the top frieze and in the background anglesite (lead sulfate) was used instead.



Fig. 3 – Egyptian Ushabti. The white paint with an underlayer of calcite and a finishing layer of tridymite can be seen near the waist.

this produced a surprise: the white pigment identified proved to be tridymite, which is a metastable form of quartz, usually associated with the high-temperature decomposition of alpha-quartz. As a result of this, we decided that this apparently simple white pigment required further study: The pigment micro sample used for the diffraction work was transferred to a stub and examined in low vacuum mode in the ESEM. The first scanning electron photomicrograph showed the presence of rhombohedral calcite crystals, which was confirmed by EDAX analyses.

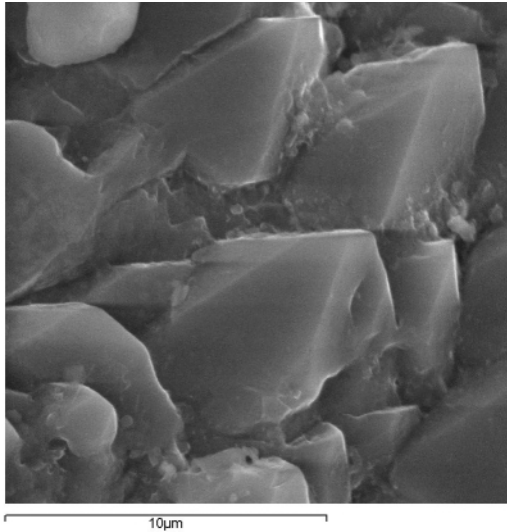


Fig. 4 – View under the ESEM of the tridymite crystals forming the outer white pigment layer overlying calcite in the Ushabti shown in Figure 3.

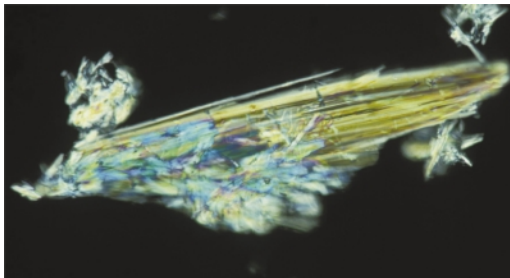


Fig. 5 – Verdigris curved crystal array of acicular aggregates (cross polars x120) from a laboratory synthesis of the verdigris used on the German Von Ems manuscript.

However, when the particle on the stub was rotated into a different orientation, the scanning electron image revealed an assemblage of tiny hexagonal prismatic crystals, obviously not calcite. Further study showed that the Egyptians had used calcite for the ground of the Ushabti, and had employed tridymite as the final white paint, since the white of the tridymite is even purer and more intense than calcite. The two whites can be clearly differentiated by crystal morphology.

Tridymite actually forms hexagonal crystals as a pseudomorph after beta-tridymite, and is itself monoclinic, but the preservation of the pseudohexagonal variety is quite common and an ESEM photomicrograph of the tridymite from the Ushabti is shown in Figure 3. Where does this tridymite come from? The mineral forms from quartz on heating to temperatures between 870-1470°C and can be found as a natural mineral or could have been prepared from heated and crushed quartz. Tridymite is a metastable polymorph of quartz, but the fact that it has survived here on the Egyptian Ushabti shows that it can remain stable for thousands of years without change. Until further examples are found and studied, we will not know how common the use of this white pigment was in ancient Egypt. (See Fig. 4).

Another difficult case is provided by a German illuminated manuscript of the 14th century AD in the collections of the J. Paul Getty Museum (Scott *et al.*, 2001). This manuscript, the Barlaam und Josaphat, by Rudolf Von Ems, with illustrations by the Diebolt Lauber Atelier dates to 1469 AD. The manuscript is on paper, which has become embrittled, with the result that many small pieces have broken away. One of these detached fragments with red, light green and dark green pigment was available for taking a micro sample for further study. The red pigment exhibits a pronounced craquelure, including severe cupping and cracking in some areas and a fine white precipitate, having the appearance of a salt, can be seen on the red under the binocular microscope. We attempted to identify the green pigment using *in situ* examination on a Siemens D5005 x-ray diffractometer equipped with Gobel mirrors. This was not successful in giving a good diffractogram, given the extremely small amount of pigment. We next tried FTIR with similar problems: no identification could be made from the spectrum obtained. Application of 0.2 microlitres of water also failed to produce any extractable components. Because of these difficulties we prepared a micro sample of the green pigment for polarized light

microscopy, which showed particles of RI less than 1.662 which were not malachite, since the refractive index of malachite is greater nor of chrysocolla, whose colour and conchoidal fracture are characteristic. A micro sample of the green pigment was then examined using Debye-Scherrer x-ray powder diffraction, when a reasonable set of d-spacings could be measured, but once again there was a problem: the set of d-spacings did not match any known mineral defined in the ICDD files or other pigment types published in the conservation literature. The problem was only solved since for the three years prior to this study we had been working on issues of identification and synthesis of verdigris pigments, both from literature sources and historical recipes that were replicated in the laboratory. The XRD data showed a close match to verdigris salt B4, of nominal composition $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ which is a water-soluble verdigris variety, made by the action of sour vinegar on copper strips at high humidity. The binder that had been used for this pigment was found to be egg by GC-MS, and since the proteins in the egg media interacts with the verdigris pigment to produce a copper proteinate green, this could help to explain some of the difficulties of general identification, as well as the embrittlement of the paper support due to the leaching of the soluble acetate and cupric ions, well-known to be very damaging to cellulose fibers. A darker green copper-containing pigment layer which had been applied over this underlying green was also examined and its binder determined to be glue by GC-MS analysis. This material, which is non-crystalline appears to be made from a verdigris pigment dissolved in glue to make a thicker, more opaque dark green paint to apply over the verdigris in egg tempera medium used for larger green areas of the design. The red pigmented area also proved to be very difficult to identify. ESEM studies showed that the pigment consists of a very uniform layer with sharp-edged cleavage. ESEM-EDS examination revealed mostly calcium, aluminum, sulfur, oxygen and carbon

as the major elements present. The results of further studies suggested that an organic red pigment had been laked onto an aluminum-based mordant, such as alum, (potassium aluminum sulphate), which was well-known from early periods. Initially we used non-destructive fluorescence spectrometry employing remote sensing with a fiber optic probe to identify the red colourant. This was not successful and our attempts to match a micro sample employed for UV/Vis spectroscopy with known standards also failed. We eventually succeeded using thin layer chromatography. The sample was evaluated together with thirty-four standards, and a match was found with rhubarb. To further evaluate the data from the UV/Vis spectrometry, a new spectrum of rhubarb root in concentrated sulphuric acid was run and found to be a close match to our manuscript sample. Rhubarb root (colouring agent chrysophanic acid), is a red in either acidic or alkaline conditions. Since rhubarb was used as a fabric dye it is possible that this pigment began as a clothlet dye that was then extracted and laked with alum for use on the manuscript. The palette of this German manuscript is quite restricted and uses a limited range of colours and inexpensive materials; which may explain the use of simple verdigris and rhubarb as the principal palette for this impressive manuscript. Instead of expensive cinnabar and ground malachite, the restricted palette makes good use of what were probably locally made materials. The description of this analysis may give an idea of how difficult the identification of a pigment could be. (See Fig. 5).

Further difficulties with green pigments were found with a late Greco/early Roman Egyptian cartonnage fragment from the Archaeology Research Collection of the Department of Religion at the University of Southern California. A light green was analyzed by XRF *in situ* and showed strong peaks for iron, with minor peaks for potassium and magnesium, suggesting that this pigment is a green earth. XRD also *in situ*, using a Siemens D5005 and Gobels mirrors showed that this green was a mixture of celadonite and glauconite, typical

for green earth pigments, but very rarely mentioned in Egyptian contexts where the usual greens encountered are malachite or Egyptian green frit. The eye of Horus on this cartonnage is painted in a dark olive-coloured green which is an unusual shade, and has in places decayed to a brown discoloured surfaced. XRF analysis showed the presence of copper, while polarized light microscopy revealed isotropic particles, clearly non-crystalline which could either be a copper resinate or proteinate. GC-MS analysis revealed the presence of a glue media and the presence of copper in the green pigment suggests that it was either made with a verdigris pigment dissolved in glue to make a copper proteinate, or the verdigris has reacted with the glue media over time to form the copper proteinate green. Since the reaction between verdigris and glue is fairly rapid, this would soon have been noticed and may have been deliberately employed by the ancient Egyptians.

CONCLUSIONS

As the above examples show (and the list can be much longer) the task of identifying pigments on art objects can be very interesting and challenging. It is a common mistake to think that the number of pigments used by man is limited and therefore their identification is straightforward. In fact, often what remains on the decorated surface is not the original pigment but an alteration, which depends upon the substances which came in contact with the work of art accidentally, from the exterior world, or that were used during the manufacture of the object for various tasks. When this happens in general any reference standard from the pigments class is lost and the search extends to a much larger set of chemicals. Unfortunately, all the restrictions in sampling dictated by the necessity of non-intrusive analysis remain. This is perhaps why, beside the beauty of dealing with wonderful masterpieces, pigment analysis still remains a very fulfilling and challenging endeavor.

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