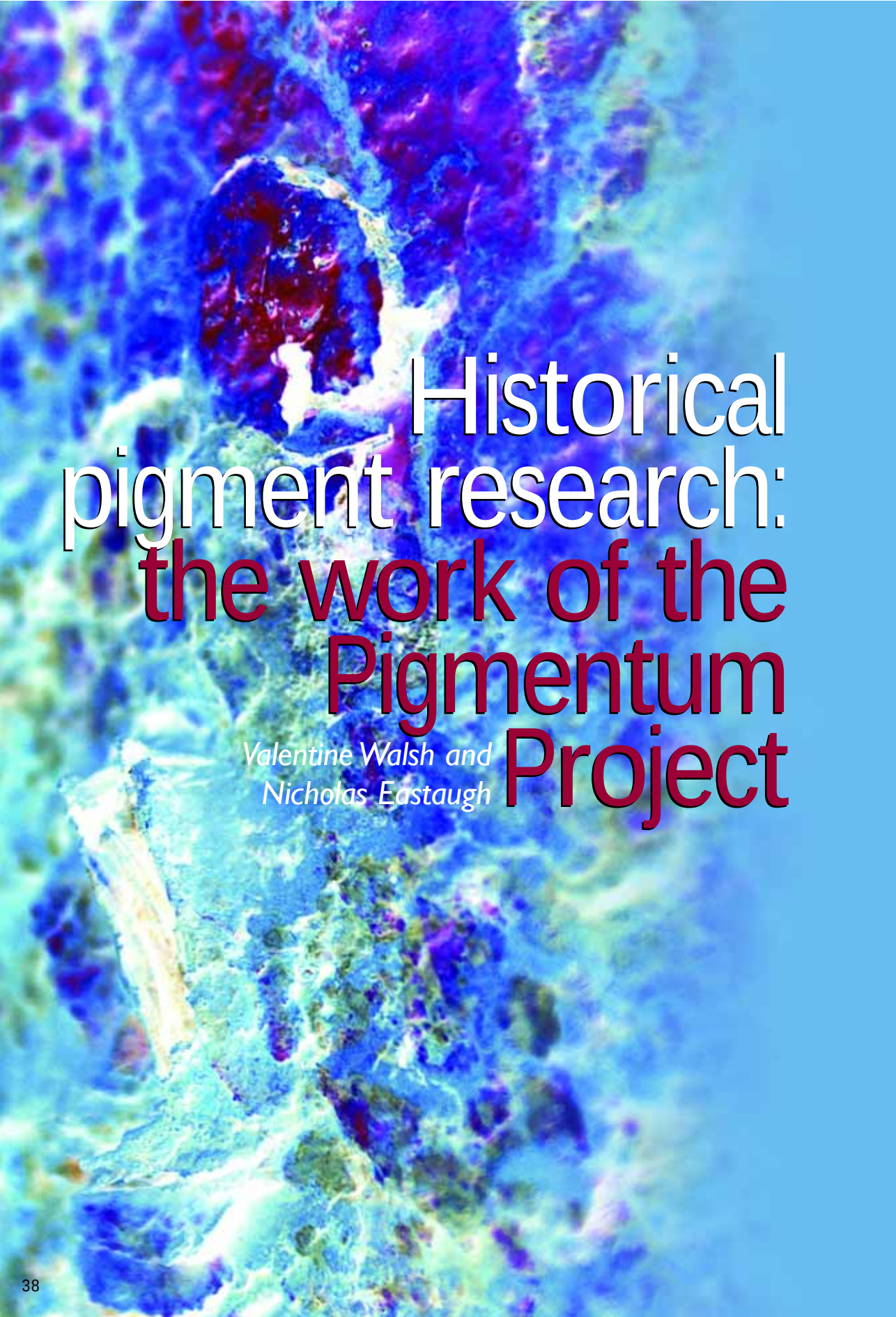




Historical pigment research: the work of the Pigmentum Project

*Valentine Walsh and
Nicholas Eastaugh*

Research into historical pigments, particularly as they are used on works of art, is an expanding field. It aids not only a growing understanding of artist's techniques, but also historical pigment manufacture and trade. The Pigmentum Project was established to investigate historical pigments, bring sense to their characterisation and thence their categorisation, and otherwise shed light on their history, use and manufacture. The project has grown from its original remit of creating a reference work on the optical microscopy of pigments to encompass a far greater range of analyses and documentary research. Presented here is a short overview of the work of the Project.

Historical pigment research is one of those fields that fall under the heading of new subjects that have been around for a long time. While analysis of pigments used in the past can be traced back until at least Sir Humphrey Davy¹ in the early Nineteenth Century, it is perhaps only with the first short monographs on specific pigments in the 1960s-70s² that we have had systematic modern studies from which this analytical discipline can grow. Consequently the scientific examination of historical materials of art (along with documentary research into materials and techniques) is now

a highly dynamic field. Extending from the appreciation of an individual painting's creation or the common working practices of a specific artist, to the broader materials and techniques of a particular time and place, to the wider questions of the trade in ideas and materials that took place historically, knowledge of what paintings are made of connects us directly to the past. It increases our knowledge of historical, social and economic production of art and artefacts as well as being crucial to objective accurate dating of many objects.

We cannot (and should not) separate the descriptions of the past, from what we gain from contemporary 'hard' analysis.

Currently the field is at a stage of development where the lessons of the first generation of analysts have been absorbed, leading to a degree of re-evaluation. For example, a number of major collections in national galleries around the world have been sampled extensively for analysis in the past 30-40 years in support of conservation and art historical scholarship. This has provided us with great insight into these paintings. However, it also means that there is a resource that we can now re-visit with today's analytical tools, developing and refining new understanding for the emerging field of 'technical art history', where the materials and techniques of paintings and other works of art are studied.

It will probably come as some surprise to those in other disciplines that there has not (until recently) been any comprehensive study of historical pigments – the full range of materials that has been used in the past for pigments, how to organise or

name these systematically, how to characterise them fully, and so forth. As a response to this gap the Pigmentum Project was established in 2000 as a collaborative venture between a paintings conservator, a scientist who works on analysing art, an 'archaeo-geologist' and a specialist in Raman spectroscopy of historical pigments. The original aim was to develop a resource for polarised light microscopic (PLM) analysis of historical pigments (a standard method in the field), but it was realised from the outset that larger questions needed some coherent response if the effort was to have any enduring utility.

Since that time the original aim of the Project has achieved fruition through the publication of two books, one on the history, chemistry and terminology of pigments, the other to satisfy the initial desire for an atlas of historical pigments under PLM. However it has acquired a life of its own, and we continue to pursue broad research



Fig. 1. A drawer from the Historical Hafkenschied Collection, Teylers Museum Haarlem.



Fig. 2. Goeree¹⁴ Painting handbook, 1756.

topics in the area. Here we will outline some of the key sections of the project's work and describe the directions in which we are going.

Historical documentary research

The discovery of past use of methods and materials by artists can be approached in several ways. Essentially either through looking at what people say they did, or by analysing their surviving artefacts. Both are equally instructive and we cannot (and should not) separate the descriptions of the past that are left to us, from what we gain from contemporary 'hard' analysis. The historical documentary record provides us with explicit evidence of what artists in the past considered special or distinctive about materials, why they chose to use one, in a particular way, over another, what they were called, where they thought they came from, and (not least) what they paid. Conversely, our analyses reveal what they actually used and how, as well as perhaps where they came

from and what has happened to them over time. In the process we can also illuminate much of the social and economic structure of art production.

In the pursuit of the definitive pigment list the Project reviewed many sources, from the earliest classic texts such as Theophrastus³ and Pliny⁴, through mediaeval and Renaissance treatises such as Cennini⁵, to 'modern' books for artists and the pigment trade from Field⁶ to Buxbaum⁷. In parallel we studied our colleagues' publications on the results of analyses of artefacts, as well as modern chemistry and geology as it related to the compounds and minerals that we came across. In all, approximately 2500 separate sources were examined, from which we culled a similar number of pigment terms, both historical and scientific. Our ultimate list of compounds runs to around 700 (though this excludes several modern categories such as azo compounds, which are hugely varied), far more than previous lists which stop at ~100.

Taxonomies and thesauri

If a sign of maturity in a field is that it has its own descriptive systematics, then historical pigments has just reached that point. Although there have been partial attempts in the past to arrive at a list of pigments used historically, none had rigorously tackled both terminology and the underlying chemistry until our own survey. Even those

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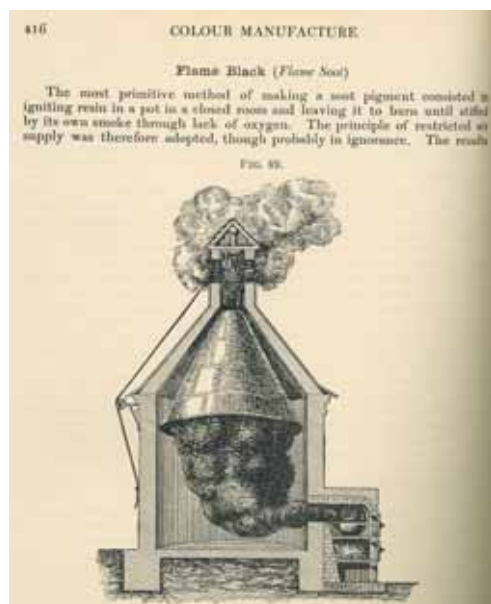


Fig. 3. A page from Zerr and Rubencamp¹⁵, a treatise on Colour Manufacture, showing the recipe for making flame black.

commonly cited, such as the *Colour Index*, did not serve the purposes of organising historical pigments so as to understand the underlying relationships and groupings. Consequently, we devised a new taxonomy⁸ that specifically dealt with the chemistry of pigments. With terminology, use of names has been so loose in the past that we found the most appropriate means of expressing relationships was through developing a thesaurus⁹.

Our taxonomy is based on the chemical composition of elements, functional groups and crystal structure, but further differentiates according to source or preparation. It also distinguishes clearly between materials derived

directly from natural sources (minerals and dyes) and those that are manufactured synthetically. Hence we categorise the blue mineral lazurite as fundamentally distinct from its synthetic analogue ultramarine, important for us since the mineral was used widely historically, but the synthetic product only appeared in the 1820s. Additional levels of characterisation then reflect different manufacturing processes or mineral sources.

The pigment thesaurus on the other hand evolved as we catalogued the many terms we discovered. By extensive examination of names, and investigating and recording the connections between them, a network of relationships and ambiguities developed. Now embedded in our *Dictionary of Historical Pigments*, links of different types (broader and narrower terms, related terms of different kinds and so forth) were detailed.

The pigment collection

The Project also set about systematically acquiring a reference library of pigment related books and papers (including some rare antiquarian texts) and, more importantly, a reference collection of historical and modern pigments of good provenance that now numbers in excess of 2000 specimens.

The philosophy behind the pigment collecting process was essentially to create a resource that reflected the diversity of what we had discovered from the documentary research, mirror (as far as possible) our pigment taxonomy, and provide a set of samples on which we could base our analyses.



Fig. 4. Detail of a portrait, Studio of Holbein. Photo taken under 10x magnification, incident light.

In practice this meant not only acquiring specimens of individual compounds or minerals that we knew had been used in the past, but also multiple examples so that we could examine variability or, at least, determine whether we could

detect such differences. It was apparent that there were likely to be differences according to source (where a particular mineral had come from; what specific manufacturing process had been used), so again multiple specimens were needed.

Pigments of recent origin in the collection are largely from commercial pigment suppliers; mineral dealers and chemical supply houses, as well as being specifically manufactured pigments (according to historical recipes) by us or by colleagues who have been kind enough to share their samples and research. Others still are from mineral collections, carefully sourced and with good provenance.

Additionally, we have had the opportunity to acquire historical material. These pigments come from a series of collections held by various institutions that generously allowed us to sub-

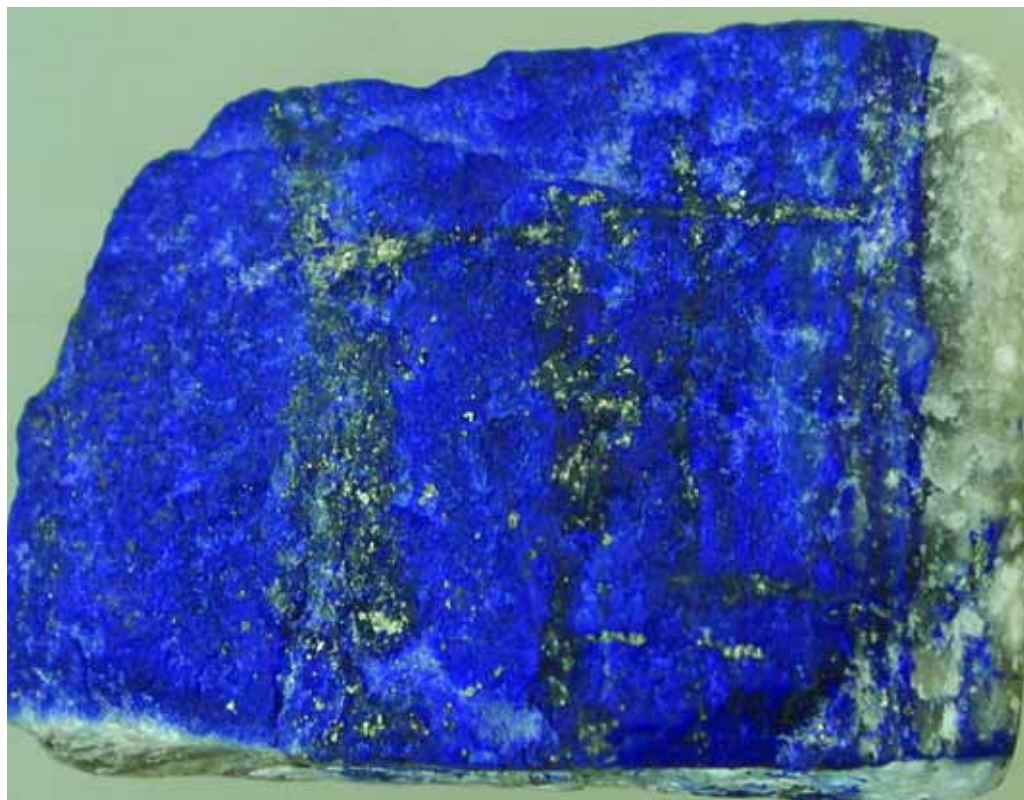


Fig. 5. A piece of lapis lazuli from which the mineral lazurite is obtained to make the pigment generally called ultramarine.



Fig. 6. Pigment pots from a 19th century travelling painter's pigment box.

sample them. Extra criteria here were that the origin of each sample must be entirely clear and that samples should not come from historical objects (where the pigment had been used in the creation of an object thus possibly leading to confusion as to what the 'pure' pigment contained). Amongst the ever-expanding collection of pigments we now have a group from the Roman site of Pompeii, where bowls of unbound pigment were preserved by the catastrophic eruption of Vesuvius in 79AD. We also have samples from the palette of the artist J.M.W. Turner, who left the contents of his studio to the British nation after his death. However, a major highlight for us is a virtually complete set from the so-called 'Hafkenscheid Collection'.

The Hafkenscheid collection belongs to the Teylers Museum in Haarlem, The Netherlands. This is a fascinating example of a physical archive that was created in the early to mid-nineteenth century by an Amsterdam trader in paint, turpentine and gums. His stock came from both Europe and further afield, including Africa, the East Indies, Brazil, Java and China, so the collection also reflects a worldwide perspective. Further, the collection's inventory (along with the specimen labels) gives insight into the wide range of names applied to pigments and through analysis, how we should interpret these traditional names. A favourite is papegaairoen, the visually arresting 'parrot green'

that in this case appears to be copper formate but which on other occasions could be the toxic 'emerald green', copper acetate arsenite.

Ours is a collection that is still growing – we have recently received a generous donation of several hundred modern azo and polycyclic pigments from the Tate Gallery, London, for example, which we will be adding to our Raman database. Further pigments will be acquired as we research particular topics. An example of this is systematically prepared pigments such as samples from our research into the formation of lead chromates under different manufacturing conditions.

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Data collation

One of the major headaches of the project was how to deal with the sheer volume and diversity of data that we were collecting. Although this is not an uncommon problem, we did nonetheless have an especially diverse set of requirements, which meant that no convenient off the shelf solution existed. For example, it was essential for us to be able to combine highly formatted text (including multiple languages and chemical formulae), microscopy and other images, analytical data in various formats, and so forth.

The primary solution has been to develop our own database system. Now having evolved through several cycles, we operate a program written by one of the team in-house known as *Lazurite* (after the blue mineral within ultramarine). A reduced, read-only version is used to distribute the CD-ROM version of the *Pigment Compendium* books, while the full version is run on a network so that team members can query and update information on an ongoing basis, or run their own independent copies. In this way it is hoped that common data formats will provide a basis for standardisation of analytical protocols in the field and reliable exchange of information between researchers, be

they art historians, scientists, conservators or even artists. We aim to make this generally available later this year.

The analytical database

As mentioned, the project initially set out to illustrate pigment characteristics by polarised light microscopy. Conservators and conservation scientists, the community in which we most often work, have adopted PLM widely as it can distinguish numerous pigments. Moreover, a polarising microscope is also a relatively affordable tool. Many of the techniques used though derive from geologists who apply PLM to identify

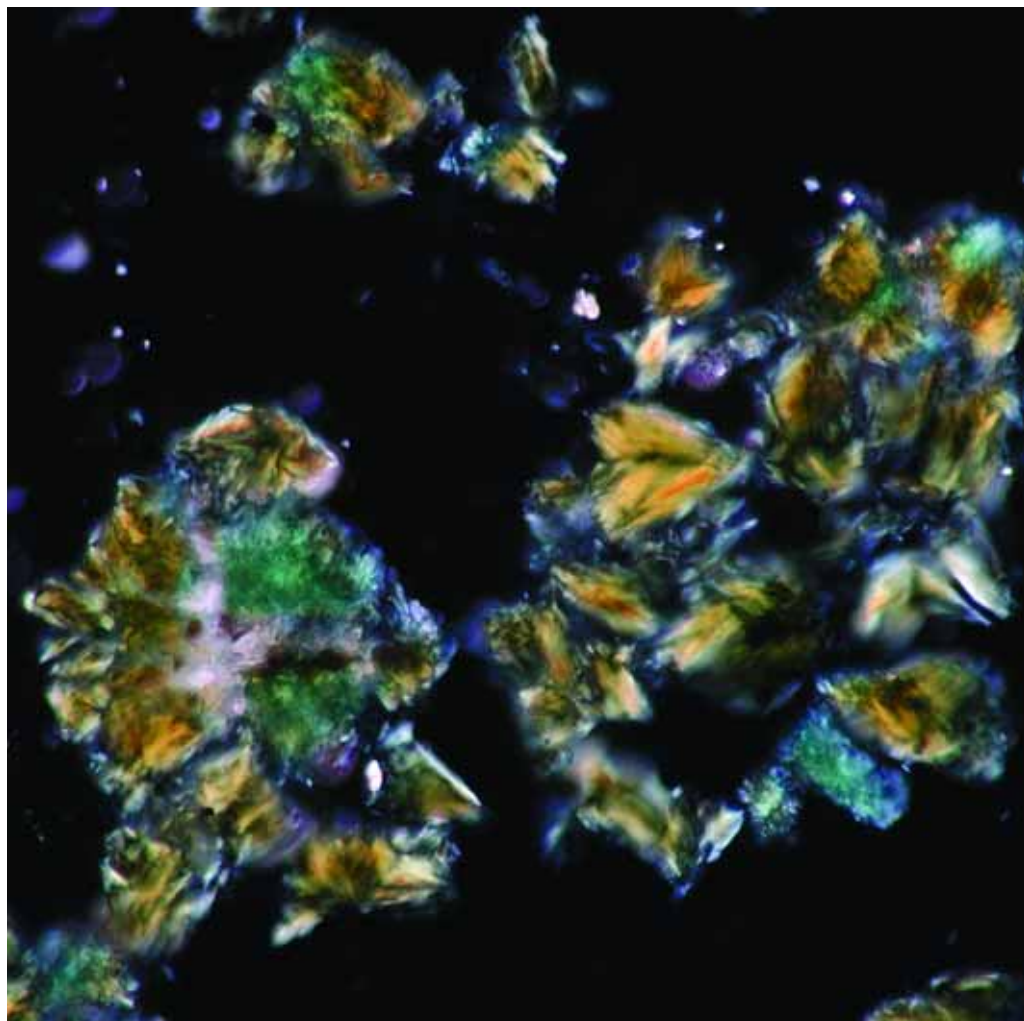


Fig. 7. Dispersion of variolitic aggregates of celadonite pigment, in cross-polarised light (fieldwidth 350 μm).

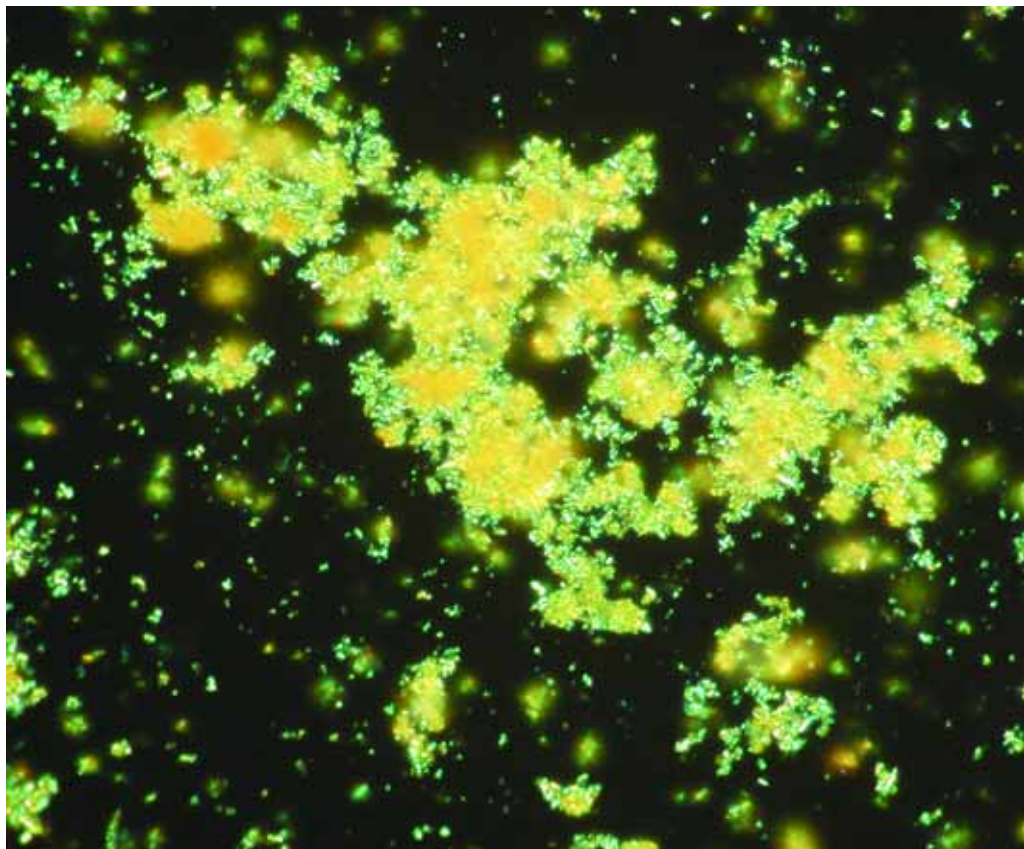


Fig. 8. Dispersion of lead chromate pigment, phoenicochroite type, in cross-polarised light (fieldwidth 143 μm).

minerals; it is a natural extension to identifying pigments as these also have, in the great part, crystalline structures. Examining pigments however poses some distinct problems when compared to minerals, such as the fact that pigments taken from works of art cannot be sliced into thin sections but must be mounted as particulate dispersions ('grain mounts' to the geologist). These have varying size and thickness of particle and the normal characteristics expected of thin sections are hence often more difficult to distinguish. At the same time particle morphology has much to tell us about the pigments, from revealing characteristic features that aid identification, to telling us about formation and modificatory treatments.

However, the utility of the pigment collection has not finished with the completion of this. A major

element underpinning the PLM publication was confirmatory analysis by complimentary techniques, primarily (but not exclusively) with a combination of elemental analysis and crystal structure determination. It became clear though that, at the very least, a proper understanding of some items in the collection required other forms of analysis. Moreover, the utility of a comprehensive, systematic, set of data using multiple independent methods of analysis was not lost on us. Thus it was a natural development to establish a full and systematic survey of the collection by a range of standard analytical techniques used in this field.

The primary set now includes:

- Polarised light microscopy
- Scanning electron microscopy
- Energy dispersive X-ray spectrometry

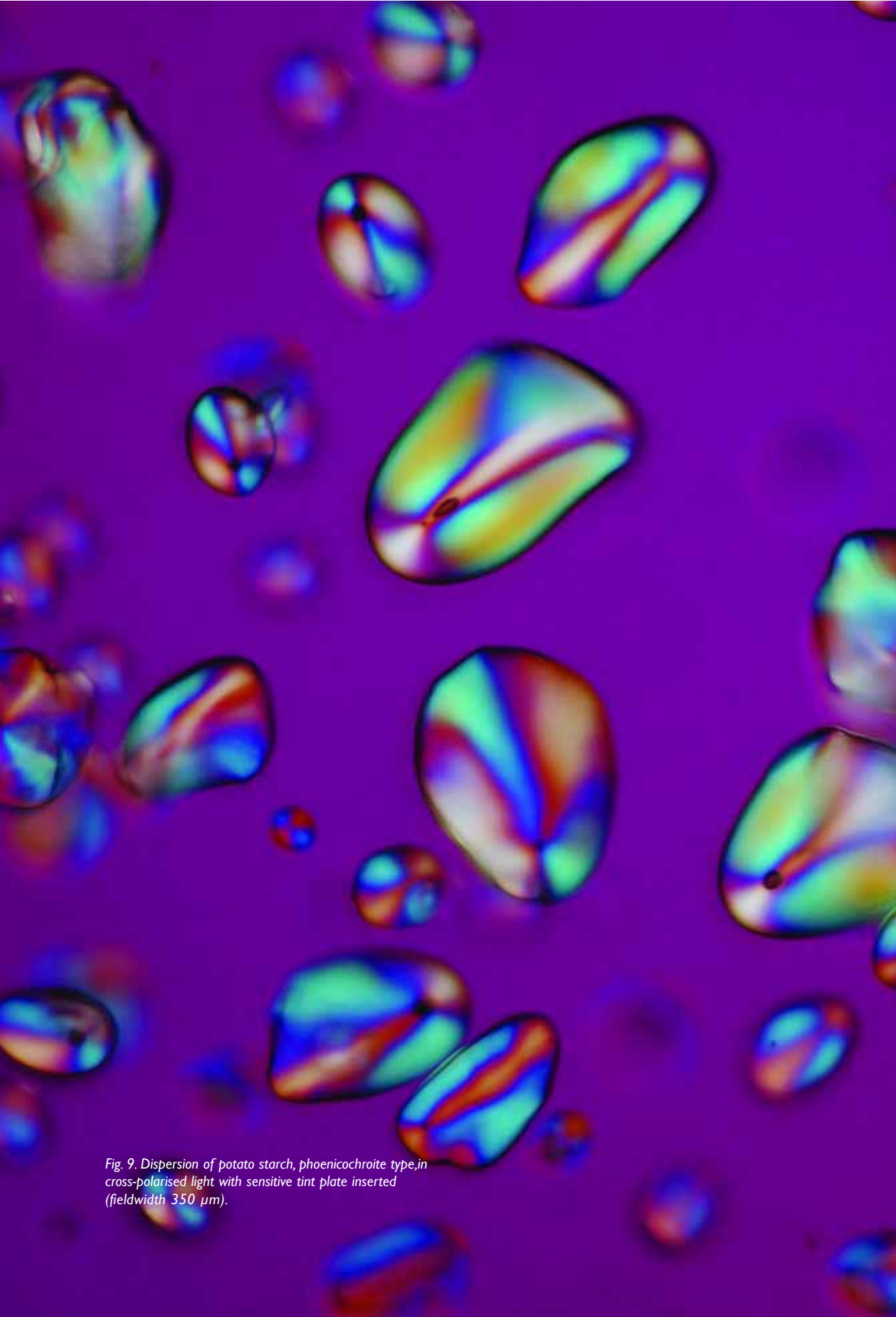


Fig. 9. Dispersion of potato starch, phoenicochroite type, in cross-polarised light with sensitive tint plate inserted (fieldwidth 350 μm).

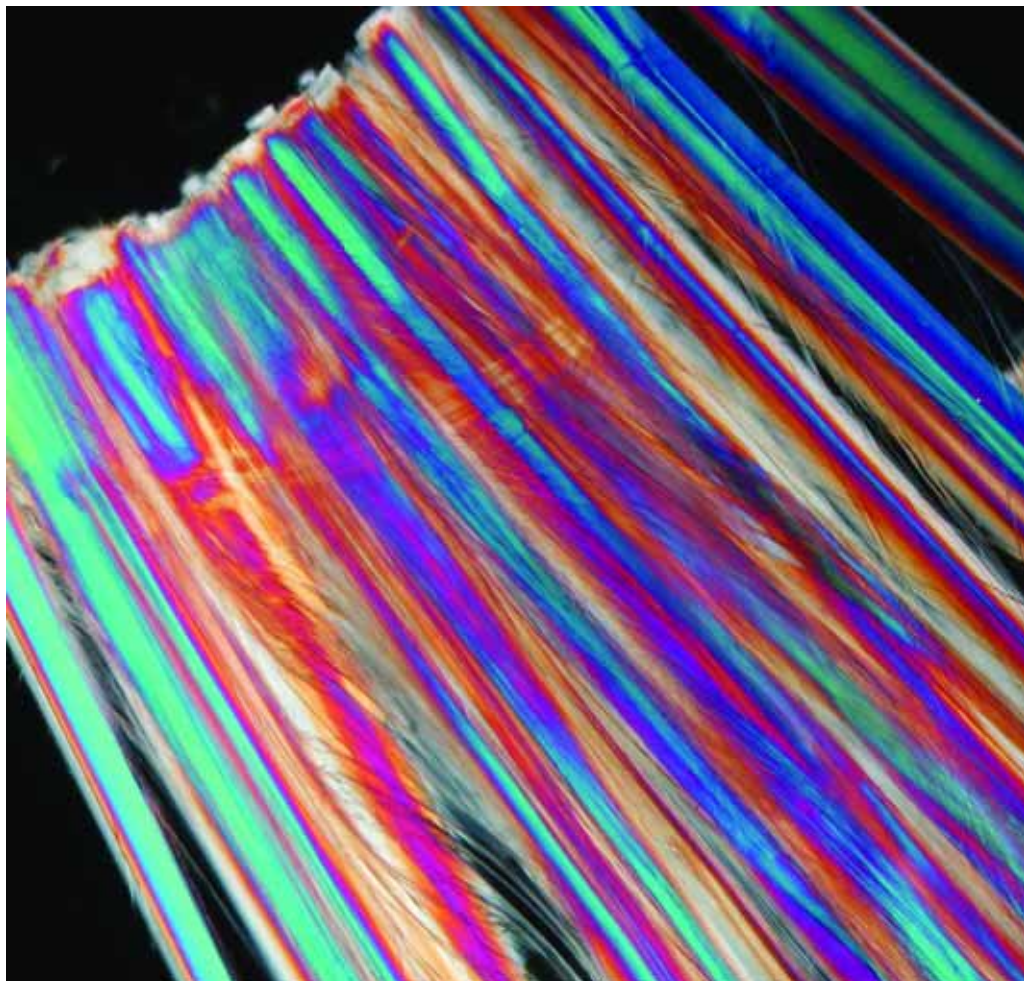


Fig. 10. Dispersion of asbestiform mineral, chrysotile, in cross-polarised light (fieldwidth 1.432mm).

- Fourier transform infrared spectroscopy
- Raman microscopy
- UV-visible-near IR (micro)spectrophotometry
- X-ray diffraction

In addition, various other techniques are used as and when necessary. For example, it is appropriate to analyse so-called 'lake' pigments (dyestuffs deposited onto an insoluble substrate such as aluminium hydroxide) using methods of organic analysis such as high performance liquid chromatography (HPLC) and a number of samples in the collection have been studied by this or related means. Many of these rely on microscopical methods of course, the quantities of some samples we have being almost vanishingly small. We intend to make the results of the analysis

generally available so that standards evolve and comparisons become possible.

Such systematic research has brought about a number of benefits. The ready availability of a strongly proven collection of data is obvious; we can, for example, not only make studies of pigment types or classes but also determine and disseminate the most effective means of characterising specific pigments to the degree of detail required. Three projects carried out with MSc students illustrate this.

An example of our development of analytical methodology is a recent study on green earths.

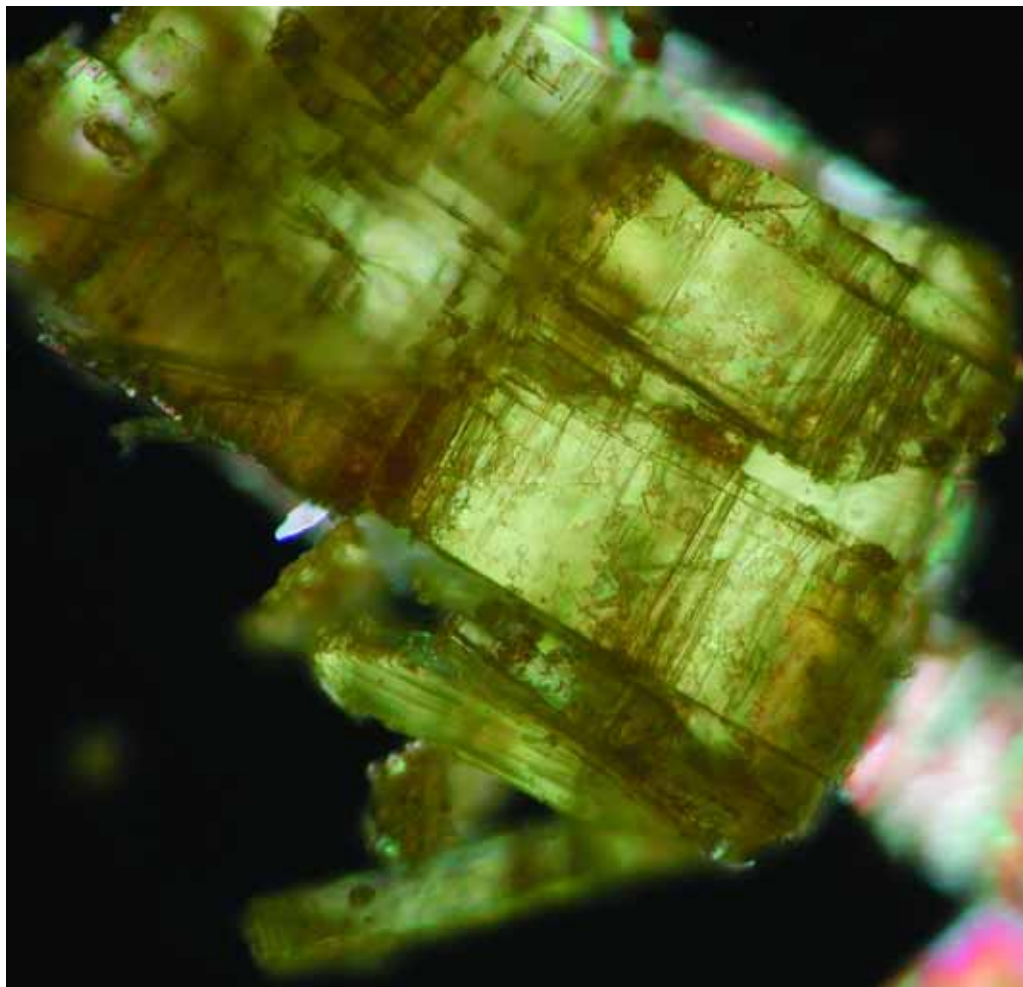


Fig. 11. Dispersion of orpiment pigment in cross-polarised light (fieldwidth 350 μm).

Green earth is derived naturally, gaining its characteristic colour primarily from several minerals, most commonly celadonite or glauconite (to a lesser extent chlorite and cronstedite also). Distinguishing these minerals is very difficult as they have very similar chemical composition and morphology. Given that we usually also have exceedingly small amounts of material to work with, characterisation beyond 'green earth' is highly problematic. However, working with our collection, Lisa Sertic¹⁰ has recently researched the formation of these minerals and proposed that differences in their geological formation can be exploited to differentiate them in a systematic manner. As a first step samples are examined by PLM, from which we

can ascertain the presence of characteristic associated minerals. Three further techniques can then be used selectively or in combination to provide the most reliable results. FTIR microscopy can give spectra where celadonite and glauconite are distinct. X-ray diffraction also gives a means for differentiation, however we found, in practice, that this relies heavily on the experience of the analyst for interpretation. Finally, elemental analysis can show clear chemical differences. From applying such an approach to the pigment collection we can now assign samples more reliably into their correct categories. This has also made a better methodology available for day-to-day analyses of paintings.

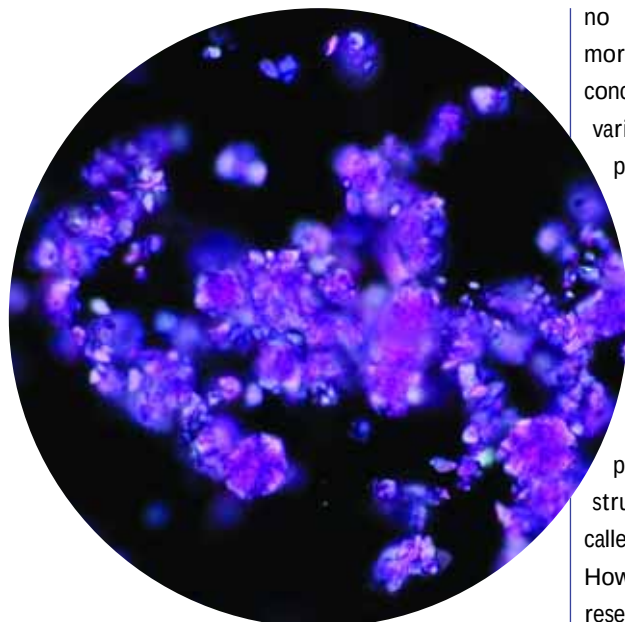


Fig. 12. Dispersion manganese phosphate pigment, in cross-polarised light with interference colours masked by pink-violet body colour (fieldwidth 143 μm).

Two further examples of studies of individual pigments and pigment groups follow. The first, lead chromate, shows how study of the chemistry (in this case the formation conditions) affects the final particle morphology. The second, 'Prussian blue' (various hexacyanoferrate compounds) reveals a deeper understanding of both the past manufacture of these and the appropriate analytical methods to use in differentiating the historical types.

Joanne Lau has recently found that it is possible to discern differences in chromate pigments according to their conditions of manufacture¹¹. Various lead chromate pigments were made according to historical recipes and these, along with the chromate pigments in the Pigmentum collection, were examined morphologically using field emission scanning electron microscopy and X-ray diffraction. Various factors were altered in the manufacture. The pH and temperature as well as concentration of sulphuric acid were varied incrementally in the formation of lemon chrome samples. It was found that there was

no clear relationship between the resultant morphology and variation of temperature and concentration of potassium dichromate, however variation of concentration of sulphuric acid did produce a weakly but statistically important correlation, and the pH variation showed a strong correlation.

The group of pigments generally known as Prussian blue is not well characterised. The primary form(s) are iron(III) hexacyanoferrate(II), with variable inclusion of potassium or sodium ions into the cage-like structure, the latter affecting whether the so-called 'soluble' or 'insoluble' types are formed. However, it was clear from our documentary research that analogous pigments were also made and marketed historically that had other metal ions substituted into the structure (such as antimony, copper and zinc), some of which are not even blue (we ended up referring to these as the 'hexacyanoferrate pigments group'). Moreover, it has been known for some time that the earliest production of Prussian blue involved the use of

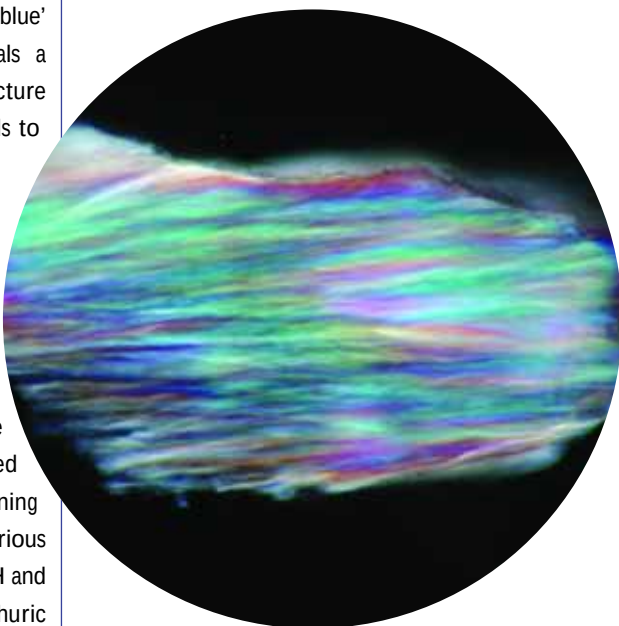


Fig. 13. Dispersion of crysocola pigment, a finely fibrous aggregate, in cross polarised light (fieldwidth 143 μm).

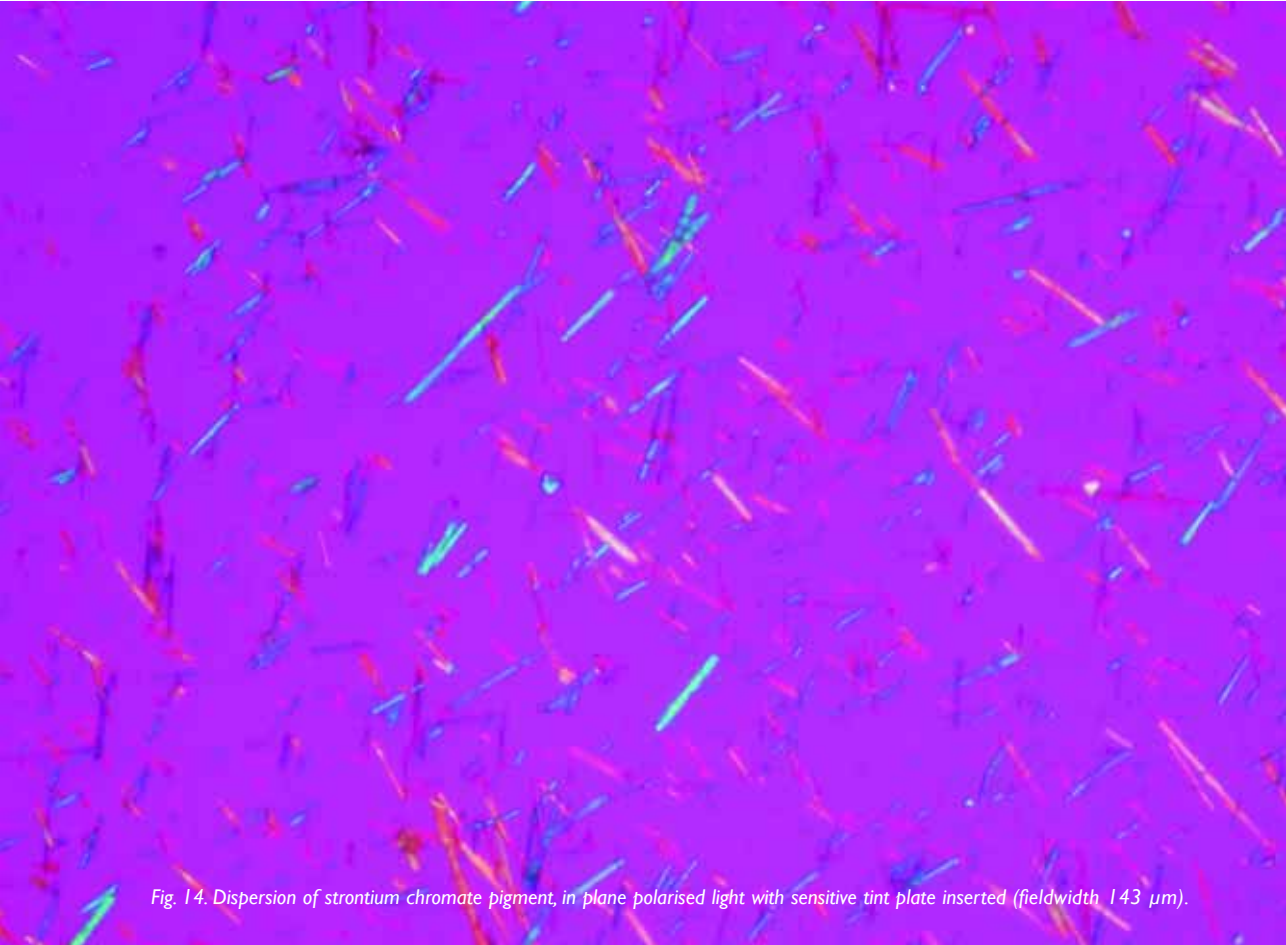


Fig. 14. Dispersion of strontium chromate pigment, in plane polarised light with sensitive tint plate inserted (fieldwidth 143 μm).

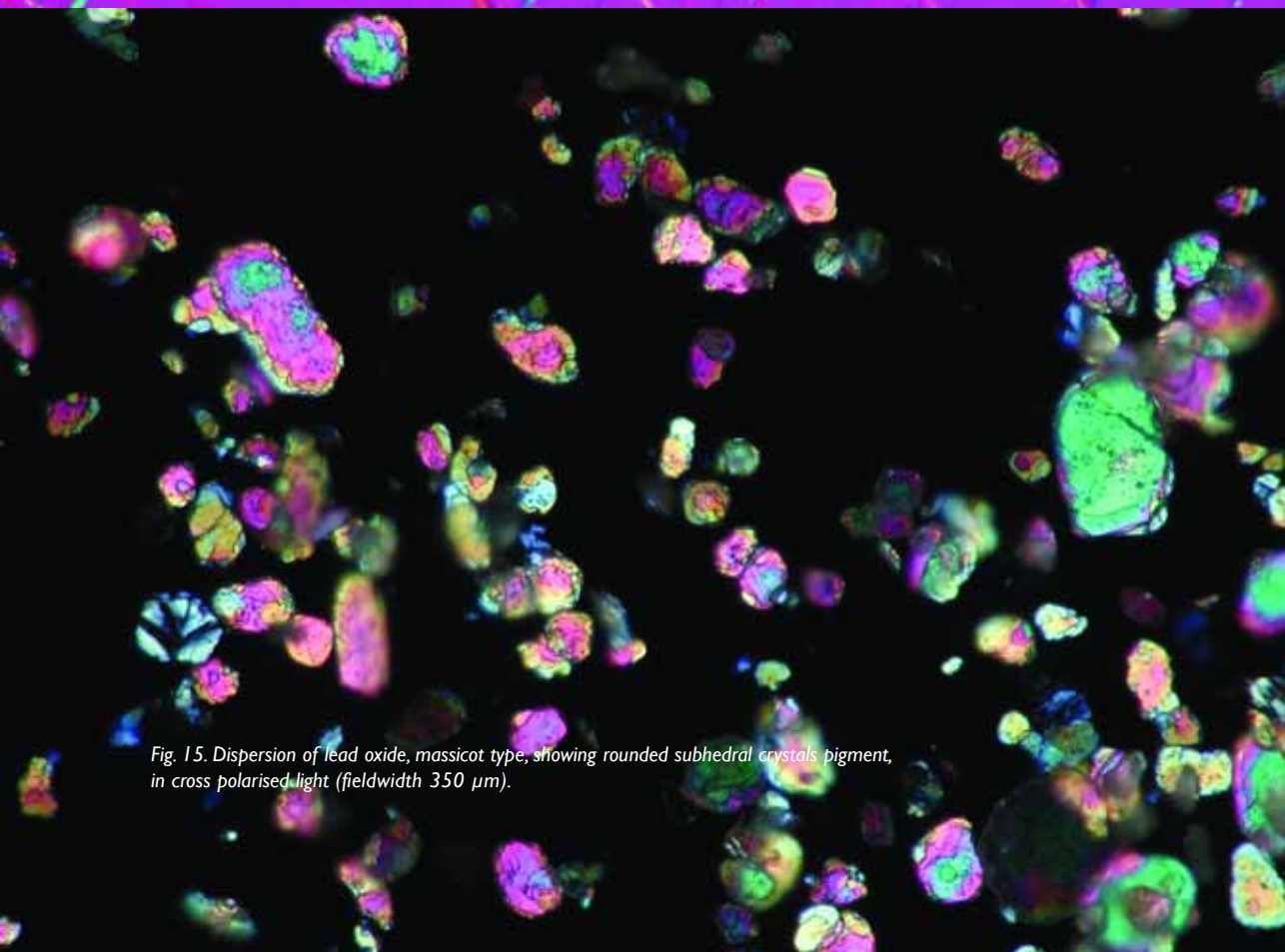


Fig. 15. Dispersion of lead oxide, massicot type, showing rounded subhedral crystals pigment, in cross polarised light (fieldwidth 350 μm).



materials such as blood. What effect do these variations have and how can we best analyse for them?

The aim of the work carried out by Juliette Middleton¹² and David Sethatho¹³ was to synthesise a range of these compounds, determine whether identification of the different forms is possible, establish which techniques best achieve this, and ultimately to provide characteristic analytical fingerprints for our database. To begin with, a good number of samples of Prussian blue variants were replicated from different documentary sources (as well as according to modern chemistry!) and then characterised by elemental analysis, X-ray diffraction, FTIR and Raman spectroscopy, and optical microscopy.

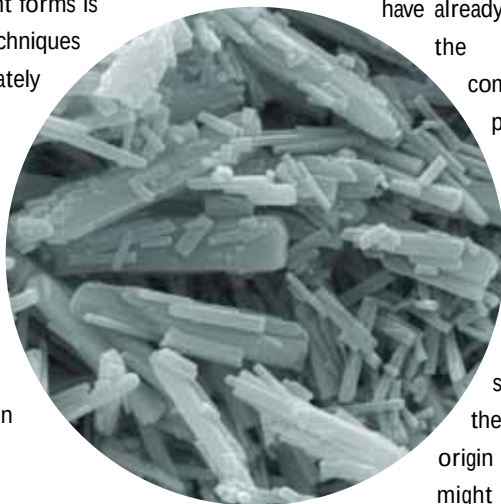


Fig. 17. SEM image of lead chromate produced under laboratory conditions at 76° C. (fieldwidth 2.0 µm).

We were able to show that a number of ions such as the antimony, copper and zinc mentioned before, are freely substituted into the structure. It is also shown that FTIR and Raman spectroscopy produce fingerprints characteristic of iron (III) hexacyanoferrate (II) and its substituted compounds that can be readily used to identify these pigments in historical artefacts.

Other examples of the work of the Pigmentum Project in specific areas have been published in the previous and current issues of *infocus Magazine*, such as that on pigment chronologies by Nicholas Eastaugh (Issue 1 pp 30) and “*Not a day without a line drawn*”: Pigments and painting techniques of Roman Artists by Ruth Siddall (Issue 2 pp 18).

The way ahead

The project is currently at a crossroads as it transforms itself from a group of like-minded colleagues writing a book into a stable and long-term research group. Having recently become a part of the University of Oxford we are now setting our goals for the future. Some of these have already been alluded to; notably the completion of our comprehensive survey of the pigment collection, but we have ambitious plans to develop a much wider series of research topics.

One of these is the subject of provenance, in the sense of determining the origin of materials. An example might be the restricted geological occurrence of certain minerals such as lazurite, which (as far as we know) came

exclusively from Afghanistan, but which is also found in Russia and Chile. To be used in European paintings this had to be traded over vast distances. This type of information can be studied more

Analysis of isotopic abundances and trace element contents provides a powerful tool for learning about our economic history.

widely among pigments – by having the analytical means of differentiating the physical sources of materials, so we can learn much about historical

Fig. 16. Detail of an Early Italian Nativity Painting (Lorenzo di Bici, c. 1440) showing green earth pigmented undercolour.



Fig. 18. Cross-section through a painting showing layers of paint containing pigment particles bound in oil medium, ordinary light. (fieldwidth 350 μm).



Fig. 19. Specially manufactured SEM stubs to take 72 samples, Pigmentum Project.

trading patterns. Analysis of isotopic abundances and trace element contents provides a powerful tool for learning about our economic history.

A second area is to extend our understanding of the relationship between pigment chemistry and the materials that we find on artworks. The aim here is to try to tease out whether we can make any inferences about the use of particular manufacturing processes in the past through detailed observations of pigments from artefacts.

A third research strand addresses questions of pigment use and chronology – say, when and where a particular compound was used. With direct application to independently establishing dates of artefacts for authenticity studies, it is also (and profoundly) again a means of studying the

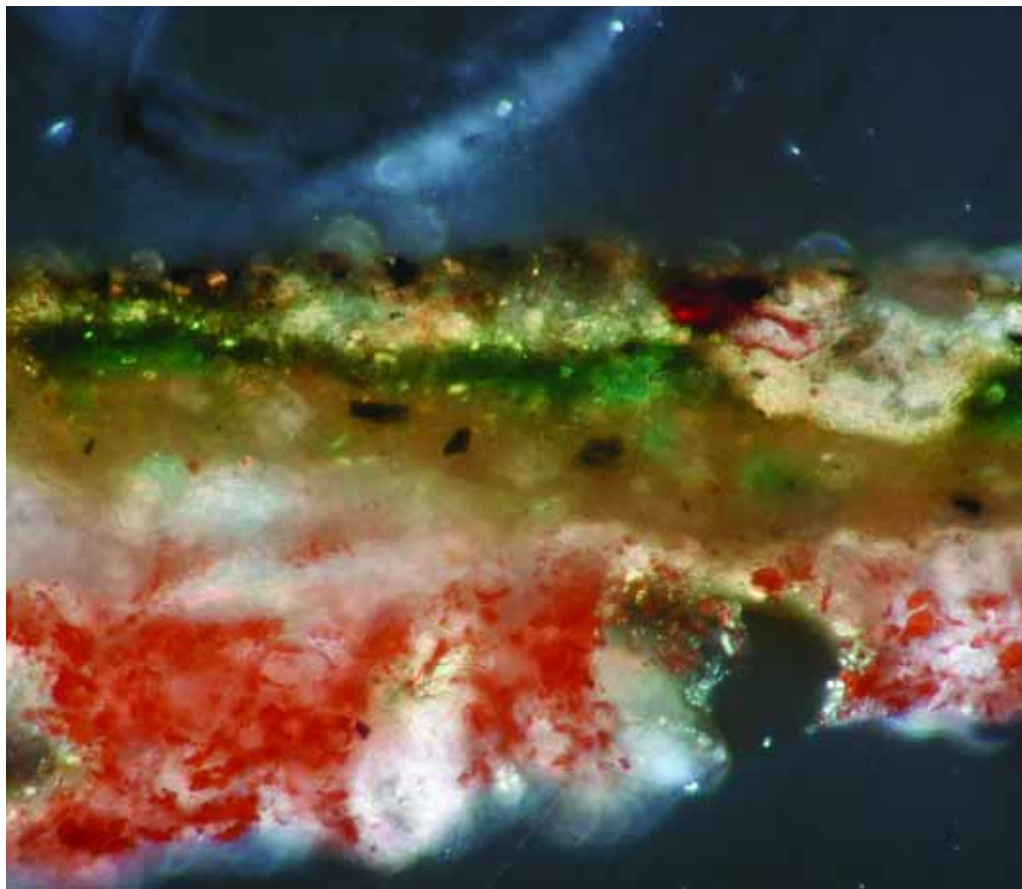


Fig. 20. Cross-section through a painting showing layers of paint containing pigment particles bound in oil medium, thin section ordinary light, transmitted, (fieldwidth 350 μm).

choices made by artists in the past. We might ask questions such as how rapidly use of a pigment spread, or why we get certain patterns in usage and how that might relate to the relative perceived benefit of one material over another.

Fourth, the Project has always taken an interest in developing knowledge about historical pigments more widely. Consequently in addition to our academic publication programme and public lectures, we have also for some years now taken in students at masters and doctoral level. We have encouraged students from courses in conservation (Institute of Archaeology, University College London) and forensic sciences (Department of Forensic Science, Kings College London) to spend time with us working on specific research topics; some of the examples above were chosen as a

showcase for this. Further, we run short courses for our colleagues to help in their continuous professional development programmes. We see this as a vital part of our work.

An article such as this can only ever give a taste of the work, but hopefully we have conveyed a cross-section of our interests. Historical pigment research is now at an exciting point, developing from a loose alliance of like-minded people of related disciplines into its own coherent field. We hope to make some significant contributions to this field in the next few years.



Fig. 21. Dispersion of starch granules and turmeric dye, in plane-polarised light (fieldwidth 1.432mm).

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Valentine Walsh is a paintings conservator with her own practise and 30 years experience working on paintings for museums and the private sector. This has led her to have a profound interest in the analysis of paintings and their materials. Consequently she co-founded the Pigmentum Project and co-authored the Pigment Compendium.

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