NY CARLSBERG GLYPTOTEK — THE COPENHAGEN POLYCHROMY NETWORK

Tracking Colour

The polychromy of Greek and Roman sculpture in the Ny Carlsberg Glyptotek

Preliminary Report 1, 2009

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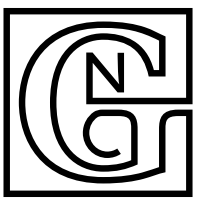

NY CARLSBERG GLYPTOTEK

Ny Carlsberg Glyptotek & the Copenhagen Polychromy Network

Tracking Colour
The polychromy of Greek and Roman sculpture in the Ny Carlsberg Glyptotek
Preliminary Report 1, 2009

The Copenhagen Polychromy Network is an interdisciplinary body formed in 2004 on the initiative of the Ny Carlsberg Glyptotek to conduct research on ancient sculptural polychromy in the collections of the Glyptotek.

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Preface

From 2004 to 2008, the Ny Carlsberg Glyptotek and the Copenhagen Polychromy Network (CPN) carried out a Pilot Project in the museum's collection of Greek and Roman sculpture. In June 2008 we started the so-called Main Project which will run until 2011. The first phase of visual examination began in January 2009 and lasted until this summer.

Some provisional results of these activities are published in this first Preliminary Report. The Report also contains an introduction to the CPN and outlines of both the Pilot Project and the Main Project. The protocol followed in visual examination and documentation is not the subject of a separate article, but is presented instead as applied in practise.

On a practical note, the system of citation and abbreviation in this Report is not homogenous.

This first Preliminary Report will be followed by (at least) two more, to be published in 2010 and 2011. The format will be electronic and the publications will be freely available for download from the Glyptotek website at www.glyptoteket.dk. At present, financial restrictions allow only a quite unsophisticated pdf-solution.

It has been our idea for some time that the following Reports should have two sections: Section I with preliminary publication of the actual project results; and a Section II containing other contributions on ancient sculptural polychromy, whether related to our results or not.

We fully realize that the advent of bibliometrical methods of academic 'rating' will make it even less attractive to publish in a forum such as ours. It is therefore our ambition to see the following Reports appear as e-publications under the auspices of an accredited Danish academic publisher. Such a publisher has already been found and initial discussions have taken place with positive results. A number of colleagues on our international advisory panel have agreed to undertake peer-reviewing of articles appearing in Section II. It remains to be seen whether the necessary funding can be found.

As it is, we invite contributions to section II of the Preliminary Report 2, 2010, to be received no later than May 1, 2010. Editorial guidelines will be made available on request to the Editor.

It goes without saying that any critical comments on this first Report and suggestions for improvement will be much appreciated.

Our thanks go at this point to all those within and outside the Ny Carlsberg Glyptotek who have contributed to bringing our project thus far – especially to the Kirsten and Freddy Johansen Foundation for providing us with microscopes and camera, to Leica Microsystems Denmark A/S and Lars Hvalsum for untiring support and a donation to the project. Moreover, to the Statens Museum for Kunst which has generously lent us glass partitions for the project work space. Finally, we express our appreciation of the interest and support shown by the members of our International Advisory Panel.

Jan Stubbe Østergaard
Editor

On behalf of the Ny Carlsberg Glyptotek and the Copenhagen Polychromy Network

Introducing the Copenhagen Polychromy Network

Jan Stubbe Østergaard[1]

The Copenhagen Polychromy Network (CPN) was formed on the initiative of the Ny Carlsberg Glyptotek, Copenhagen, in the wake of the exhibition 'ClassiColor – the colour of ancient sculpture.' The exhibition was shown at the museum from March to May, 2004.[2]

FACTORS DETERMINING THE ESTABLISHMENT OF THE NETWORK

The decision to form the network was taken in the light of a number of different, but interrelated factors:

- The exhibition project mobilized awareness of the importance of polychromy studies within the museum.
- The exhibition was successful in reaching a wide audience, in terms of both visitor numbers and media coverage. Among other things, this served to generate interest and understanding among a variety of important audiences, such as institutions with scientific resources relevant to this field of archaeological and art historical research.
- The collection of ancient sculpture in the Ny Carlsberg Glyptotek has, since 1991, been the subject of systematic documentation resulting in a digitally produced, printed catalogue series available also in an English version.[3] Relevant data on the collection, in the form of texts and high quality photography, are therefore now accessible to international scholarship. The catalogue contents are in the process of being made available via an object database on the museum's website, www.glyptoteket.dk.
- The only aspect of the collection not yet systematically examined and documented is that of traces of ancient polychromy.[4]
- The collections have good potential for providing information on ancient sculptural polychromy. Many works were acquired on the art market in Rome from the middle of the 1880s to the early years of the 20th century. In the same period acquisitions were made on the art market in Munich and in Athens. A fair proportion of these acquisitions were recent finds. Dealers were aware of the importance placed by the Glyptotek on acquiring works in as pristine a condition as possible.

  Over the years, subsequent treatment in the Glyptotek's department of conservation has seen the application to many pieces of methods of cleaning which would not be acceptable today and casts have been taken of a number of important works. It is likely that this has caused some damage. Apart from works acquired from old collections, ancient sculptures

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1 Research curator, ancient art, Ny Carlsberg Glyptotek, Dantes Plads 7, DK-1556 København V. jso@glyptoteket.dk.

2 This was the Copenhagen version of the exhibition shown first in the Staatliche Antikensammlungen und Glyptothek, Munich, in 2003 (Bunte Götter. Die Farbigkeit antiker Skulptur) and later in the Musei Vaticani, in 2004/5. Under the auspices of the Stiftung Archäologie, Munich, and through the efforts of Vinzenz Brinkmann and Ulrike Koch-Brinkmann, continually revised and expanded versions of the exhibition have since been presented at a number of other venues. The contribution thus made to generating both public and professional interest in the subject can hardly be overestimated.

3 The catalogue series is available from the museum eShop at www.glyptoteket.dk

4 As is the case for all other major collections of Greek and Roman sculpture.

have however generally not been subjected to 'rigorous' cleaning. Many pieces retain traces of polychromy.[5]

- The museum houses collections of polychrome works in other art forms and from other cultures whose relevance as comparative material is becoming increasingly clear. We have Greek, Etruscan and Roman terracottas; Etruscan stone sculpture, Egyptian stone sculpture of all periods as well as Egyptian terracottas of the Hellenistic and Roman periods and painted mummy portraits from Roman Egypt.
- The museum had become aware of the fact that traces of ancient polychromy on the stone sculptures in its care were deteriorating and have in some cases disappeared. The processes at work in the deterioration of ancient pigments are not yet been precisely understood. Action to document traces of polychromy in the collection was therefore agreed to have a high priority.
- The disciplines needed to conduct research in ancient polychromy in a museum collection was available in Copenhagen.

The above mentioned factors determined the Network's aims and structure.

THE NETWORK'S AIMS

The CPN's aim is to contribute to an increase of data available to the study of ancient sculptural polychromy through systematic documentation of traces of polychromy in the collection of Greek and Roman sculpture in the Glyptotek, in-depth conservation scientific and natural scientific study of sculptures identified as having special importance, and publication of the acquired data.

It was decided that the project publications should appear in open access electronic formats whose sophistication would depend on available funding. A high degree of interactivity with readers was aimed for.

THE NETWORK'S STRUCTURE: PARTICIPATING INSTITUTIONS AND COMPETENCES

The participating institutions are:

- The Ny Carlsberg Glyptotek
- The Departments of Painting and Monumental Art at the School of Conservation of the Royal Danish Academy of Fine Arts, Copenhagen
- The Geological Museum and Institute of Geology, University of Copenhagen (Natural History Museum of Denmark)
- The Institute of Chemistry, Technical University of Denmark, Copenhagen.

5 Visible remains of pigment have been observed on c. 120 Greek and Roman sculptures, from miniature to colossal formats. Since experience has shown that close examination reveals remains not seen by the naked eye, the number of sculptures in the collection that are relevant to this field of research is certainly higher, but difficult to estimate.

Together, these institutions provide the competences needed in this field of research, namely:[6]

- *Classical archaeological, curatorial competence (1)*. A research curator of ancient art at the Ny Carlsberg Glyptotek directs the project, and is responsible project management, strategy and priorities in collaboration with the museum's curatorial department and its Director. He is in charge of archaeological documentation, contact with museum conservation, network partners and an international collegial network.
- *Museum conservation competence (2)*. This member of the team is in charge of a variety of conservation tasks: Visual examination and documentation (ambient light, raking light, IR and UV photography; microscopy; cross-section preparation and investigation; documentation of samples; organisation of digital data), and dialogue with the curatorial department and external partners in conservation science.
- *Conservation and natural scientific competences (external network partners)* represented by (3) an experienced conservator, contributing in the field of scientific conservation photography; instrumental pigment analyses (SEM/EDX; FT-IR), chemical spot tests and pigment and binding media analysis. The network partners in natural science offer SEM/EDX, SEM/XRD, XRF and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) for pigment identification and pigment localisation through isotopic trace element analysis and comparative analyses of provenanced specimens (4), and chemical analyses using Raman Laser Spectroscopy (5).

These external network partners offer their service free of charge. They also on occasion activate their contacts in other fields, in Denmark and abroad.

THE CPN'S OVERALL STRATEGY

A simple overall strategy consisting of three stages was established at the outset. First, to carry out a Pilot Project study, proceeding as the resources of the CPN might allow. This was then to provide a platform for stage two, a more ambitious Main Project, planned according to the resources that might be allotted by the museum or raised by other means. The last stage was to comprise a final publication of the accumulated results and the communication of these results to the public in the form of an exhibition at the Ny Carlsberg Glyptotek.

PROGRESS HITHERTO

As it turned out, by early 2008 the results achieved by the Pilot Project led to a decision by the museum to go ahead with the Main Project. The Pilot Project and some of its results are dealt with elsewhere in this Report.

The museum's main contribution to the project was a full-time position as research curator for the three years 2008–2011, and a half-time position as project conservator for the same period. Applications for additional funding have not so far met with success – the exception being a generous donation made by the Kirsten and Freddy Johansen Foundation for the acquisition of instruments.

6 In the following, the persons involved are referred to by numbers in brackets. They are (1) Jan Stubbe Østergaard, research curator, MA; (2) Conservator Rebecca Hast and subsequently Maria Louise Sargent BA conservation and classical archaeology, post graduate student in conservation, (3) Mikkel Scharff, Head of the Paintings Department and of the Monumental Art Department. School of Conservation, The Royal Academy of Fine Arts, Copenhagen (with attached advanced students), (4) Prof. dr. Minik Rosing, Natural History Museum of Denmark, (5) Associate professor Rolf W. Berg, Phd, Institute of Chemistry, Technical University of Denmark.

The Main Project is outlined in a separate article, together with a report on the first sculpture to have been examined.

Work on the final publication is to take place 2011–2012 and the exhibition is scheduled for the spring of 2013.

CHALLENGES

Of the challenges facing the CPN's activities, the greatest is that of ensuring the continuation of coherent and systematic research on ancient sculptural polychromy in the Ny Carlsberg Glyptotek after the close of the Main Project.

It has by now become clear that within the framework of the Main Project, it will only be possible to investigate a limited number of the sculptures which can supply us with evidence of the polychromy of Greek and Roman sculpture – furthermore, the polychromy of the museum's rich holdings of Egyptian and Etruscan sculpture remains unexplored.

If we do not succeed in meeting this challenge, the results achieved by the CPN will thus stand as a torso; the experience and expertise acquired by the CPN will dissipate, and, worst of all, we will be unable to offer younger Danish archaeologists and conservators a platform allowing them to take over from those leaving the field in the foreseeable future. To nourish research 'Nachwuchs' is essential, as always.

Despite the seminal contribution made by such scholars as Vinzenz Brinkmann, Ulrike Koch-Brinkmann, Philippe Jockey, Brigitte Bourgeois and many others, research in ancient sculptural polychromy still finds itself in a formative phase. Its interdisciplinary character and the considerable resources it requires, makes it the more difficult to find a footing of any permanence at humanistic academic institutions. It is indicative of this that, as far as I know, the only organization wholly dedicated to sculptural polychromy research is a foundation, namely the Stiftung Archäologie in Munich.[7]

VISIONS

The CPN should therefore meet the challenge described above by developing visions of how the research it has initiated may be continued in the future. Such visions must be based on some established, key factors:

- The size and research potential of the collections of ancient sculpture in the Ny Carlsberg Glyptotek.
- The museum's long-standing policy of welcoming research on its holdings by scholars from outside the institution and allowing open access to works in the collection – combined with an open-minded attitude to the taking of samples for analysis elsewhere.
- The availability of relevant research facilities at the museum, including a first-rate library, office space for visiting scholars, a mini-auditorium for scholarly research meetings, as well as work space and equipment for visual examination and documentation.
- The not inconsiderable international, interdisciplinary network of contacts developed by the CPN.
- The existence of up-coming Danish conservators and archaeologists with the necessary talent and enthusiasm.

7 Founded in 2005 on the initiative of Vinzenz Brinkmann and Ulrike Koch-Brinkmann (www.stiftung-archaeologie.de).

AN INTERNATIONAL RESEARCH CENTRE IN COPENHAGEN

Taken together, these key factors allow one to envision the creation in Copenhagen of a research centre for ancient sculptural polychromy. In outline, such a centre could be described as follows:

- The centre has its base in the Ny Carlsberg Glyptotek. It is interdisciplinary in character and international in outlook. It focuses its research on ancient sculptural polychromy as represented in the collections of the Ny Carlsberg Glyptotek. The centre conducts a research programme, including research training of young scholars, and a variety of activities connected with ancient sculptural polychromy. This involves collaboration with other museums and relevant universities. The centre issues relevant publications and organises scholarly meetings. The possibility of offering courses on aspects of ancient sculptural polychromy on relevant academic levels should be explored.
- The centre is directed by a classical archaeologist, a museum stone conservator and a conservation scientist.
- The mission of the centre is to promote, expand and consolidate research on ancient sculptural polychromy in the academic world and communicate research results to a wider public. The centre aims to:

1 Establish a visible and explicit research profile with national and international references, setting standards for future research on ancient sculptural polychromy.
2 Explore and consolidate international knowledge of ancient sculptural polychromy by inviting colleagues from abroad to conduct research in the collections and by establishing collaboration with research projects in other museums.
3 Achieve new results by conducting research programmes, and by inspiring young scholars and scientists to include ancient sculptural polychromy in their research.

- In carrying out this mission, the centre collaborates closely with the CPN and an international advisory board.

Some of the elements of this vision were present on a modest scale at an international, interdisciplinary Round Table on ancient sculptural polychromy held in the Glyptotek in September 2009. A couple of participants arrived some days prior to the meeting to examine sculptures in our collection. The sculptures were brought to work spaces set up for the purpose. In connection with a second round table meeting next year, one might imagine this activity expanded. At the meeting itself, scholars directly involved in research projects presented and discussed results. Participation, by invitation only, included Danish archaeologist and conservators.

To discuss, develop, adjust and refine such visions for the future is a vital part of the work now being done by the CPN and the Ny Carlsberg Glyptotek.

The CPN Pilot Project: a brief introduction and evaluation

Jan Stubbe Østergaard

The provisional results of the Pilot Project are reported on in the articles below. Here, I restrict myself to some general remarks on the aims of the project and some comments in the way of evaluation.

Three sculptures from our collections were chosen for study following two criteria: the presence of traces of ancient polychromy, and the potential for throwing light on sculptural polychromy in poorly documented periods – namely Classical and Hellenistic Greek original sculpture and Roman ideal sculpture. Through the study of these works, we hoped to:

- Acquire experience in structuring and operating an interdisciplinary network.
- Develop a protocol for visual examination.
- Acquire data on the expenditure involved in visual examination and documentation and in-depth conservational and natural scientific study, in terms of time, personnel resources and instrumental examination costs.
- Produce primary research data on the objects chosen for the Pilot Project.
- Establish contact with others working in the field.
- Provide a platform for a more ambitious, long term research program.

Looking back, the Pilot Project served its purpose in most respects.

However, in the matter of operating the network, examination of the sculptures was not carried out in a work space specifically designed for the purpose, but at various locations – in situ in the galleries, in the museum conservation workshop, in our photo studio and in work spaces at the School of Conservation. As a result we did not develop a clear idea of how to establish and equip a dedicated work space in the galleries, for the Main Project. This was eventually to cost us time in preparing that facility.

As far as the planning of non-invasive or sample analyses to be carried out by, or using the instrumentation of, our external partners in conservation and natural science, we did not come to fully recognize a basic condition. Namely that such analyses could only take place to the extent allowed by the internal work programmes of the institutions involved, and already hard pressed in the matter of resources. For perfectly understandable reasons, they were not – and are not – in a position to allot agreed resources to a project such as ours with the regularity needed for any kind of planning. This in no way affects our gratitude for the unstinting external network support generously given to the project.

Within the framework of the Main Project, appropriate measures have now been taken to make the best possible use of the resources of external partners. In practise, this means the batching of the analyses we need, rather than waiting for analyses when examining an individual sculpture.

Furthermore, we did not gain any proper idea of the amount of time the examination of an individual sculpture would involve. During the Pilot Project, work was done ad hoc, as conditions permitted, and no log was kept; the development of a protocol went ahead as hoped, but in a way which did not result in an understanding of the time required to implement the protocol. This has influenced the planning of the Main Project, which has turned out to be unrealistically optimistic as regards the number of objects we would be able to examine.

As a result, a shorter, so-called Survey Protocol, has now been developed to increase the number of sculptures examined during the Main Project.

The experience gained during the Pilot Project has served to strengthen the conviction that the way forward in the study of ancient sculptural polychromy is to establish committed interdisciplinary networks formed around major collections of ancient sculpture, in their plurality forming a 'network of networks' in synergetic collaboration. It has also served to clarify that such networks will be of at least two different types.

The CPN is an example of a network made up of some competences existing in the museum, while others are provided by external partner institutions – with the limitations this entails. Other collections are in the keeping of museums which have the prerequisite interdisciplinary organisation in-house and are therefore able to allot resources in a more organized manner once the decision has been taken to give polychromy research the necessary priority. Networks of this type are likely to become the leaders in the field.

Some museums will have to establish networks like that of the CPN, created through decisions taken by the keepers of their collections and their conservators, and by those in charge of institutions of conservation science and natural science.

In both types of network, decision makers are faced with many different well-reasoned, urgent applications for allotment of resources to a variety of projects. It comes down to establishing priorities. In this situation, the case for interdisciplinary research in ancient sculptural polychromy must be forcefully made.

The Pilot Project was successful in cementing network collaboration and producing research data. Without this, it would not have been possible to fulfil the aim of launching the Main Project.

Investigating the polychromy of a Classical Attic Greek marble female head NCG IN 2830

Mikkel Scharff, Rebecca Hast, Nicoline Kalsbeek, Jan Stubbe Østergaard[1]

One of three sculptures selected for the CPN Pilot Project was a fragmentary marble head of a woman[2] (Fig. 1), chosen as a representative of the Greek Classical Period. The suggested date of c. 425 BC and proposed Attic origin is based partly on stylistic analysis, partly on the Athenian provenance of the head. As preserved, the head is 23 cm high, 16 cm wide and 21 cm deep; if it comes from a statue, the height of this can be calculated to c. 2 m, or slightly over life size.[3] The marble has been identified by isotopic analysis as 'probably Parian Lychnites; Ephesian a possibility.'[4]

Fig. 1: Ny Carlsberg Glyptotek IN 2830.

1 Mikkel Scharff, conservator, Head of the Departments of Painting and of Monumental Art, Royal Danish Academy of Fine Arts, The School of Conservation
Jan Stubbe Østergaard, research curator, Ancient art, Ny Carlsberg Glyptotek, Copenhagen. Jan Stubbe Østergaard's contribution is limited to the archaeological comment.
Rebecca Hast, stone conservator, MSc in Conservation, Copenhagen
Nicoline Kalsbeek, chemist, ass. prof., Dr., formerly The School of Conservation, now Teamleader Novozymes, Bagsværd, Denmark.

2 IN 2830. Poulsen 1941, pp. 111–118, pl. 13; Poulsen 1951, p. 219, no. 298a; Moltesen et al. 1995, p. 70, no. 16.

3 Poulsen 1941, p. 112; Berger 1956, p. 171, no. 11 for additional measurements.

4 Sample taken 1993 for isotopic analysis. Result: d13C, 5,13 – d18O, -3,26; Poulsen 1941, p. 112 'Pentelic'

INTRODUCTION – TECHNICAL EXAMINATION, PILOT STUDY

Prior to selecting relevant examination techniques for the Pilot Project, literature on examination of the polychromy of Greek and Roman sculpture was studied.[5] The technical examination of ancient polychromy has concentrated on studying the composition of paint fragments and the traces they left of the stone surface. The authors have summarized their findings of pigments, established hypotheses concerning the original appearance of the sculptures and tried to verify these hypotheses by reconstructing the polychromy of the sculptures.[6]

The published studies of ancient polychromy[7] left us with the impression that most painted surfaces were made with paints composed of a selection of a total of 15–20 basic pigments (with variations) and a few organic colorants[8] made into lakes/dyes and all mixed with binding media of a rather limited variation but including animal glue.

Apparently the same set of pigments, binding media and stratigraphy were found in the ancient Greek and Roman sculptures, in other ancient cultures (e.g. Xi'an[9]) as well as in European medieval polychromy.[10] This led us to assume that we may trace the origin of medieval painting technique in ancient sculpture. This view is supported when studying the materials and the development of some of the recipes in medieval treatises from the 8th century Mappa Clavicula to 12th century Theophilus.[11]

The typical stratigraphy in European medieval polychromy on wood would be a so-called ground structure, covered with one or two layers of paint. Occasionally metal leaves and some more specialized materials (e.g. semi-precious stone) were applied to the surfaces. This is also the rule for medieval painting or decoration of stone supports. Scharff has previously suggested that the origin of certain kinds of ground structures (lead-containing grounds with drying oil as binding medium) in European medieval wooden polychromy has been developed from using the same composition on stone surfaces.[12]

Since literature on the examination of ancient polychromy is relatively limited it was decided that the examination techniques chosen for the pilot study were to be based on an existing tradition of studying polychromy on European medieval polychrome wooden sculpture and panel paintings,[13] as well as the general techniques developed for examining paint lay-

5 Bourgeois – Jockey 2005; Brinkmann 2003; Brinkmann – Wünsche 2003 (version 2008 from Liebieghaus Skulpturensammlung, Frankfurt 2008); Chrissoulakis – Queyrel – Perdikatsis 1989; Kakoulli – Kottaridou – Minos 2001; Graeve – Preusser 1981; Nielsen – Østergaard 2004; Santamaria – Morresi 2004; Santamaria – Morresi – Delle Rose 2004; Wallert 1995.

6 Brinkmann – Wünsche 2003 passim.

7 Cf. note 11; Thieme – Emmerling 2001, pp. 335–369; Wu – Zhang – Petzet – Emmerling – Blänsdorf 2001.

8 Grzywacz – Su – Fan – Wouters 2008, pp. 534–541.

9 Cf. note 13.

10 Plahter 2002, pp. 446–454.

11 Hawthorne – Smith 1974; Hawthorne – Smith 1979.

12 Scharff 1999, pp. 47–52.

13 Nadolny 2006; Tångeberg 1986; Kühn – Straub 1984, pp. 7–54, pp. 125–260; Scharff 1995, pp. 83–91.

ers on various supports.[14] Published literature of paintings on stone or plaster (however not traditional wall paintings in lime or fresco techniques) was also studied.[15]

While there were expectations about the pigments to be found in an examination, the uses of binders for the pigments are less well established and we had fewer prior ideas about what binders might be found during analyses. Proteinaceous glue and egg tempera have been analytically identified in some cases, while Plinius the Elder describes a technique using wax (encaustic technique).[16] In European medieval sculptural polychromy a variety of binders were used[17] and a certain system seems to have been applied: if a painted sculpture was to be left outside it was painted in a somewhat weather resistant technique (e.g. a drying oil binder) while water soluble techniques (e.g. proteinaceous glue) was sometimes used and accepted for indoor sculpture; other techniques included egg tempera or oil. The same may or may not have been the case in Greek and Roman polychromy technique: however, it would make sense to use a weather resistant technique out of doors. If so, it might become possible – by determining the nature of the binding medium – to be able to suggest the original positions of a sculpture (outside or inside: weatherproof painting technique or not) when this is not known about a specific object.

Other features of antique paint layers not very well understood are the surface appearances: matt or glossy, opaque or translucent, or variations on the same object as it is sometimes seen on medieval sculpture? The state of most of the surviving paint fragments or painted areas on ancient sculptures are probably not representative or reliable concerning the surface appearance. It is assumed that the surfaces have been degraded or changed in numerous ways and for a number of reasons.

Some problems are related to a general lack of provenance in the older part of many collections. Greek and Roman sculptures in old collections have been acquired from dealers, the sculptures are generally without provenance and thus the condition of the sculptures when found is not known. When paint traces/samples are located on the surface it is not possible to ascertain whether they were present at the time when the sculpture was found or if paint or other surface treatments have been added (deliberately or not) after the object had been found. Neither is it known whether the surfaces of the paint traces are as when found or they have been tampered with.

As a working hypothesis for the pilot study we assumed that paint layers (composition and stratigraphy) on polychrome sculpture does not differ widely between various geographical locations, cultures and timelines. If so, we should be able to use the same examination techniques for ancient polychromy as for European medieval polychromy and we assume that stratigraphic features on Greek and Roman sculpture could be interpreted and compared with European medieval practice. When we started the Pilot Project examination we thus expected to find pigments, binding media, stratigraphy, and perhaps even metal leaves which appear in published literature on ancient as well as European medieval polychromy. If such similarities were to be found, we might gain an idea of the original surface appearance of ancient polychromies.

14 Khandekar 2003, pp. 52–64; Autenrieth 1990, pp. 215–233; Walmsley 1993, pp. 57–62.

15 Katz 1998, pp. 27–33; Sauerberg 2003, pp. 189–199.

16 Naturalis Historia XXXV, 149.

17 Binding mediums identified – and referred in Eupopean medieval painting treatises (see e.g. note 11) – include proteinaceous glue, starch, waxes, (drying) oils, egg, gums, perhaps resins, resinous compounds or balsams – or mixtures such as in various types of tempera.

We hope – through further examinations and analyses – to gain insight into the original appearance of the ancient polychrome sculptures, and through this to better understand the present state and deterioration phenomena. This would enable us to assess the risk of further deterioration and establish a strategy for future preventive means of protection.

The medieval polychromy examination techniques applied in the Pilot Project are described in the following.

METHODS & MATERIALS

The examination of the female head in the Ny Carlsberg Glyptotek (IN 2830) is divided into various steps: visual examination/analysis, photographic documentation, paint sampling, light and UV-fluorescence (UV-FL) microscopy, scanning electron microscopy (SEM) with EDX and SEM imaging, Fourier transform-infrared spectroscopy (FT-IR), and gas chromatography-mass spectrometry (GC-MS).

VISUAL EXAMINATION/ANALYSIS

The visual examination/analysis consisted of a visual examination with the naked eye of the surface of the head beginning with the face and subsequently turning around and examining the sculpture clockwise 360 degrees. The visual examination was supported by a magnification glass and the use of an operation microscope[18] to examine in detail various phenomena. The light and radiation types used at this stage were: tungsten light in symmetric setup (in order to distinguish visible colour differences on the surface); raking light over the surface in order to examine surface phenomena such as tool marks, incisions and traces of paint; UV-radiation causing UV-FL to examine the surface for surface fluorescence phenomena.[19]

PHOTOGRAPHIC DOCUMENTATION (DIGITAL) AND EXAMINATION

Systematic documentation was made of the sculpture and furthermore photography of the detail phenomena observed during the visual examination, supplemented by examination and documentation by means of infrared reflectography (IRR) and UV-FL. Photographic documentation in colour[20] was made of the sculpture in 6 stages (beginning with the face) and subsequently in 60 degree steps. One image using a colour reference standard[21] for subsequent colour balancing was made for each new set-up, and grey background used on all images. Digital photographs were saved in the camera as RAW-files, post-processed, colour corrected and saved as 16 and 8 bit TIFF images. In all cases the photographs were made using fixed exposure time and aperture. Exposure details of the photographs are embedded as EXIF-data with the digital tiff images.

18 Operations microscope, Carl Zeiss Jena.

19 The UV-radiation system builds on the principles described in the paper: Autenrieth 1990, pp. 215–233.

20 A Nikon D100 digital camera (3008 × 2000 pixels CCD-array), 60 mm Macro-Nikkor lens was used for capturing photographs, symmetrically positioned and balanced halogen light provided form and shadows.

21 GretagMcBeth ColorChecker® chart, a 24-patch reference standard to reproduce colours.

ULTRAVIOLET FLUORESCENCE (UV-FL) PHOTOGRAPHY

The same 6 images were taken under UV radiation[22] as well as some details. The photographs were saved in the camera as RAW-files, post-processed and colour-corrected using a grey card and saved as 16 and 8 bit TIFF images.

IR-REFLECTOGRAPHY (IRR)

An IRR-camera system[23] was used to examine areas on the surface where colour/paint was found in order to subsequently document whether the paint or surrounding areas provided information otherwise invisible.

PAINT SAMPLING

Four samples each with a surface area of circa 0.25–1 mm^2 were taken, one from each of four surfaces with pigment remains. Approximately half of each sample was embedded in polyester resin and prepared for paint cross sections.[24] The remaining parts of the four samples were left for subsequent analysis.

MICROSCOPY

The four embedded paint samples as cross sections were studied in dark field light and UV-FL microscopy[25] using two sets of filters[26] in order to examine the stratigraphy and obtain the first idea of the pigments and fluorescence phenomena from pigments and/or binding media. The cross sections were subsequently photographed.[27]

SEM/EDAX

To determine the chemical elements present in the various layers in the samples, a JEOL 5310 LV SEM with a Link EDX unit was used for the analyses. Low vacuum (LV) was applied with a pressure of approx. 20 Pa, the acceleration voltage was 15 kV. Backscatter (BSE) pictures were taken of all samples. Contrast differences in BSE pictures are caused by relative differences in atomic number Z of the elements constituting the sample. Heavier elements (higher Z) appear lighter and brighter in the picture than elements with lower Z. During EDX analysis single elements are mapped or monitored across the sample surface, the lighter

22 Camera, see note 27; UV-radiation system, see note 25; filters in front of lens: Wratten 2A (cutting around 400 nm), Wratten 2A + Wratten 85B (cutting off some of the blue part of the spectrum).

23 IRR camera (Inframetrics InfraCam SWIR®) with a 256 x 256 pixel PtSi-detector array, lower threshold 1100 nm, equipped with a band pass filter 1500 nm to 1800 nm and as source of IR radiation a tungsten bulb were used in the study. Via a frame grabber, the 8-bit signals were transferred to a computer, subsequently processed in the image processing software VIPS/nip2 (GNU) and saved as 8 bit TIFF images.

24 Paint samples were embedded in Serifix® polyester resin with MEKP hardener, cured at 50° C, prepared with Si-based wet-grinding paper 240, 800, 1000, 1200 mesh and dry-polished using 4000 mesh; see Christensen – Scharff 1986, pp. 10–12.

25 Zeiss Axiotech 100 HD microscope, ×20/0.40 Epiplan HD lens, used in dark field technique, halogen light and UV-radiation.

26 3SP395 + LWP420, FT510 + LP520.

27 Olympus OM-1 camera, Ectachrome 64 ISO and 200 ISO film (EPY for tungsten light, EPD for UV-FL), auto exposure; the colour slide films were developed and afterwards scanned.

the colour of an area of the sample the higher is the concentration of the investigated element in that specific area.

FT-IR WITH ATR MICROSCOPY[28]

To determine the chemical composition of selected elements, individual layers on the four samples were analysed using the FT-IR microscope with ATR directly on the cross section of the embedded samples. Typically, 6–10 areas or specific grains on each layer were examined. The results were determined immediately or compared with references, mainly the IRUG database.[29, 30]

GC-MS

To determine possible organic binders. Derivatisation was done by making an alkaline hydrolysis. Next the sample was acidified and extracted with ether, transferred to an autosampler vial and the solvent evaporated. Finally the sample was re-dissolved in t-butyl methyl ether containing diazomethane (1) and injected on-column at 64° C. The temperature is programmed to initially 190° C @ 10° C / min, and from there to 320° C @ 4° C / min. Data are collected in 'full scan' on a Saturn Ion Trap.[31]

SEM IMAGING

This was done in order to examine calcium-containing layers on sample 1 and Sample 3 for possible presence of coccoliths. Specimens were prepared for SEM imaging by coating with Platinum-Palladium in a JEOL JFC-2300HR high resolution coater prior to scanning at 7kV in a JEOL JSM-6335F Field Emission Electron Microscope.[32]

RESULTS AND DISCUSSION

The following results and discussions are based on the Pilot Project examinations and analyses described above. A certain margin of error or uncertainty is due partly to the minute sample size and partly to lack of parallel samples that might – through repetitions – have made some analyses more reliable.

28 FT-IR Perkin Elmer Spectrum One, Autoimage FT-IR Microscope, ATR.

29 Infrared and Raman Users' Group (IRUG); for further information and the IRUG database, see: www.irug.org

30 Special thanks to Dr. Jan Jørn Hansen, School of Conservation, for performing and interpreting the FT-IR spectra.

31 Glastrup 1998, p. 133; Special thanks to Dr. Jens Glastrup, the National Museum of Denmark, for performing and interpreting the GC-MS analyses.

32 Special thanks for performing SEM imaging to Dr. Nikolaj Scharff, the Zoological Museum at the Natural History Museum of Denmark (The University of Copenhagen). Thanks as well to Prof. Dr. Minik Rosing, the Geological Museum at the Natural History Museum of Denmark for help in interpreting the images.

VISUAL EXAMINATION AND PHOTOGRAPHIC DOCUMENTATION

As a result of the visual examination – which confirmed the presence of paint fragments – five areas with paint fragments were selected for further study:

1 A few fragments of presumed skin coloured paint on the right cheek in minute hollow grates were identified, one was extracted (Fig. 2, sample 1);
2 A few fragments of skin coloured paint in the area around the left eye were identified, one was extracted (Fig. 3, sample 3);
3 An area around and below the left ear with skin coloured paint was identified, no sample was extracted;
4 A number of red-brown paint fragments were identified in the cavities of the hair above the left ear and in other parts of the hair. One sample was extracted from the area above the left ear (Fig. 3, sample 4);
5 An area with brown paint was identified on top of a putty-like material covering what was assumed to be an old damage and subsequent repair at the top of the forehead at the edge of the hairline (Fig. 2, sample 2).

The general condition of the sculpture surface could – based purely on the visual examination – be divided into five fairly distinct levels:

1 A level of the assumed original, relatively smooth surface of the face where skin colors might have been applied – 'warm' greyish appearance;
2 A level of smooth surface of the face around the left eye where the marble surface is considerably more white. Such surface characteristics are usually interpreted by archaeologists as a later re-working of the surface in order to make damaged areas less conspicuous;
3 Areas of relatively white but fairly rough surface apparently at protruding areas like the hair, eyebrows and nose, interpreted as the wear and tear of the surface rather than proper breaks;
4 Obviously damaged areas exhibit a rough break surface and a colour somewhat darker than the supposedly original cheek area. This is the case on most of the hair-area as well as most of the left lower half of the cheek, and the bottom of the head where the break is located between the existing part of the head and the now lost parts of the head, i.e most of the mouth, chin and neck;
5 An area above the forehead and at the hairline, seems to have been damaged and has been filled with a putty-like substance that has been covered with a dark red-brown layer of paint of which fragments are still seen.

ULTRAVIOLET FLUORESCENCE (UV-FL) enhanced the presence of some of the paint fragments (Fig. 4), and showed three other phenomena:

1 The area of the right cheek, the forehead, the area around the right eye and the nose assumed to be the original surface showed a discreet fluorescence while the white area of the right eye exhibited a strong yellowish-whitish fluorescence while the iris showed the same discreet fluorescence as e.g. the cheek (Fig. 5).
2 The discreet fluorescence of the face was specked with scattered dark red-violet fluorescing spots at places where in normal light brown spots were seen. This was also evident in the re-worked or damaged areas.
3 A prominent difference in fluorescence was seen between the above mentioned discreet fluorescence in areas considered to be the original surface and in areas considered to be

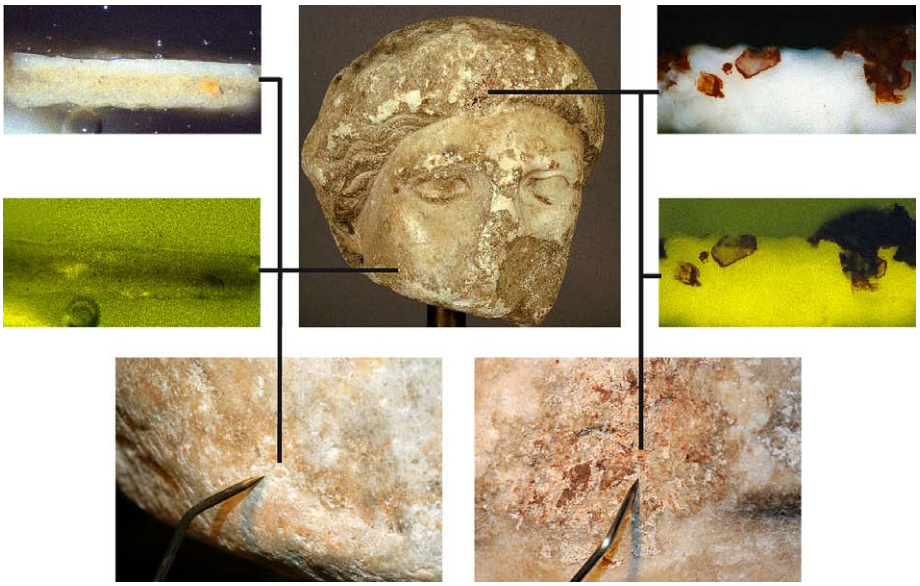

Fig. 2: IN 2830. Paint samples 1+2, top center: head with location of samples (bottom left and right are details); top and centre left: Sample 1 (flesh colour) in tungsten light and UV-FL; top and centre right: Sample 2 (damaged area at forehead and hairline) in tungsten light and UV-FL.

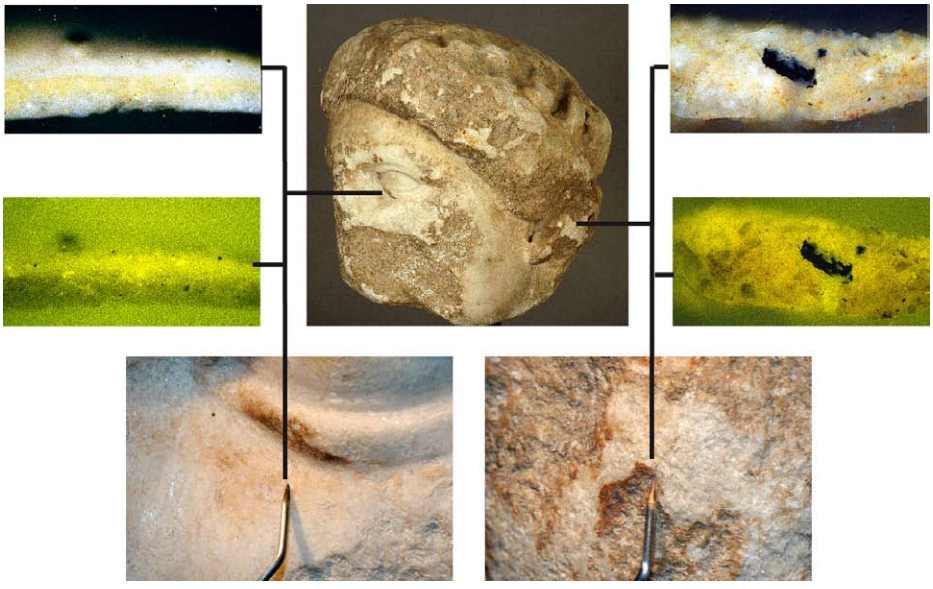

Fig. 3: IN 2830. Paint samples 3+4, top center: head with location of samples (bottom left and right are details); top and centre left: Sample 3 (flesh colour) in tungsten light and UV-FL; top and centre right: Sample 4 (hair colour) in tungsten light and UV-FL.

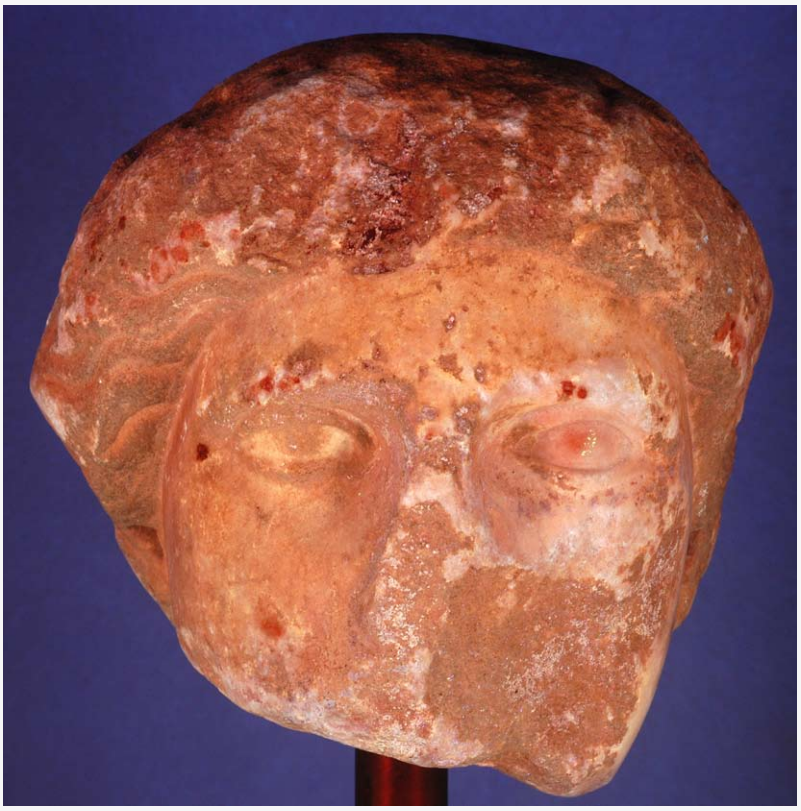

Fig. 4: UV-fluorescence (UV-FL) of female head, IN 2830.

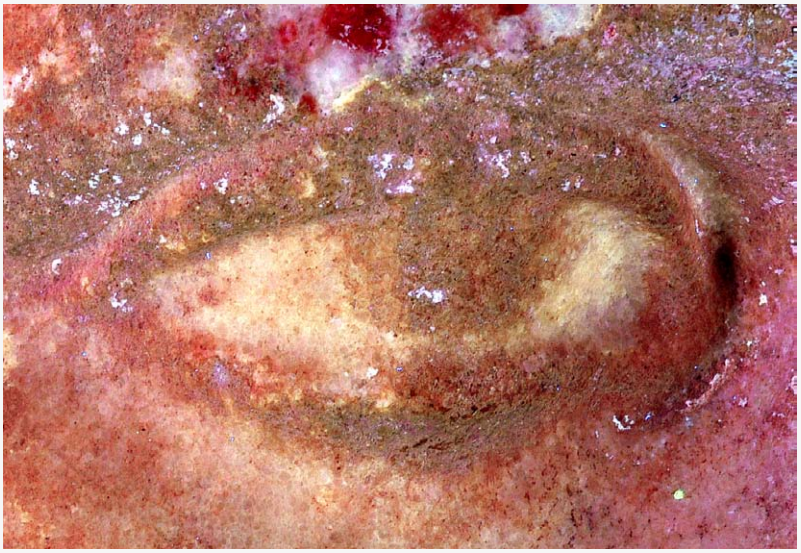

Fig. 5: UV-FL of white in the right eye and iris of female head, IN 2830, detail.

later re-worked areas – i.e. most of the left eye and cheek. In the re-worked areas the fluorescence was brighter, bluer.[33]

INFRARED REFLECTOGRAPHY (IRR) images were captured of relevant areas (as documentation) but on this sculpture the technique did not reveal information that was not visible in tungsten light or in UV-FL.

CROSS SECTIONS

The four cross sections of paint exhibited the following features under microscopy:

Sample 1 (from area of presumed skin colour on right cheek): A three-layer structure with a white layer at the top and bottom and a light ochre layer as the middle layer. Each layer is approx. 100 micrometer thick (with some variation), the top and bottom layers being finer grained than the middle layer. At the right side of the cross section are a relatively large orange-red grain and some fairly small grains scattered over the entire ochre layer (Fig. 2, left part). In UV-FL the middle ochre layer absorbs more UV than the top and bottom layers and none exhibit a strong fluorescence. The orange-red grain absorbs while a few other grains fluoresce vividly.

Sample 2 (from damaged area above forehead): Consists mainly of two layers with the majority of the sample being a thick white layer and at the top of the white layer large red-brown grains. Some of these grains appear semi-transparent, the white layer apparently shining through. The white layers fluoresce vividly with a yellowish fluorescence. The large red-brown grains exhibit a nearly full UV-absorbance thus appearing dark (Fig. 2, right part).

Sample 3 (from area of presumed skin colour under left eye): As in Sample 1, a three-layer structure with white layers at the top and bottom of the cross sections. Contrary to Sample 1, only the white top-layer appears finely-grained while the middle ochre layer and the bottom ground layer appear comparatively coarse; each layer is approx. 100 micrometer with variations. While the two lower layers show a discreet fluorescence the upper layer exhibit a fairly strong yellow UV-FL (Fig. 3, left part).

Sample 4 (from area of presumed hair colour): A relatively coarse layer structure with many large and small white grains mixed with a variety of small ochre, brown, red and orange grains. Mixed into this are some small black grains and one large black grain. While most of the layer has a discreet UV-FL an area on top of the structure and partly downwards through the center exhibit a yellowish UV-FL (Fig. 3, right part).

VISUAL EXAMINATION, UV-FL, IRR AND CROSS SECTIONS provided a considerable amount of information as well as some yet unsolved problems. No tool marks or surface phenomena that could be related to local colours were found when examining the surface. Paint fragments were confirmed visually in normal light and in UV-FL. A few were sampled and made into cross sections. Summing up the results of the visual analysis and cross sections it appeared that the skin colours were three-layer structures, the hair exhibited a one- or two-layer structure and the putty-like material with red-brown paint on the forehead had a two layer structure.

At the bottom of the two skin colour samples a white layer was present, assumed to be a ground layer. Compared with a typical European medieval ground layer often exceeding 1 mm this sculpture had a thin ground layer. This may be explained by the very careful finish of the surface of the face – on medieval sculpture the wood carver usually left the surface

33 This is in accordance with similar observations, see Rorimer 1931, p. 15ff.

fairly coarse, relying on the persons producing the thick ground and paint layers to level out the unevenness. From a technical point of view this is remarkable: it must have been more labour intensive for the sculptors to have produced a smooth surface e.g. on the skin area of the marble than if a painter were to produce a similar smooth surface (on top of a more coarse marble surface) using calcium carbonate in a binding media.

The two samples of skin colour – very alike – had a fairly thin layer of light ochre on top of the ground, and in both cases a white layer on top. The top white layer could either be a secondary addition or it could be a thin white layer to regulate the effect of the ochre - perhaps make the ochre appear more light and lifelike? One might also consider the light refracting impact of the crystalline structure of the marble through the very thin paint layers. No obvious comparison with medieval European painting technique could be identified with regard to a white layer on top of a skin colour.

UV-FL made the difference between the apparent original surface with the discrete UV-FL and other parts with a more white-blue UV-FL stand out – the latter interpreted as secondary surfaces. While it can be assumed to be a characteristic for an original surface to exhibit discrete 'warm' grey UV-FL there is no simple explanation for the reason. Deterioration phenomena of the stone itself as a possibility has been suggested by Rorimer[34] but remains from the paint layers (e.g. micro particles and binding media, or microbiological deterioration) may also play a part. UV-FL revealed important information when studying the white of the eye in the right eye in UV-FL. The white of the eye showed a prominent fluorescence while no pigments particles were visible leading to the assumption that the white part of the eye was painted with a pigment and binding media layer that has left a fluorescing substance in the stone surface.

SEM/EDAX

SAMPLE 1: The BSE picture of sample 1 is given in Fig. 6 (top left). The magnification is × 1000, meaning that the sample is approx. 0.15 mm in cross section. From Fig. 6 it is evident that a coarse thick middle layer is bounded by thin fine grained layers at the top and the bottom. Maps with the distribution of Ca, Mg, Fe, S, Cl, Na, Si and P are shown in the remaining part of Fig. 6.

All three layers in sample 1 consist of calcium carbonate ($CaCO_3$) with a number of grains in the middle coarse layer that are very rich in Ca (the white grains in the Ca map).

From the Fe distribution it is evident that the concentration of Fe is higher in the coarse middle layer especially in the right side of the sample. The presence of Fe indicates that an ochre paint was used for the colour of the skin.

Si originating from silicate aggregate like quartz (SiO_2) is concentrated in the lower layer of the sample, but Si is also observed outside the sample in the embedding material, hence originating from a Si containing abrasive used in the manufacture of the sample. A large salt grain (NaCl) is observed in the upper right part of the sample.

An interesting feature is observed in the S map. A sulfur containing material, probably gypsum ($CaSO_4 \cdot 2H_2O$) is observed in high concentrations on top of the upper layer and running through the coarse layer. This second S containing layer, that is parallel with the first, reveals that the coarse middle layer consists of more than one single layer. A gypsum layer like the one found indicates that this layer for a period of time was the surface of the sample. Between the two highly concentrated S layers, the concentration of S is slightly elevated compared to the rest of the sample.

34 Cf. note 24.

From the EDX results there is no explanation for the very bright orange colour found in the tungsten light photograph of sample 1 (Fig. 2, upper left).

SAMPLE 2: The red-brown colour of the damaged area at the forehead presumed to be a secondary surface appears as very bright red large grains in the tungsten light photograph (Fig. 2, upper right). BSE pictures of the two halves of sample 2 are shown upper left in Fig. 7a and 7b. The magnifications are ×350 and ×200, meaning that the sample is approx. 0.5 mm in cross section. It is evident from the pictures that in the right area of the sample the red grains look very white in Fig. 7a (upper left); this means that a heavy element is observed in relation to the red colour. In the left part of the sample (Fig. 7b, upper left), the red grains appear much darker indicating lighter elements. Here the darker grains are coated by heavier elemental compounds. As a consequence the two parts of the sample were examined separately.

A BSE picture and element maps of Ca, Ba, S, Fe, K, Al, Si, Na and Cl in the right part of the sample are shown in Fig. 7a. From the maps of Ba and S it is evident that these two elements are responsible for the compound found in connection with the red layer. Ba and S are found as barite ($BaSO_4$), which is white and not red. From the map of Fe it seems that a Fe compound is coating the barite grains. If this Fe compound is responsible for the red colour, it is a hematitic red ochre compound (Fe_2O_3). The Ca map reveals that the white matrix is calcium carbonate, and maps of Na, K, Al and Si show that large grains of potassium feldspar ($KAlSi_3O_8$) are used as aggregate in the chalk. The other alkali feldspar mineral albite ($NaAlSi_3O_8$) is not present.

A BSE picture and element maps of Ca, Ba, S, Fe, K, Al, Si, Na and Cl in the left part of the sample are shown in Fig. 7b. In this part of the sample only one grain of barite is found, implying that in the left part of the sample, the red colour has a different origin. The map of Fe shows that a Fe compound, again red ochre (hematite is presumed), is responsible for the red colour. The Fe compound is coating large grains, as is evident from the BSE picture of the left side of the sample and from the Fe map. This is contrasted by the tungsten light picture of sample 2 in Fig. 2 (top right image), where entirely red grains are observed. The ochre is coating grains of quarts (SiO_2) and potassium feldspar ($KAlSi_3O_8$) and again no albite ($NaAlSi_3O_8$) is observed, see the maps of Na, K, Al and Si in Fig. 7b. The Ca map confirms the presence of calcium carbonate.

We are not familiar with earlier findings of red ochre on barite grains or on silicates responsible for red paint layers. Examination of the red colour of the grains in Fig. 2 (top right image) reveals that they do not have an ordinary ochre colour, the red looks rather as an organic lacquer or cinnabar (HgS) or some lead red. However no traces of either Hg or Pb are found in the sample by EDX analyses. A red lacquer precipitated on barite or silicate would be expected to fluoresce in UV pictures; this is not the case, as evident from Fig. 2 (center right UV-FL image).

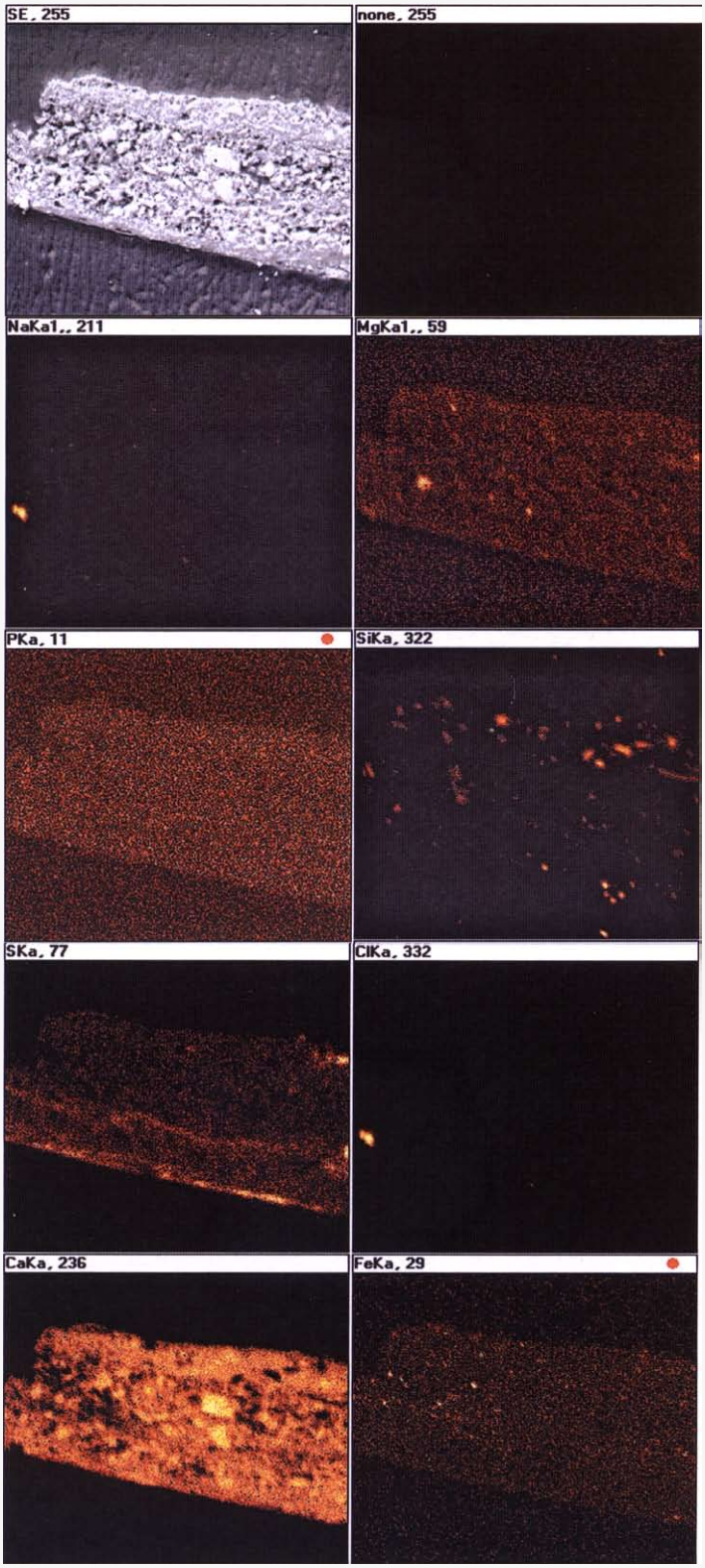

Fig. 6: Sample 1 flesh colour on cheek; SEM/EDX, ×1000, 20 kV. From top left to bottom right: BSE picture (top left) and element maps with the distribution of [none], Na, Mg, P, Si, S, Cl, Ca and Fe (bottom right).

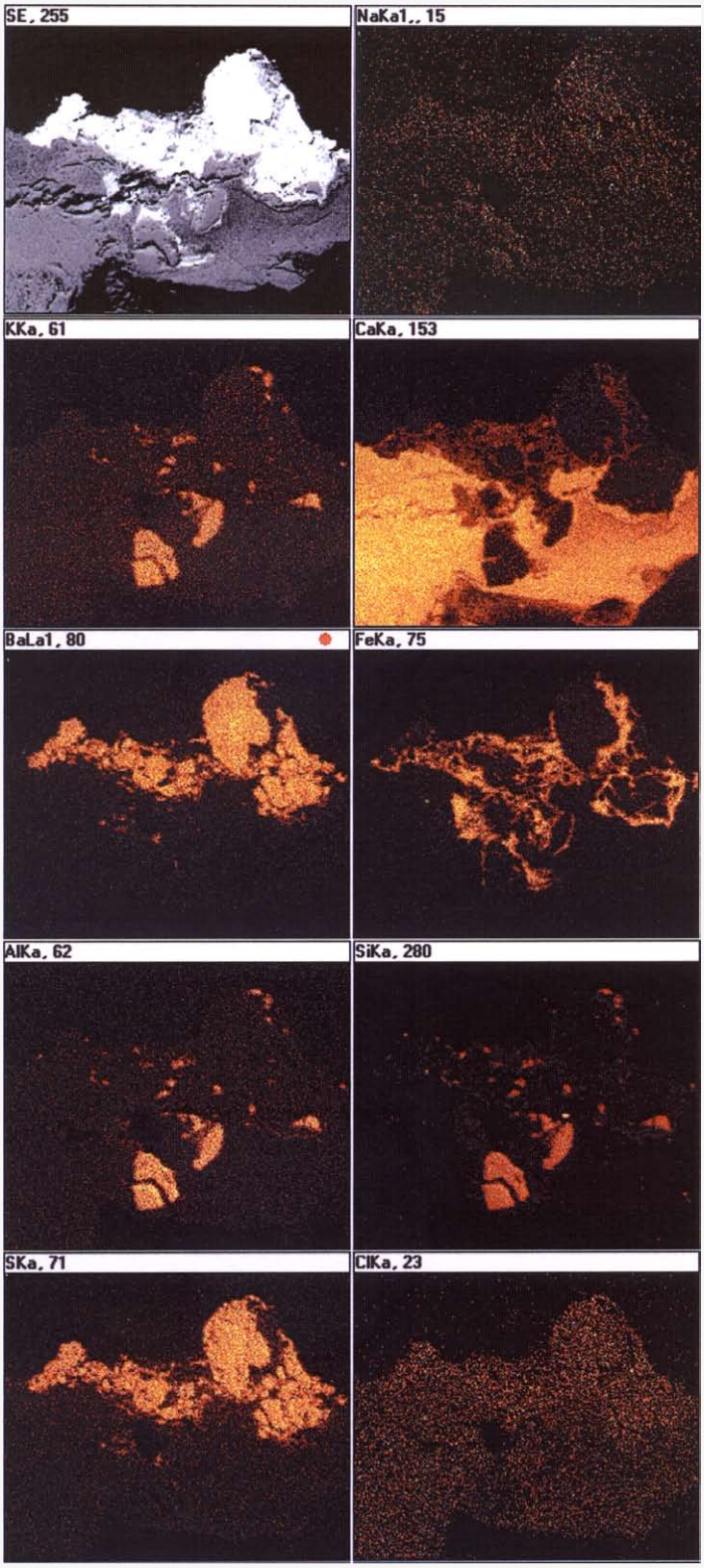

Fig. 7a: Sample 2 right part, damaged area at forehead; SEM/EDX, ×350, 20 kV. From top left to bottom right: BSE picture (top left) and element maps with the distribution of Na, K, Ca, Ba, Fe, Al, Si, S and Cl (bottom right).

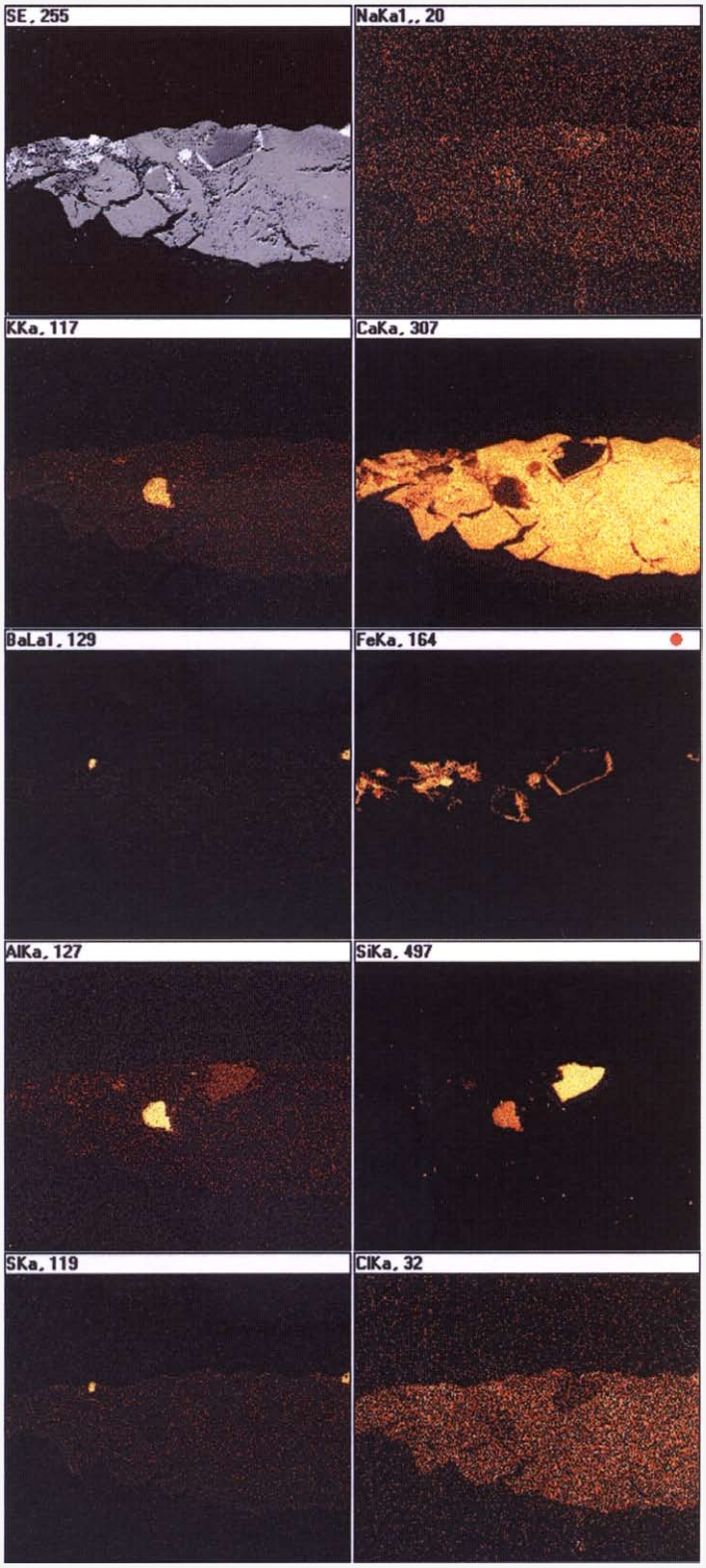

Fig. 7b: Sample 2 left part, damaged area at forehead; SEM/EDX, ×200, 20 kV. From top left to bottom right: BSE picture (top left) and element maps with the distribution of Na, K, Ca, Ba, Fe, Al, Si, S and Cl (bottom right).

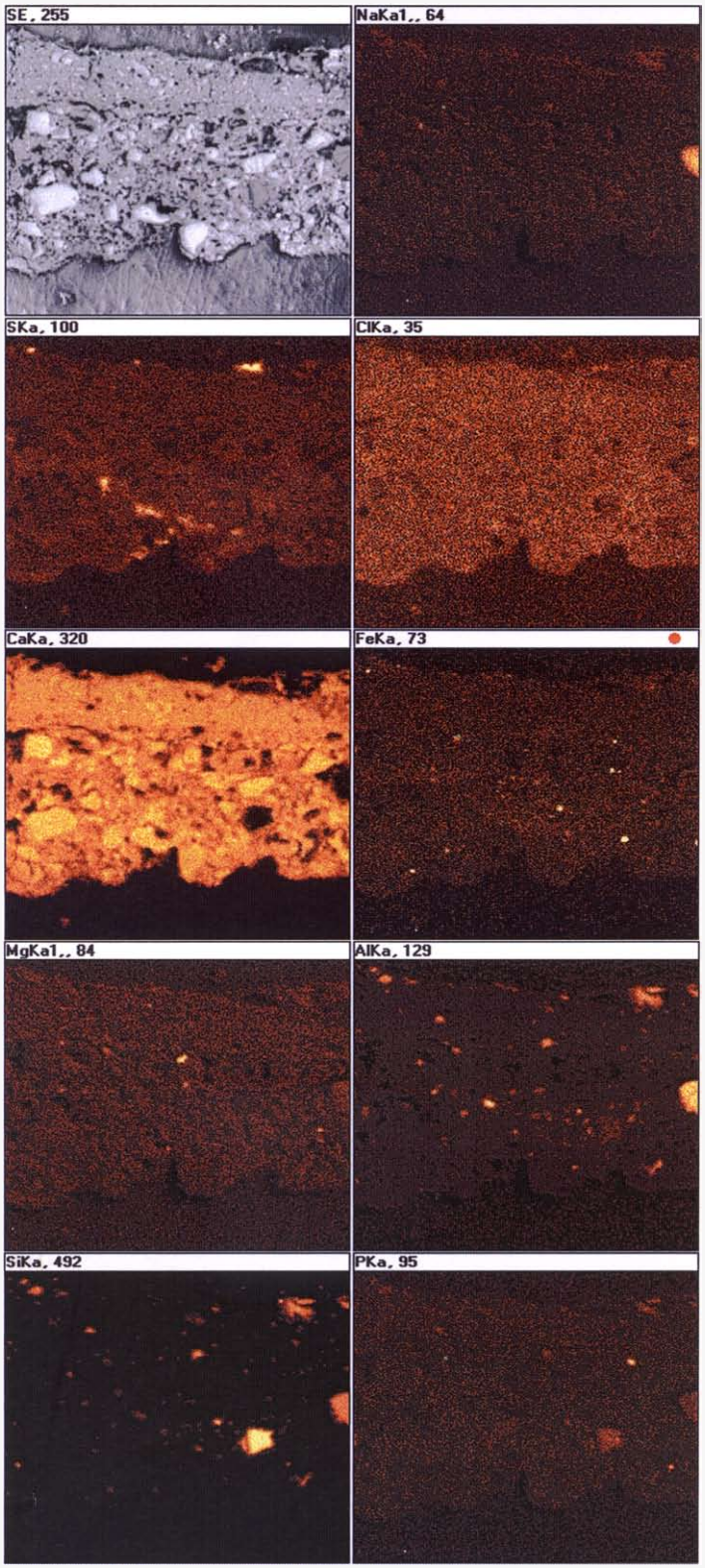

Fig. 8: Sample 3 flesh colour near left eye, SEM/EDX, ×750, 20 kV. From top left to bottom right: BSE picture (top left) and element maps with the distribution of Na, K, Cl, Ca, Fe, Mg, Al, S and P (bottom right).

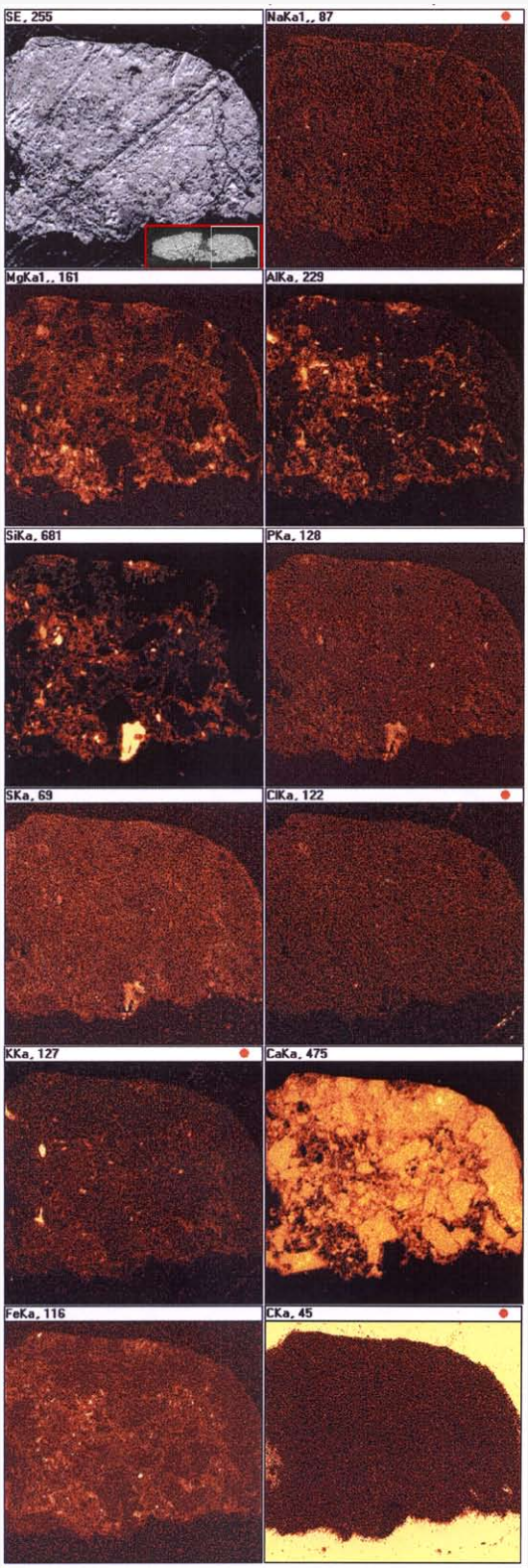

Fig. 9: Sample 4 hair above left ear (detail of sample), SEM/EDX, ×500, 20 kV. From top left to bottom right: BSE picture (top left, with miniature BSE picture of the whole sample inserted) and element maps with the distribution of Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe and C (bottom right).

SAMPLE 3: The BSE picture of sample 3 is given in Fig. 8, the magnification is ×750, meaning that the sample is approx. 0.25 mm in cross section. From Fig. 8 (top left) it is evident that a coarse thick layer is overlain by a thinner finer grained layer. Maps with the distribution of Ca, Mg, Fe, S, Cl, Na, Si, Al and P are shown in the remaining part of Fig. 8.

Both layers in sample 3 consist of calcium carbonate with a number of grains in the lower coarse layer that are very rich in Ca (the white grains in the Ca map). Al is distributed in both layers probably originating from clay minerals. A few large grains are rich in Na, Al and Si indicating the feldspar mineral albite ($NaAlSi_3O_8$) in contrast to the potassium feldspar found in sample 1 and 2, and quarts grains are also observed. A peculiarity is P found in connection to the silicates. Fe, probably as a yellow ochre, is responsible for the skin coloured appearance of the sample. Sulfur (S) observed in sample 3 is concentrated in spots on the top of the sample and in two thin layers that are angled approx. 45 degrees to each other; one layer is in a crack. We believe that these layers have been exposed as surfaces, where S from the environment is able to react with the calcium carbonate resulting in the formation of gypsum on the surface.

SAMPLE 4: BSE pictures of sample 4 are given top left in Fig. 9, with the whole sample in miniature and a detail of the paint layer. The detail is from the left in the sample.[35] The magnification of the detail is ×500, meaning that the sample is approx. 0.45 mm in cross section. The BSE picture of the whole sample reveals a rather homogeneous surface (with respect to element number) with a part in the middle of the sample that is much darker, implying significantly lighter elements. Maps with the distribution of Ca, Mg, Fe, S, Si, Al, K, Na, Cl, P and C are shown for the detail of the sample in the remaining part of Fig. 9.

The tungsten light picture in Fig. 3 (top right) shows a whitish coarse grained sample with orange pigment grains and one very large black grain in the middle of the sample.

The C map in Fig. 9 identifies the black grain as charcoal. Visual identification of the orange grains in the sample would indicate a pigment like minimum (Pb_3O_4), however no lead (Pb) was discovered in the sample. The orange colour is attributed to Fe present in the sample (Fe map in Fig. 9) where Fe rich particles are observed.

The white matrix is Ca rich (Fig. 9) and consists of calcium carbonate. The left part of the sample (Fig. 9) is relatively richer in Mg than the rest of the matrix, indicating the use of dolomitic limestone, i.e. the chalk containing mineral dolomite $CaMg(CO_3)_2$.

Quartz grains SiO_2 (Si map) and potassium feldspar grains $KAlSi_3O_8$ (K, Al and Si maps) have been used as aggregate (Fig. 9). Salt NaCl (Fig. 9, Na and Cl maps) is observed in the lower right part of the sample.

A grain with an elevated content of S and P is observed in Fig. 9. We have no obvious explanation for this.

FT-IR + ATR

The main pigments/fillers in all layers in all four samples were determined by carbonate bands to be some form of calcium carbonate ($CaCO_3$).

While the pigment composition appeared the same in the white top and bottom layer in *Sample 1* (skin colour) a certain physical difference could be seen between these two layers. The top layer of Sample 1 appeared a little less dense judged by a slightly higher amount of esters from the (polyester) matrix had penetrated the top layer than the bottom layer and the mid ochre layer. The mid ochre layer in *Sample 1* and *Sample 3* (skin colour) did not show traces of iron oxides or silicates as expected.

35 The SEM/EDX analysis was done with the sample positioned upside down.

The white (main) part of *Sample 2* (damaged part at edge of forehead) again comprised of calcium carbonate (very much like in *Sample 1* and *Sample 3* and as these with no traces of silicates). The various red grains were examined and gave slightly different results. At the right side of the sample the main part of the grains was calcium carbonate while on the left side it appeared more like a mixture of calcium carbonate and silicates such as feldspar. In three grains to the right no calcium carbonate was detected at all. Bands suggesting sulphates were detected. Comparisons with IRUG tables like IMP00194 anglesite and IMP00197 anorthite supported these observations. Barium was not detected in the grains by FT-IR. The red color of the grains appeared to be linked to iron oxides.

Sample 4 (hair) consisted mainly of calcium carbonates as well but was distinguished from *Samples 1–3* by the presence of silicates with the calcium carbonate. The brownish color of the sample was due to iron oxides, silicates (ochre) as well as small black particles (carbon black) and a fairly large black grain.

FT-IR was used to examine the four samples for traces of organic materials like binders. In general it was necessary to distinguish between traces that may be linked to the matrix polyester and possible original organic materials. In most cases – examining layers of the four samples – there were no traces of binding media. Neither proteins, carbon hydrates nor resins could be found but in a few cases a hint of a possible wax or (more likely) oil were found. Oil was partly judged by tops around from 1700 to 1715–20 cm^{-1} and some CH groups around 3000 that appeared a little stronger than the groups in the matrix ester. That a possible oil was partly deteriorated was determined by the shift of tops from around 1730–40 to a lower level. These observations were made on Samples 1, 2 and 3 while hardly any significant tops around 1700 were found in Sample 4.

The FT-IR analysis of the samples confirmed the calcium compound to be calcium carbonate ($CaCO_3$). Although a number of analyses were done with the ATR on small areas (approx. 35 × 35 micrometer) on the cross sections in order to verify or exclude the presence of possible organic binders only weak signals were found and thus no definite conclusions could be drawn. However, in a few cases – on a few spots on the uppermost layer of sample 1 and sample 3 – some indications of either traces of oil or a wax could be found. It might be correlated with the fact that the uppermost white layer appeared more porous – a fact that caused some discussion as it might also have allowed the embedding media to be absorbed in the same layer. Repeatedly, the embedding medium (polyester) seemed to create false signals of an organic binder near edges of the embedded sample which led to considerations about alternative embedding strategies and materials.

GC-MS

GC-MS extended the analysis of organic materials in the samples and indeed showed the presence of the fatty acids P (Palmitine) and S (Stearine) thus indicating oil. This may also complement the weak signal of possible oil in some of the FT-IR analyses. However no A (Azlaine) was found and thus the oil appears not to have been a drying oil.

There are some possible explanations for this. One is that a non-drying oil may have been applied in antiquity, another that the non-drying oil has been applied in recent time, either as a part of the preparation of the sculpture for sale or a treatment done by the two known owners in recent times.[36] It is likely that a treatment with a non-drying oil (or a composi-

36 The person who bought the sculpture in Athens at the beginning of the 20th century or staff at the Ny Carlsberg Glyptotek.

tion where such oil were included) has been applied to saturate a recently cleaned or a lean or dusty surface.[37] It has not been verified if such oil is present in non-painted areas of the sculpture. The background analysis exhibited a fair amount of pollution and for that reason it is included in the chromatogram.

SEM IMAGING

26 images of calcareous fragments from paint sample 1 (17 images captured[38]) and sample 3 (9 images captured[39]). On one fragment a possible organic form was identified, length approx. 15 micrometer, width approx. 10 micrometer.[40]

No coccoliths were identified on the surface of the 26 images of calcareous fragments from paint sample 1 and sample 3. On one fragment an organic form was identified. The possible organic form has not been further identified; it might be a fragment of a fungus or spore?[41] The well-defined calcium-crystals in the fragments and the lack of coccoliths led to the assumption that the calcium containing grounds and pigments derived from marble – or rather marble-dust.[42]

When combining and discussing the results from the visual examinations, UV-FL, IRR and cross sections with the instrumental analysis it appeared that the stratigraphy of the original sculpture may have had only two layer structures. In the skin colour areas a ground and a paint layer – light ochre – while the white top layer might be secondary as a thin line or spots of gypsum between the layers indicate. It is, however, not possible to determine the age difference between the original and the possible secondary layer. The chemical composition of the layers was mostly determined – in terms of pigment/filler – to be calcium carbonate, dolomite, some clay minerals, ochre and black. The calcium carbonate probably is marble powder as no coccoliths were present. Nothing definite was found concerning binding media in the four samples. Only traces of a non-drying oil were identified: such oil has with all probability not been used as the paint layer would not have dried and thus may have been a late addition. Although nothing was identified the paint may have contained one or more of a number of possible binding media including animal glue, starch, egg, waxes, (drying) oils, gums, perhaps resins, resinous compounds or balsams – or mixtures. However, most such organic compounds may have deteriorated by now to a point beyond analytical detection. One reason for deterioration could be the possibility that NCG IN 2830 – as is the case with other antique statues – may have been exposed to e.g. bacteria while buried underground. Furthermore it can probably not be ruled out that an 'al fresco' technique has been used to bind the pigments.

37 For a survey of possible traditional surface treatments to marble sculptures, see Plenderleith – Werner 1971, p. 311ff.

38 Images NCG 2830 sample 1a – NCG 2830 sample 1q.

39 Images NCG 2830 sample 3a – NCG 2830 sample 3h.

40 Images NCG 2830 sample 1m, 1n (overview) + NCG 2830 sample 1o (detail).

41 Oral communication from Prof. Dr. Minik Rosing.

42 Marble dust is known to have been used in some cases for ground materials and is referred to in painting treatises, see for example 'Mappa Clavicula' (note 11), chapter 122B with a description of powdered marble and glue.

CONCLUSION

Traces of colour was confirmed as being paint, applied to a ground layer. The most prominent paint layer is the skin colour. The general stratigraphy and pigment composition has been affirmed while the binding media is yet not confirmed. The techniques used during the Pilot Project has led to adjustments to the protocol to be applied in the examination of sculptures within the framework of the Main Project. Some uncertainties may be related to the fact that most sculptures in older collections have been acquired without information about excavation and prior treatment. Furthermore, few collections have record of earlier in-house treatments (if any) making an assessment of previous condition complicated and making it difficult to evaluate materials present (or not present) on the surface. Hopefully the results of the Main Project as well as results from similar investigation campaigns in other collections or by contemporary field archaeology will create a better knowledge basis concerning the original state and visual appearance of the sculptures as well as a better understanding of the deterioration process – the latter in order to enhance the protection and preservation of the remains of colour on the ancient sculptures.

ARCHAEOLOGICAL COMMENT

This fragment of a female head (Fig. 1) was bought c. 1910 at Athens by the Danish architect Sven Risom and acquired for the Glyptotek in 1940. The marble is probably Parian Lychnites.[43] On stylistic grounds, it is unanimously held to be a Classical Greek original, made at Athens c. 425 BCE.

The head is related by its style to a group of other Attic female marble heads and fragments associated with the Parthenon sculptures and sculptures of the immediate post-Parthenonic period.[44] Like the Glyptotek head, a number of these pieces have drill holes in the hair for the attachment of metal ornaments such as diadems and wreaths. This feature and the slightly over life size format suggest that the head is that of a goddess.

Compared to that of the Greek Archaic and Early Classical periods, the sculptural polychromy of the Classical and Late Classical period remains poorly documented. The summary offered by Reuterswärd in 1960[45] has not been substantially challenged by subsequent research.

The results related above have special bearing on one of the most contested issues, namely how the nude parts of marble sculptures were dealt with. Was a skin colour applied or not?

For the Archaic period, the evidence available remains meagre and its interpretation debated.[46] In the light of the present state of our knowledge, it would seem advisable to be very open-minded and avoid generalizations. The decision to apply a skin colour or not may

43 Cf. note 4. The use of Parian Lychnites marble by Attic sculptors was widespread.

44 Berger 1956. See also two other fragments in Athens: National Archaeological Museum inv. 4491 (reference in Moltesen 1995) and 3739 (Kaltsas 2002, p. 123, no. 228 w. bibl.).

45 Reuterswärd 1960, pp. 85–88.

46 Reuterswärd 1960, p. 68, lists the Archaic (and Classical) instances of a skin colour known to him, with page references to his treatment of the sculptures concerned; the polychromy of the period is summarized pp. 69–70 and 70–74 (on surface treatment with wax, ganosis), and pp. 74–80. Reuterswärd's discussion of skin colour lacks focus and structure. Brinkmann 2003, pp. 43–45 asserts that a skin colour was the rule. This position is strongly challenged by Schmaltz 2005, pp. 24–30. To my knowledge, the question of skin colour has not been addressed as a separate subject since the still important studies by Richter 1928/29 and 1944. A concise presentation and discussion of the evidence now available is needed.

have been influenced by factors such as material, monument type, context, formats and regional traditions.

As for the Classical period, evidence is even thinner. The number of sculptures known to have or have had a skin colour is very small and none have been investigated in depth. To my knowledge – which may well be too limited – the monuments in question are the following:[47]

- *Hephaisteion*, east and west frieze, Athens, c. 450 BCE. Traces of red on male figures.[48]
- *Funerary relief of Philis*, from Thasos, c. 450–44 BCE. Skin colour on the cheeks.[49]
- *Reliefs from Myra*, Lycia. Grave 81, entrance room. 4th century BCE. Skin colour on adult male, woman and boy.[50] (Fig. 10)
- *Mausoleum at Halicarnassos*. Mid 4th century BCE. Skin colour on Amazon Frieze and coffer reliefs.[51]
- *Sarcophagi from Sidon*. 4th century BCE. Male skin colour on Alexander Sarcophagus and female skin colour on lid pediment reliefs on Mourning Woman Sarcophagus.[52]
- *Attic funerary relief with horse and black groom*. 4th century BCE. Bluish-black skin colour on groom.[53]

47 Cf. Reuterswärd 1960 as in note 52. On the colour of skin in 4th century BCE written sources see Villard 2006, pp. 43–54, focusing on the word 'andreikelon' meaning both a statue of a man and the colour of skin. Cf. Theophrastos, De lapidibus, 51, 6 on the painters use of ochre ('miltos') in preparing skin colours, 'ta andreikela', Villard 2006, p. 48.

48 Athens, in situ in the pronaos of the temple. Reuterswärd 1960, p. 52, cf. Koch 1954, p. 101, with his own observation of reddish skin colour on both friezes (no colour reproduction). I do not know of any visual documentation in colour.

49 Paris, Louvre Ma 766. Reuterswärd 1960, p. 58 (not Louvre Ma 706 as in his note 129); Hamiaux 1992, p. 108, no. 97, 'the colour mentioned in earlier literature has disappeared.' No colour reproduction of earlier state exists.

50 Reuterswärd 1960, p. 58; Borchhardt 1975, pp. 135–146, Farbtafel I, 1–2 (colour photographs of Relief II and IV in Tomb 81). Borchhardt's description of preserved colour traces does not include skin colour. Cf. the now lost (see Borchhardt 1975, p. 135) painted casts of the British Museum BM Cat. 954 of the tomb 81 reliefs Borchhardt 1975, 81, II, III and IV as described in Reuterswärd 1960, loc.cit., n. 130. The only existing visual documentation of the polychromy of these three reliefs is now the colour plate reproduction of water colour renderings by G. Scharf in Fellows 1841, p. 198ff.

51 Bodrum and London, British Museum. Reuterswärd 1960, p. 59; Jenkins et al. 1997, especially p. 38, right column, with mention of skin colour on the Amazon frieze, but no colour reproduction; Cook 2005, p. 30. Skin colour on the relief sculptures of the Mausoleum remains to be visually documented. For polychromy on the free-standing sculptures of the Mausoleum see Waywell 1978 and Higgs 2006, pp. 190–193 (Colour on the Amazon Frieze and free-standing sculpture).

52 Istanbul, Archaeological Museum, inv. no. 368 (Mourning) and 370 (Alexander). Reuterswärd 1960, pp. 60–62, p. 60 w. references to early colour reproductions in note 133. For the Alexander Sarcophagus cf. V. Brinkmann in Brinkmann – Wünsche 2007, pp. 150–162 and H. Piening, ibid., pp. 168–171, with documentation in colour. For the Mourning Women sarcophagus cf. now Fleischer 1975, p. 60 reporting skin colour still visible (no colour illustrations). For colour photographs of near-present state: Pasinli 1989, pp. 14–17 (Mourning), pp. 18–33 (Alexander).

53 Athens, National Archaeological Museum, inv. no. 4464. Reuterswärd 1960, pp. 62–64; Kaltsas 2002, p. 206, no. 415. No colour reproduction.

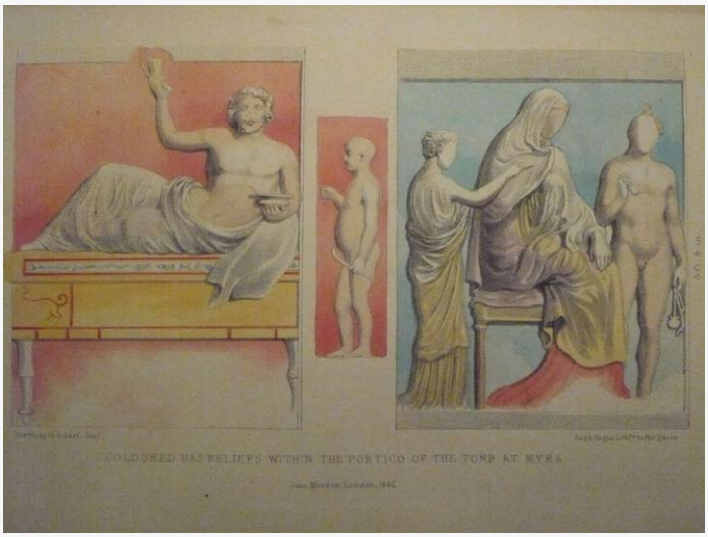

Fig. 10: Tomb 81, Myra. Reliefs in the entrance room. 4th century BCE. Water colour by G. Scharf as reproduced in Charles Fellows' An Account of Discoveries in Lycia, 1841.

These monuments have in common the fact that they are all reliefs, rather than free-standing sculptures in the round. From this, no conclusions can be drawn at this point as to whether the polychromy of classical reliefs differed from that of sculptures in the round: far too few sculptures in the round of the Classical period have so far been examined in-depth with the technology now available.[54]

To date, we have therefore no published study of samples taken from skin colour remaining on Greek marble sculpture of the Classical period. The cross sections of the skin colour of NGC IN 2830 and the data obtained from them therefore have no parallels with which they might be compared. Consequently, this skin colour may in principle have been applied in post-classical or even post-antique times. Further comparative data must be accumulated in order to reach firmer ground.

In this regard, coordinated, systematic and not least, interdisciplinary study of polychromy in museum collections of Greek and Roman sculpture, conducted to some agreed standards, is needed. A pilot study of sculptures in the British Museum, launched in the summer of 2009, is the more welcome.

One among many important issues to be faced is that of the taking of samples. The use of invasive methods[55] needs to be discussed in the light of present day technology, in a forum composed of curators and conservators.

In such a discussion, it needs to be recognized that the size of a sample as needed for cross section analysis and further in-depth instrumental examination is minute to the point of being invisible to the naked eye, i.e. on an average c. 0.3–1 mm^2. One should obviously not remove the last remaining shred of ancient pigment, but have some agreed standard to determine when the taking of a sample is permissible.

54 It is instructive to read Bourgeois – Jockey 2005 reporting on their study of Late Hellenistic sculptures in the round from Delos. Examination under high magnification reveals evidence not visible to the naked eye – though not of a skin colour. The hypotheses put forward in existing literature on the possibly differentiated polychromy of the various classes of Classical Greek sculpture will be discussed in forthcoming publications by the authors of this article.

55 To be distinguished from 'destructive methods,' a term which relates to the impact on samples of the analytical methods employed.

If, on ethical or other grounds, the taking of samples is disallowed, it must be realized that we are thereby prevented from gaining data pertaining to essential aspects of ancient sculptural polychromy.

As far as our work at the Ny Carlsberg Glyptotek is concerned, the taking of samples is not ruled out a priori. Conditions allowing, it will be part of our standard protocol.

Just as important is an increased awareness among archaeologists and conservators working in the field, of possible, usually minute and very fragile remains of polychromy on finds of sculpture and architectural members.[56]

56 Discoveries of ancient sculpture and architecture with remains of polychromy are regularly reported from sites around the Mediterranean (i.e. Aphrodisias, Bet Shean, Corinth, Herculaneum, Gortyn, Narona, Oudna, Rome,Tarragona). But to my knowledge excavation directors, field archaeologists, field conservators and specialists in ancient sculptural polychromy have so far not met to discuss and formulate guidelines for best practise when dealing with such finds. A meeting should be organized as soon as possible.

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Preliminary results from geochemical analysis of pigments on ancient Greek & Roman marble sculptures

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INTRODUCTION

This is the report on analyses carried out within the framework of the Copenhagen Polychromy Network Pilot Project.[3] The aim was to use geochemical methods and geological reference materials to determine the mineralogical identity of ancient pigments, and to test whether specific regions of provenance of specific pigments can be identified. The latter could be addressed through major and trace element and isotopic compositions or by differences in the mineralogy of impurities in the pigments. When classifying ancient pigments, is important to keep in mind that classification of minerals in the present meaning of the word is a rather new concept, which probably had no meaning in Classical Antiquity. Likewise, the understanding of chemical components was also sketchy at best, at the time of manufacturing of the pigments. For these reasons, pigments would probably have been classified according to colours and technical properties and perhaps according to the site of their origin.[4] We may therefore introduce a scheme of classification that transgresses ancient classification schemes and which only reflects poorly the factors upon which ancient artists would have based their choice of pigments for a given project.[5] However, a classification based on modern geochemical and mineralogical principles may provide insight into the origins and processes of manufacturing of the pigments. In this Pilot Project, two sculptures in the Ny Carlsberg Glyptotek with red pigmentation were investigated by two different approaches.

IDENTIFICATION OF RED PIGMENTS

The first was a colossal marble head of Zeus/Jupiter (Fig. 1–5),[6] which carries a red pigment on the beard, cheeks and eyebrows. A sample of the pigment and its substrate was scraped from the sculpture. The powder from the beard was investigated under the microscope and by qualitative analysis by EDS (energy dispersive X-ray spectrometry) in a SEM (scanning electron microscope). The powder was fixed on sticky tape, gold coated and investigated under the SEM. This showed discrete pigment grains mixed with small particles of carbonate presumably derived from the substrate. Quantitative analysis of the pigment grains could

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3 See the introduction to the Pilot Project.

4 On ancient pigments and terminology: Koch 2000, 37–50 and Anhang II (Die Pigmente der griechischen Malerei); Der Neue Pauly IV (1998) s.v. Farben (N. Hoesch).

5 See for example Pollitt 2002.

6 Inv. no. 1664. Moltesen 1996, 227–229, no. 101. The reported find spot is a locality in southern Latium. The suggested date is c. 100 BCE. See archaeological comment below.

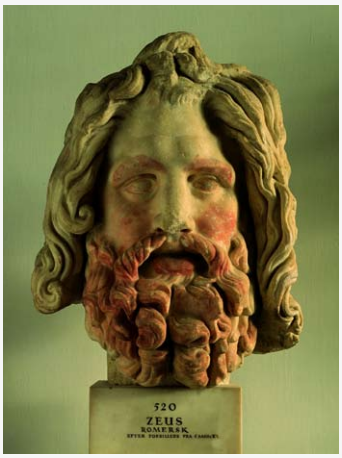

Fig. 1: Head of Zeus/Jupiter, Ny Carlsberg Glyptotek IN 1664. Marble. Height 54 cm, width 45 cm. From an acrolith statue. Front view. Museum photo.

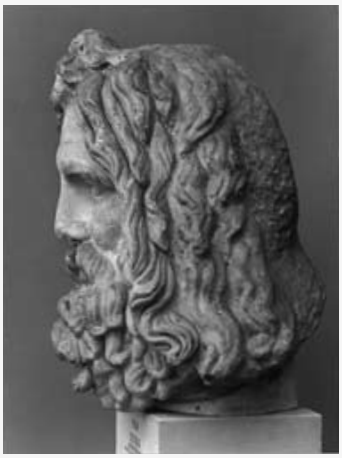

Fig. 2: As Fig.1. Left profile. Museum photo.

Fig. 3: As Fig.1. Right profile. Museum photo.

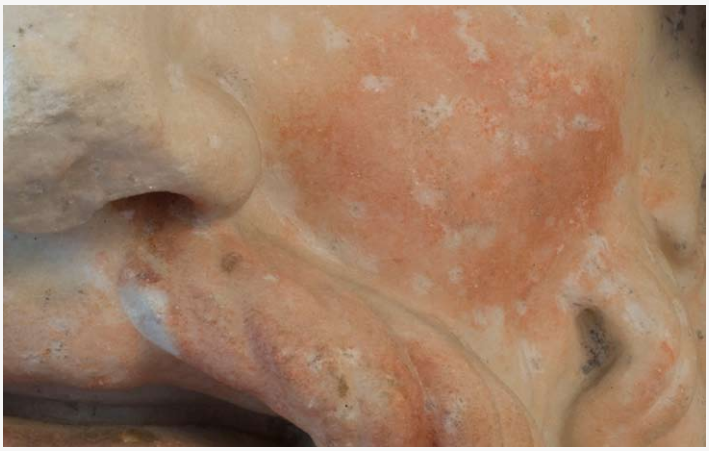

Fig. 4: As Fig.1. Detail of the left side of the face with red on cheek and beard. Photo courtesy M. Abbe.

Fig. 5: As Fig.1. Detail of red in the area of the left eye. Photo courtesy M. Abbe.

not be carried out by this method. The qualitative analysis showed that the pigment grains have high concentrations of Pb (lead), most likely in the form of lead oxide. Chlorine and traces of barium (Ba) and sulphur (S) were found in varying proportions in association with the Pb. This suggests that the pigment could be an impure Pb-oxide mineral powder containing other minerals derived either from an impure source, or formed by reaction of the primary Pb-oxide with agents from the environment during the millennia passed since the application of the paint. It is likely that Ba and S represent the mineral barite ($BaSO_4$), which may have been used as a white pigment or may be a constituent of the marble substrate. In addition to the Pb-rich pigment grains, the mineral chromite was also identified in the powder. This may possibly be a contaminant from the preparation of the pigment, as this mineral does not commonly occur with Pb-ores. Chromite is a common mineral in serpentine rocks that are found throughout the Mediterranean region, but could also be derived from gabbro or other dense massive rocks hypothetically used as mortars during crushing of the pigment.

INTERPRETATION

The simplest interpretation is that the red pigment is the lead oxide mineral red lead or minium (Pb_3O_4). The term minium has previously been applied to both Pb oxide and to the mercury sulphide mineral cinnabar. Pliny distinguishes between true scarlet minium, which was probably cinnabar, and an inferior product called minium secondarium derived from silver and lead foundries.[7] The latter was probably the lead oxide mineral we now call minium. The high content of Cl in some grains might hypothetically be due to the presence of the mineral laurionite (PbClOH), which may have been present in the source of the pigment, or perhaps have formed by reaction of primary minium as a consequence of exposure to saltwater. This has been the case in the slag piles around the mines of Laurion SE of Athens where from a number of secondary Pb minerals including Laurionite have been described. The provenance of the Pb in the pigment has been tested by Pb isotopic analysis by ICP-MS (inductively coupled plasma mass spectrometry[8]). The Pb isotopic data unambiguously shows that the Pb cannot be derived from Laurion or the Aegean region and recent contamination by modern industrial lead products can also be ruled out as a source of the lead. In a Pb-isotope discrimination diagram by Kylander et al.,[9] the isotopic composition of the lead in the pigment plot lies outside the fields of any Roman lead ores mined at the time. This might suggest that the minium was indeed prepared as a by-product of silver production. In antiquity silver was produced by a process called cupellation.

The process involves two steps. Firstly, the silver ore is heated with metallic lead, which dissolves the silver, and forms an alloy that can be separated from the slag. Secondly the lead–silver alloy is heated in a furnace. During this process the lead is oxidized to the white lead oxide litharge (lithargyrus = silver stone) which separates as a froth that floats on top of the silver metal. The litharge is subsequently converted to minium by heating in air to c. 450° C. The litharge and the minium produced from it therefore contain a mixture of lead from both the ore and the lead added during the first step of the process. Following the rationale

7 Plinius the Elder, Naturalis Historia 33, 111–119 (trans. H. Rackman, Loeb Classical Library, Vol. IX, Cambridge, MA, 1952); Walton and Trentelman 2009, 846–847.

8 Analysed at a VG Elemental Axium instrument at the University of Copenhagen, and the data corrected for mass bias using a Ta spike. T. Kokfelt personal communication 2004.

9 Kylander 2005, 467–485.

of Walton and Trentelman, 2009,[10] the isotopic composition of the pigment on Zeus's beard has been compared to Pb from the Rio Tinto silver ore and lead from the lead mine at Murcia in Southern Spain. Lead ingots stamped with 'Nova Carthago' have been found in excavated silver smelting plants near the ancient Roman silver mines of Rio Tinto in southern Spain.[11] This lead was probably extracted from the Murcia mine by Cartagena. The isotopic composition of the red lead pigment used to colour Zeus's beard plots on a mixing line between the Murcia and the Rio Tinto lead compositions (Fig. 6), and is therefore most likely manufactured from litharge from the silver mines at Rio Tinto. The mass balance suggests that about 1/3 of the lead used in the process was lead metal from Cartagena, and 2/3 was lead carried by the lead – silver ore.

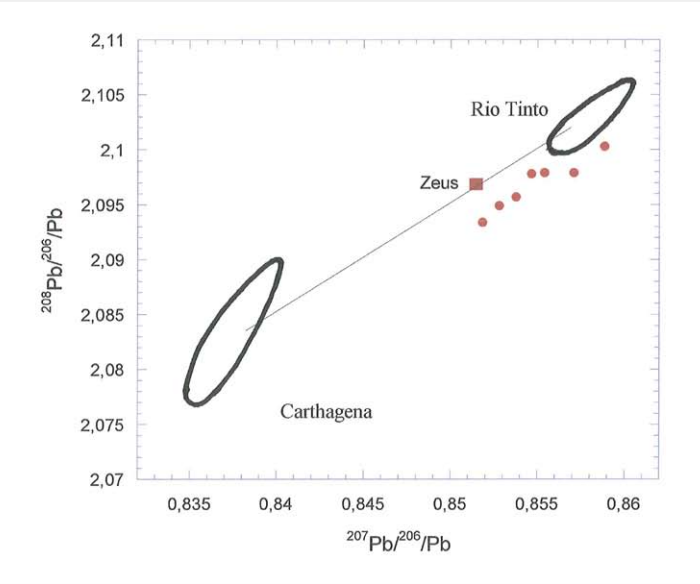

Fig. 6: The isotopic composition of Pb from the red pigment of Zeus's beard (open square). Also shown are compositional fields for Pb from Rio Tinto and Cartagena together with analysis of red pigments from Egyptian mummies shown as open circles from Walton – Trentelman, 2009. The Pb from the Zeus pigments plots on a mixing line between the Cartagenian and the Rio Tinto lead, and is dominated by lead from the Rio Tinto source.

The second sculpture investigated in this Pilot Project was an Archaic Greek limestone Sphinx from Attica[12] with traces of red colour. Here we used a hand-held XRF (X-ray fluorescence spectrometer[13]). This instrument has a ca. 1 cm^2 area of analysis. The analysis of a faint red pigmentation of the Sphinx showed higher levels of Fe in these areas compared to background, and there were no traces of Pb or other heavy elements in the fluorescence spectra from the pigmented areas, which lead to the conclusion that the red pigment on this sculpture was a Fe-oxide based pigment such as red ochre, which is abundantly present throughout the Mediterranean region.

10 Walton – Trentelman 2008.

11 Domergue et al. 2006, 14.

12 Inv. no. 1203. Johansen et al. 1994, 40, no. 4. The preliminary results of the examination of this sculpture are presented in an article further below.

13 Innov-X Alpha Series 8000 LZX/R.

CONCLUSIONS

It has proven possible to identify the mineralogical composition of pigments used on antique marbles, and, in this example, distinguish between two different red pigments, which superficially resemble each other. The analysis leaves little doubt that the beard on the Zeus head was deliberately painted with a red lead pigment. The pigment was most likely manufactured on a large scale during Roman times by secondary heating of litharge which was a by-product from silver production by cuppelation, and probably derived from Rio Tinto in Southern Spain. The litharge carried a significant amount of lead from Murcia/Cartagena added as metal during silver extraction by cupellation.

It seems that the hand-held XRF spectrometer is a very efficient exploratory tool, to guide more specific analytical strategies, such as isotopic analysis, XRD (X-ray diffraction) and EDS or WDS (wave length dispersive X-ray spectrometry) microanalysis. The XRF instrument has the clear advantage that it is easy to operate, fast and non-destructive, while the other methods require micro-sampling of the artefacts.

ARCHAEOLOGICAL COMMENT ON THE ZEUS/JUPITER IN 1664

This over life-size head in Greek (?) marble comes from an acrolithic statue (only head and nude parts in stone; dress in other materials mounted on a wooden core).[14] It was acquired for the Ny Carlsberg Glyptotek by Wolfgang Helbig in 1898, on the art market in Rome. The find spot was reported to Helbig as being the ruins of a Roman villa south of Ceprano, near S. Giovanni Incarico, in the interior of southernmost Latium.[15] There is no reason to doubt this information: the site was not of any consequence.

A couple of kilometres north of the village of S. Giovanni Incarico lay Fabrateria Nova,[16] a *colonia* of Rome's, founded in 124 BCE after the destruction of the rebellious town of Fregellae in 125 BCE. This latter important town was situated another two kilometres north of Fabrateria Nova, on the banks of the river Liri and astride the Via Latina.[17]

The head has generally been identified as Zeus/Jupiter,[18] though Poseidon/Neptune is also a possibility. It has been suggested that it is from a cult statue at Fabrateria Nova or Fregellae.[19] Stylistically, the head belongs together with a group of fragmentary above life-size sculptures from Central Italy in Greek marble, by Greek sculptors, of the mid 2nd to mid 1st century BCE. The majority are acroliths and they are generally regarded as coming from cult statues.[20]

14 The marble has not been identified. To the bibliography given by Moltesen 1996, 227–229, no. 101 add: Reuterswärd 1960, 200; Reusser 1993, 104 n. 61; Dörig 1995, 301–302; LIMC 1997; Coarelli – Monti 1998, 108 no. 101; Ghisellini 2003–2004, 514 no. 22.

15 Letters to Carl Jacobsen 11 September., 17 September. and 15 October, 1898, in the Ny Carlsberg Glyptotek archives.

16 Coarelli 1984, 207–208.

17 Cf. Coarelli – Monti 1993.

18 Cf. LIMC VIII (1997) 342 s.v. Zeus no. 219b (I. Leventi – V. Mackaira).

19 Reusser 1993, 104 n. 61; Moltesen et al. 1996, 227–228 (from the Capitolium at Fabrateria Nova?). No Capitolium or other sanctuaries relevant to Jupiter/Neptune have been identified in the two towns.

20 For the group, see Martin 1987, 207–248 (catalogue); Reusser 1993, 104 n. 104 (additions to Martin's catalogue); Ghisellini 2003–2004, 510–519 (updating of Martin and Reusser, includes pieces from elsewhere in Intaly).

These sculptures may broadly speaking be described as Late Republican or Late Hellenistic in style, and are to be seen in the context of the hellenization of Latium and Campania in the wake of the increased Roman contact with the Greek world of the Eastern Mediterranean from the early 2nd century onwards. A 'Hellenistic' and a 'Classicizing' stylistic current running side by side may be recognized. The identification and dating of individual pieces is often difficult.[21] Our head is usually dated to '1st century BCE' and seen as a variant of the Zeus Otricoli in the Musei Vaticani, a work which in its turn is often connected with a statue of Serapis in Alexandria, by Bryaxis and belonging to the late 4th century BCE.

The remains of colour on IN 1664 have so far been interpreted either as evidence of the ritual painting with red of cult images of Jupiter recorded by ancient authors, or as a mordant for gilding. Traces of gilding were not observed when the head was examined under binocular microscope in September 2009.[22] Indirect evidence that the hair of the head was given some sort of surface covering is found in the raw treatment and ancient piecing of the back. The fact that we are dealing with an acrolithic statue also entails the element of colour provided by the material used for the surfaces of the non-marble parts (drapery).

In the group of sculptures with which this piece is related, we are aware of only two instances of preserved polychromy: the head of the cult statue of Diana Nemorensis in the Glyptotek has faint traces of the pupil in its left eye, and red is preserved on the sandal sole of a foot fragment of the Fides from her temple on the Capitoline Hill in Rome.[23] Indirect evidence of polychrome elements on Late Republican cult statues are to be found in the form of inlaid eyes and piercing of ears for earrings.[24] Inlaid eyes are to our knowledge not represented among the male sculptures to which our head is related, but are found in Hellenistic male marble cult statues from Greece – a case in point being the head of Anytos from the group of cult statues in the Despoina sanctuary at Lykosoura by Damophon from Messene, of the late 3rd century BCE[25] It should be noted that a red pigment was observed on the foot of Despoina and the cuirass of Anytos; it is apparently no longer visible. The quality of the local stone used at Lykosoura would seem to recommend some sort of surface treatment.[26]

This does not affect the fact that the valuable evidence of painted sculptural polychromy provided by IN 1664 has limitations because it stands completely isolated. Comparative data from similar monuments are not available. The results of the analysis carried out would seem to confirm that the pigment was applied in ancient times, but whether it is the original polychromy or a secondary one, we cannot tell.

To make any progress, close examination is needed of the other, similar sculptures from Central Italy – and of Late Hellenistic marble cult statues from the Greek world.

21 For these aspects see Reusser 1993, 104–112 and Ghisellini 2003–2004, 479–509, both with extensive references to relevant literature.

22 Reuterswärd 1960, 198–200 w. n. 560 (ritual); Moltesen 1996, 227 (for gilding?). Microscopy by Mr. Mark Abbe, La Renta Fellow at the Fairchild Centre of Objects Conservation at the Metropolitan Museum of Art, New York.

23 Diana Nemorensis: IN 1517. Martin 1987, 236–237 no. 15; Moltesen 1996, 205–206 no. 90 (colour not mentioned). Fides: Reusser 1993, 218–219 no. 1d.

24 Inlaid eyes: Female head, Musei Capitolini inv. no. 253, Ghisellini 2003–2004, 511 no. 2. Ears pierced: Feronia from Terracina, Terracina, Museo Civico inv. no. 16, Martin 1987, 232, no. 13.

25 Most recently H. Schraudolph in Bol 2007, 190–197. 397 (bibliography). figs. 174k-m. Cf. Ghisellini 2003–2004, 490–493.

26 Faulstich 1997, 163 w. n. 682

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Raman spectroscopy characterization of colored pigments in archaeological materials

Rolf W. Berg

INTRODUCTION

Archaeological artifacts and artworks with colors are being increasingly analyzed in these years. The pigment materials used for their creation are much studied after the development of modern non-destructive micro sampling analytical techniques. Art historians, museum conservators, and archaeological scientists are now much aware of the importance of physicochemical characterization for the attribution of the historical period and genuineness of an item. Ancient technological methods used in the construction of the items may be characterized by spectroscopists with a minimal disturbance to the artifacts or artworks.

In this connection the Raman spectroscopy technique must be considered a most elegant method for pigment and materials analysis of relevant museum and archaeological materials. This is done by correlating some bands in the studied pigments with those of well characterized references. The use of Raman spectroscopy can be taken to illustrate this: It provides e.g. information of importance to art restorers and museum conservation scientists in preserving materials and the understanding of deterioration processes. It does so by identification of key components, as shown in Fig. 1.

Prior to the advent of modern Raman spectroscopy it was difficult to analyze archaeological materials, due to difficulties arising principally from the generation of fluorescence by shorter-wavelength visible radiation. There was also the real possibility of sample degradation occurring from the use of the relatively high laser powers that years ago were necessary for sufficient sample excitation. The major advantages of Raman spectroscopy over infrared spectroscopy, namely the weak Raman scattering of water, could not be fully exploited. This situation has changed recently, as shown below in this review.

The number of research papers on the subject of Raman spectroscopy applied to pigments and art has been growing very fast during the last years. To get a comprehensive overview we refer to three recent theme numbers of Journal of Raman Spectroscopy[1, 2, 3] and other dedicated texts such as e.g. Edwards et al.[4, 5]

To help the reader we start by a short presentation of some technical details in Raman spectroscopy.

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1 P. Vandenabeele, Raman spectroscopy in art and archaeology, J. Raman Spectrosc. 2004; 35 nos. 8–9: 607–609, and the rest of the special issue containing further 31 dedicated papers, pp. 606–818.

2 W. Kiefer, Raman spectroscopy in art and archaeology, J. Raman Spectrosc. 2006; 37: no. 10, 961–1237.

3 P. Baraldi and A. Tinti, Raman spectroscopy in art and archaeology, J. Raman Spectrosc. 2008; 39: 963–965 and the following 22 papers.

4 H.G.M. Edwards. Raman spectroscopy in the characterization of Archaeological Materials, chpt. 26 (p. 1111–1044) in Handbook of Raman Spectroscopy. From the Research to the Process Line. Edited by I.R. Lewis and H.G.M. Edwards, M. Dekker, N.Y. 2001.

5 Edwards, H.G.M., Farwell, D.W., The conservational heritage of wall paintings and buildings: an FT-Raman spectroscopic study of prehistoric, Roman, mediaeval and Renaissance lime substrates and mortars Journal of Raman Spectroscopy, Vol. 39, Issue 8, 987–992, 2008.

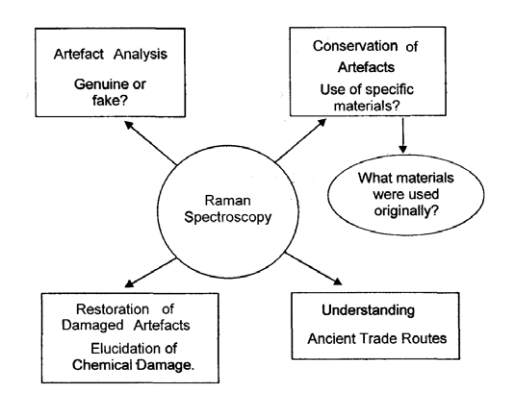

Fig. 1: The role of Raman spectroscopy in the characterization of art and archaeological materials.

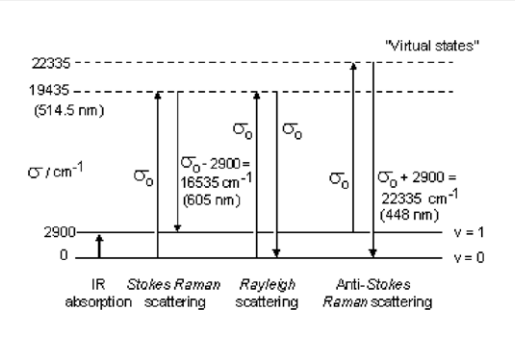

Fig. 2: The relationships between infrared absorption, Rayleigh and Raman scattering; see the text for details. The wavenumber σ is the number of waves per cm and a measure of the energy, the frequency or the reciprocal wavelength.

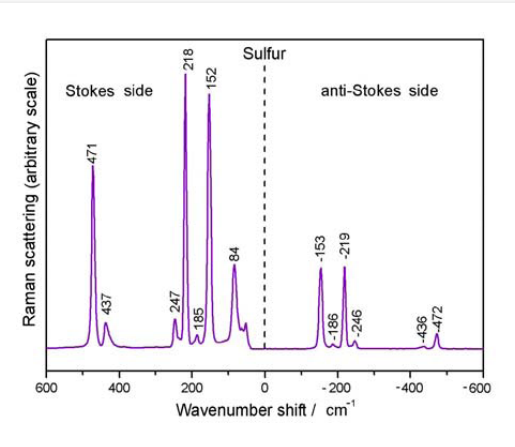

Fig. 3: Raman spectrum of sulfur crystals; a 'notch' filter takes away the light between ca. 50 and -150 cm^{-1}, so that neither the Rayleigh scattering at ca. 0 cm^{-1} nor the Raman bands in the range from ca. 70 to -100 cm^{-1} are seen. Some authors flip the direction of their wavenumber shift axis.

BRIEF INTRODUCTION TO RAMAN SPECTROSCOPY

The *Raman scattering effect* was discovered in 1928 by Indian physicists Raman and Krishnan.[6] Raman scattering may be defined as instantaneous inelastic scattering of light (electromagnetic radiation). When a *light quantum* (a kind of particle in the light, called a *photon*) collides with a sample, the *photon* may be scattered, either elastically (called *Rayleigh scattering*) or *inelastically* (called Raman scattering). In the Raman process an amount of energy is exchanged with the sample as shown schematically in the quantum energy level diagram in Fig. 2. Accordingly, the outgoing *photon* has *less* or *more* energy than the incoming one (Stokes or anti-Stokes Raman processes). The energy is measured by the frequency υ or wavenumber σ according to the relation $E = h\upsilon = hc\sigma$ (h is Planck's constant and c is speed of light). A Raman process corresponds to a (fundamental) transition among certain group vibrational states as described in the theory of quantum mechanics. For a peak (a Raman band) to occur in the Raman spectrum with a significant intensity, the molecular bond stretching or angle deformation vibration must cause a change in the so-called 'polarizability' of the molecule (the polarizability is the ability of a molecule to become polar when subject to an electric field). The ensemble of light scattering bands constitutes the Raman spectrum. Most often only Stokes-shift Raman spectra are measured and shown; i.e. the scattered photons have lower frequency than the incident radiation. The Stokes and anti-Stokes spectra of a typical sample, yellow sulfur crystals, is shown in Fig. 3.

During an *infrared* (IR) absorption process, a quantum of IR radiation is absorbed (a *photon* of a particular energy E and frequency υ or wavenumber σ, again because $E = h\upsilon = hc\sigma$). The molecular system undergoes a transition from the ground state (quantum number $\upsilon = 0$) to an excited state ($\upsilon = 1$), in the present case corresponding to e.g. a bond stretching in a CH_3 group and a wavenumber shift of ca. 2900 cm^{-1}. In contrast to this IR absorption, during *Rayleigh* and *Raman* scattering, an exciting photon of much higher energy (visible light) hits the molecular system and raises it to a virtual state, from where it 'immediately' falls back. There are two possibilities, illustrated in Fig. 2 with green Ar^+ light of 514.5 nm wavelength, corresponding to a wavenumber of 19435 cm^{-1}. In the so-called Stokes Raman scattering (not so likely), the system falls back to the $\upsilon = 1$ state (emitting a 16535 cm^{-1} photon), or in Rayleigh scattering (more likely) to the $\upsilon = 0$ ground state (emitting light at ~19435 cm^{-1}), producing the so-called Rayleigh wing. If the system is starting from the $\upsilon = 1$ state (not so likely at room temperature because of the Boltzmann distribution), similar transitions can happen. Now also a so-called anti-Stokes Raman process is possible producing photons at 22335 cm^{-1}. Most Raman spectroscopy studies report data corresponding to Stokes Raman transitions. Samples or impurities therein having energy states near the 'virtual' ones (here at e.g. ~19435 cm^{-1}) may absorb photons from the incident light and later re-emit the light as a broad intensive background called *fluorescence*.

Dramatic improvements in instrumentation (lasers, detectors, optics, computers, etc.) during recent years have raised the Raman spectroscopy technique to a level where it can be used for 'species specific' quantitative chemical analysis. Although many times not as sensitive as e.g. infrared absorption, the Raman technique has the advantage that it can non-destructively measure samples directly without touching or any sample preparation. Furthermore, by use of polarized light techniques, one can derive molecular information

6 Raman, C.V. and Krishnan, K.S., A new Type of Secondary Radiation, Nature, 121, 501, 1928.

that cannot be obtained from infrared spectra. Good starting references dealing with Raman instruments and lasers are perhaps.[7, 8, 9, 10, 11]

Raman and Infrared techniques are closely interrelated in that they both sample molecules. The spectral bands depend on characteristic 'group' motions in the molecules present in the sample. One may say that the vibrational bands in the spectra give rise to a 'fingerprint' of the molecules. As an example, bands occurring near 2950 cm^{-1} often arise from transitions for aliphatic C–H stretching vibrations (although sometimes perturbed by 'Fermi-resonance' with overtones and other nonfundamental transitions). So-called empirical group frequency charts are available, specifying the 'fingerprint' bands, that may be used to identify pure materials or the presence of a particular component in a mixture, see e.g.[12, 13, 14, 15]

Although similar transitional energy ranges occur in IR and Raman spectroscopy, different selection rules govern the intensities in Raman scattering and IR absorption spectra. Hence both types of spectra may be required to fully characterise a substance: A necessary requirement for a molecular motion (such as a vibration, rotation, rotation/vibration, or lattice normal mode) to be measurable in IR spectra it is needed that an oscillating dipole moment is produced during the vibration (in Raman the motion within the molecular system should vary the polarizability). Combinations, differences or overtones of these transitions can occur, but normally only weakly. The selection rules of the transitions are described in quantum mechanics and group theory, see e.g.[16, 17, 18, 19, 20]

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FLUORESCENCE, INSTRUMENTATION AND EXPERIMENTAL DETAILS

Applications of Raman spectroscopy have been limited by the presence of fluorescence from the samples (or from impurities in the samples). In case of strong fluorescence the use of less-energetic near-IR lasers for the excitation is often necessary. Fourier-transform (FT-) Raman instruments are available that typically apply ~1064 nm laser excitation (from solid state Nd-YAG or Nd-YVO4 lasers) to avoid the fluorescence.[21] The advantage of Raman spectroscopy over IR and other analytical techniques (if the fluorescence problems can be circumvented) stems from the ability of Raman to identify discrete species in situ. Raman spectra can be obtained directly from 'samples on the walls.'

The polarization properties of the Raman scattered light may be employed to select only the isotropic intensity of the symmetric vibrational modes, thereby helping conclusive assignment of the spectra.

The Raman effect is weak, perhaps only 10^{-8} of the photons hitting the sample are scattered in Raman. The use of high power lasers (to circumvent the low scattering efficiency) may often result in sample decomposition, and fluorescence interference from impurities must be considered a likely problem when using visible light, at least for samples that do emit much fluorescence. The development of charge coupled detectors (CCDS) and notch filters have revolutionized the Raman technique. Sampling through a microscope – under high magnification – is an effective way to collect Raman light over a large solid angle, and thus only minute sample quantities are necessary.

Museum artefacts and art pieces have been the object of several Raman spectroscopy studies as discussed in the following. Raman microscopy is, in principle, an appropriate technique, since it allows focusing on very small grains from the samples. However such samples often emit intensive broad fluorescence. In our own experiments with visible (green 514.5 or red 784 nm) laser light, also strong fluorescence was observed. Similar observations have been reported by many other researchers. Therefore to get good experimental spectra it has become common practice to use the 1064 nm near-infrared exciting lasers (e.g. a Nd^{3+}-YAG laser at 100 mW of power) and scanning FT-Raman instruments, e.g. the Bruker type Raman FT spectrometer equipped with a liquid-N_2 cooled Ge-diode detector shown in Fig. 4. In such an instrumental setup, the scattered light (excited by the laser hitting the sample) is collected – eventually at a distance by a fibre optic system, see Fig. 5 and Fig. 6 – filtered for the laser light itself and sent into the spectrometer for spectral analysis. The spectra are calculated after averaging ~200 to 500 scans followed by apodization and fast-Fourier-transformation to obtain a spectral resolution of ~2 cm^{-1} within a stable precision better than 1 cm^{-1}. The spectra may be corrected for (small) intensity changes in detector response versus wavelength but this is many times not needed.

Because efficient infrared spectrometers were developed at a much earlier date than Raman instrumentation, infrared databases for natural or synthetic materials and minerals are more comprehensive than for Raman spectra. Ancient specimens often give highly fluorescent Raman spectra excited with visible light due to impurities in coatings or previous conservation techniques. These factors have favoured the use of infrared spectroscopy, because the fluorescence emission may swamp the lower-intensity Raman signals.

21 Chase, D.B., and Rabolt, J.F., Fourier Transform Raman Spectroscopy, Academic Press, New York, 1994.

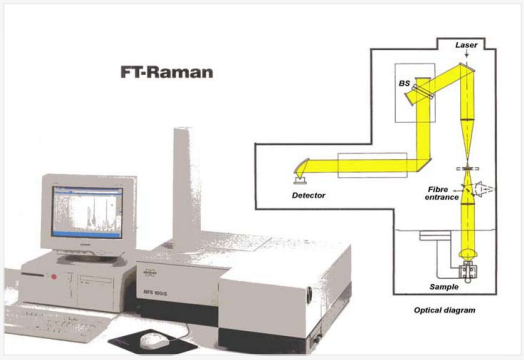

Fig. 4: Simplified optical diagram of a FT-Raman instrument operating with a 1064 nm infrared laser (beam shown going down to the right in the picture); BS = beam splitter. The sample sits at the focus in the lower right corner of the picture or at the end of a bundle of optical fibres (not shown). See references and text for details.

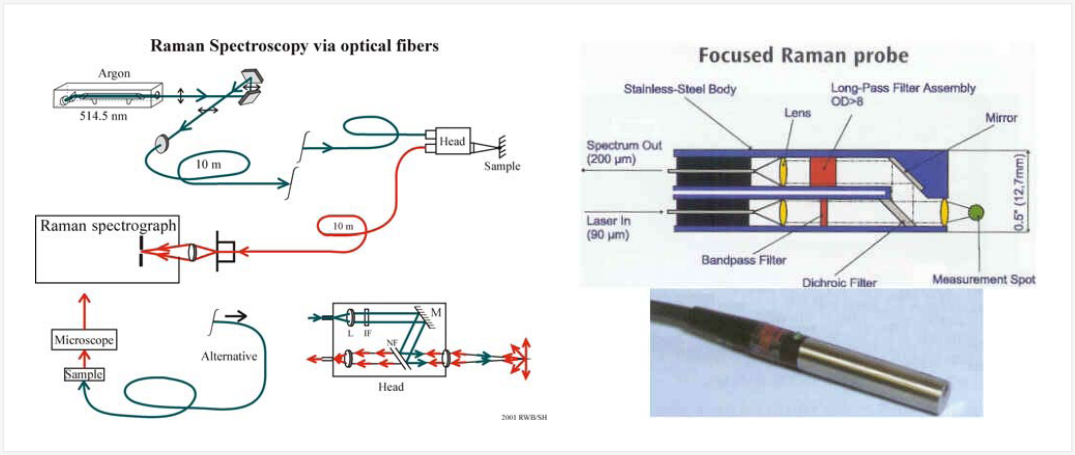

Fig. 5: Fibre optical Raman probe and the optical principles.

Fig. 6: The iris of the head of Zeus in the Copenhagen Ny Carlsberg Glyptotek is being examined with light from a fiber. The practical value of the probe is that it is easy to get the laser light to the sample, collect the Raman scattered light and send it to the spectrometer, as shown in Fig. 5.

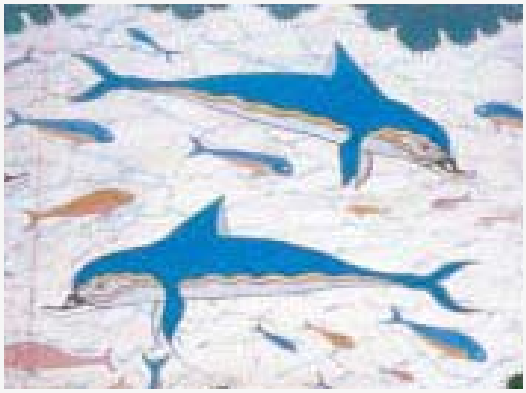

Fig. 7: An example of Mycenaean painted plaster art from Bronze age Greece (the period of roughly 1450–1200 BC): Dolphin scene from the Queen's Megaron at Knossos, Crete. Figure cited from [26].

On the other hand, in the area of paintings and manuscripts, Raman spectroscopy is used extensively because of the accessibility of the low-wavenumber region of the vibrational spectra (<500 cm^{-1}), which are most important for the characterization of inorganic pigments. This region is not easily observed in the infrared.

Many museum specimens do not allow mechanical or chemical destructive sampling – the taking of small samples by drilling, scraping, or excision is prohibited or strongly discouraged by archaeological conservators. The use of fiber-optic probes for 'remote' analysis of art objects is now advocated for many infrared and Raman applications. The obvious advantage of *in situ* recording Raman spectra in museum environments or archaeological excavation fields is now aided by the appearance of portable units, see Fig. 6.

With modern FT-Raman spectrometers or dispersive Raman spectrometers using confocal microscopy with CCD detection – characterization it is now possible via Raman spectra of samples with dimensions as small as a few µm, using visible or near-infrared excitation.

PIGMENT STUDIES

Paint is covering many museum objects. Pigments can be found on such items as statues, ceramics, frescoes, paintings, and manuscripts. In cases of ancient statues, rock art, wall paintings and mural frescoes, often only a very small part of the pigments remains, perhaps only several grains, because the items have been subjected to environmental degradation due to wear, time, local climate and restoration.

In the following we review some typical investigations made by means of the micro-Raman spectroscopy method. We start with some recent mural pigment studies, because they show most of the essential features of the state of the modern micro-Raman spectrometric method. Other examples not discussed here can be found in the literature, e.g. analysis of dated authentic wall paintings from archaeological sites representing some 6000 years of human occupation.[22, 23, 24, 25]

MURAL PAINTINGS IN MYCENAEAN GREECE

The first example to be discussed is a pilot study on Bronze age painted plaster in Mycenaean Greece discovered around the end of the 19th century.[26] An example on these fragmentary paintings is shown in Fig. 7. These kind of wall paintings are claimed to be among the first ones to have been executed in the *buon fresco* technique. This has serious implications for our general understanding and appreciation of the materials used and such early

22 H.G.M. Edwards, L. Drummond, J. Russ., Fourier-transform Raman spectroscopic study of prehistoric rock paintings from the Big Bend Region, Texas. J. Raman Spectrosc. 30:421–428, 1999.

23 H.G.M. Edwards, D.W. Farwell, S. Rozenberg., Raman spectroscopic study of red pigment and fresco pigments from King Herod's palace at Jericho. J. Raman Spectrosc. 30:361–363, 1999.

24 H.G.M. Edwards, D.W. Farwell, F. Rull Perez, S. Jorge Villar., Spanish mediaeval frescoes at Basconillos del Tozo: An FT Raman Spectroscopic Study. J. Raman Spectrosc 30:307-312, 1999.

25 H.G.M. Edwards, P. Vandenabeele, E.M. Newton, F. Rull Perez, S. Jorge Villar., FT Raman spectroscopic studies of the wall-paintings at the monastery of San Baudelio, Spain. Appl. Spectrosc, 2001.

26 A. Brysbaert and P. Vandenabeele, Bronze Age painted plaster in Mycenaean Greece: a pilot study on the testing and application of micro-Raman spectroscopy, J. Raman Spectrosc. 2004; 35: 686–693.

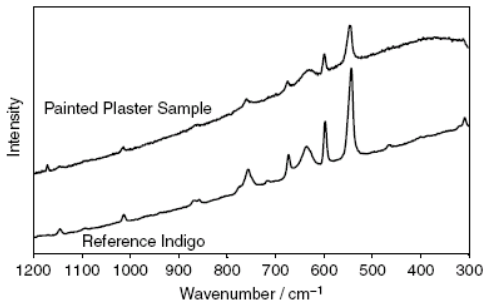

Fig. 8. Raman spectra of an *indigo* sample from Greek painted plaster and a reference of pure indigo. Cited from [26].

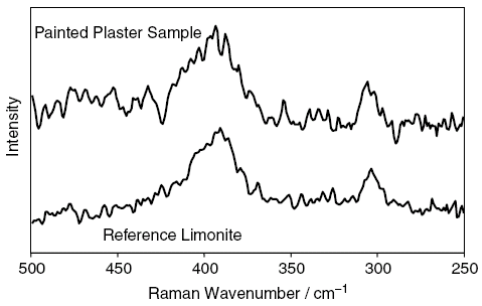

Fig. 9. Raman spectra of a *limonite* sample from Greek painted plaster and a corresponding reference. Cited from [26].

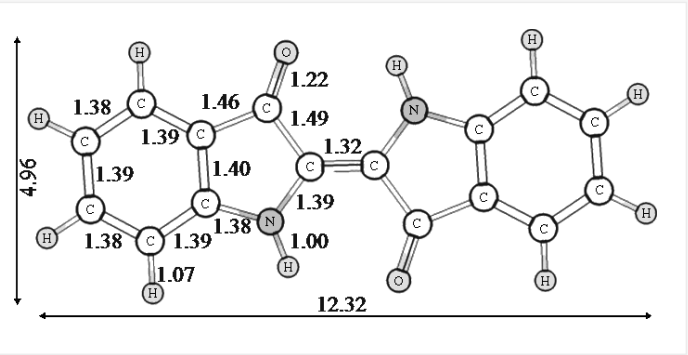

Fig. 10. Schematic representation of the organic molecule of *indigo* or *indigotin* that can be extracted from plants. The size of the molecule and interatomic distances are given in Å. Cited from [27].

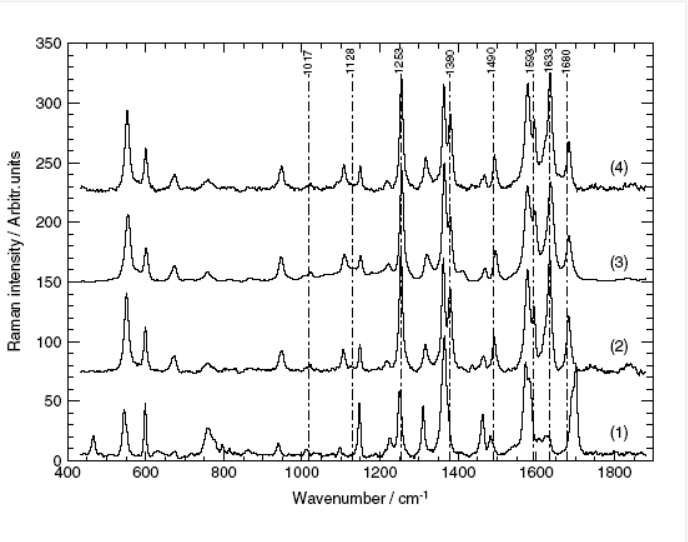

Fig. 11. Raman spectra of: (1) synthetic indigo, (2) a palygorskite (99 %) and indigo (1 %), finely ground unheated mixture, (3) a palygorskite (99 %) and indigo (1 %) heated (5 h 190° C) pigment (synthetic Maya blue), and (4) archaeological Maya blue pigment from a mural paint from Cacaxtla. Indigo is clearly present in all samples. Cited from [27].

developed technologies applied in prehistoric societies. Non-destructive sampling methods are required for analysis because very little original material remains. Consequently, micro-Raman spectroscopy was applied to this early fragmentary material.[26]

Interesting results were obtained, although not without problems. High fluorescence prevented the identification by Raman of e.g. the *Egyptian Blue*, known to be present. Egyptian blue is the most common blue in antiquity, an artificial pigment made from copper salts, *cuprorivaite*, $CaCuSi_4O_{10}$ or similar salts. Other compounds were identified, both organic (indigo, Fig. 8) and non-crystalline materials (*limonite*, an amorphous yellow form of *goethite*, FeOOH, in combination with Fe_2O_3, pointing to *ochre* and also of goethite used as pigments originally, Fig. 9). Such results are important, complementing our traditional knowledge known from ancient sources and obtained from other modern techniques. One should however be careful, because e.g. the red-purple pigments identified by other means as *haematite* α-Fe_2O_3, did not give Raman signals whereas *calcite*, $CaCO_3$, was identified probably from the lime plaster substrate. A clear identification of *indigo*, applied in blue painting materials in decorated plaster surfaces (Fig. 8) must be considered of high interest. Indigo is known as a very colorfast material and has been mentioned in Egyptian contexts from the 5th Dynasty onwards (ca. 2400 BC). It has been used as a pigment for wall paintings, executed in the *al fresco* technique in later periods (see the writings of Pliny and Vitruvius for its use in Classical times) both in Europe and in the New World. The identification of this material on painted plaster from the Aegean Bronze Age is a new knowledge that has a potential of showing trends in technological transfer, innovation and continuity featured among the Aegean and eastern Mediterranean societies.

As the sampling method tiny cotton wool Q-tips were used for removal of 1 microgram of pigment from the substrate. The Q-tip was then tapped on the surface of a cleaned microscope glass slide to release some pigment particles. By focusing the laser on to each particle using a ×50 objective, spectra were obtained. The measurements were done using a Renishaw System-1000 spectrometer with a 785 nm diode laser and a cooled charge-coupled device (CCD) detector. Grains from a total of 87 samples were measured and analyzed.

MESOAMERICAN MAYA BLUE PIGMENTS

Most organic molecules cannot be used as colorants in artworks because they fade with light, age, and react with other chemicals (oil, resins, substrates, etc.) of the artwork itself or present pollutants. On the other hand pigments made from minerals are very stable and are therefore preferred for artistic techniques, whether it is in mural paintings, oil paintings, or polychromatic pottery, etc.

Mesoamerican Maya peoples in pre-Hispanic times, at around the VII–VIII century, invented the marvelous Maya Blue artificial pigment. This extraordinary pigment was apparently obtained by encapsulating the natural organic compound *indigo* into an inorganic matrix of *palygorskite*. Indigo, see Fig. 10, is extracted from the *Indigofera suffruticosa* plants. Palygorskite is a very particular fibrous clay mineral presenting channels in its molecular structure. Palygorskite (almost free of impurities) may be obtained e.g. from a mine close to Ticul (Yucatan, Mexico). The indigo-palygorskite mixture acquires a considerable stability when a moderate thermal treatment is applied, constituting an artificial 'mineralization'.

The chemical reasons of the unusual stability of the pigment and the exact mechanism of interaction between the indigo and the clay are not entirely understood.[27, 28]

The Maya blue technology has been examined by Raman spectroscopy.[27] Spectra of different authentic samples were compared with preparations of synthetic Maya Blue and other mixtures of indigo with other inorganic materials, see e.g. Fig. 11.

Unheated or heated mixtures of indigo with palygorskite give Raman spectra similar to that of Maya blue, as do also indigo mixed with other clays, like sepiolite or montmorillonite, indicating that the indigo spectrum is not much affected during the thermal treatment making the pigment robust.[27, 28] For Raman studies on palygorskite alone, an infrared Nd:YAG laser and an FT-instrument were used, because a high fluorescence background was hiding the bands when the exciting laser was in the visible range. On the contrary, indigo produces well-defined bands that can identify this colorant, when one is using a confocal Jobin-Yvon dispersive instrument with a CCD detector and a notch filter, excited by a green laser (wavelength of 532 nm, intensity from 50 μW to 2 mW, produced by a frequency-doubled Nd:YAG laser). For the identification of Maya blue one must take into account the observed intensity increase in some indigo bands and the presence of new bands in the Raman spectrum of the archaeological pigment with respect to that of modern indigo, possibly because of interactions with palygorskite or loss of planarity of the indigo molecule introduced when the heating process took place. It may be added that also green pigments may contain indigo.[28]

NEPALESE TEMPLE MURAL PAINTINGS

To study materials and techniques used by ancient Asiatic artists, pigments present in painted mural decorations in a monastery temple from the 15th century located in Lo Manthang, upper Mustang, Nepal, have been scientifically examined by micro-Raman methods.[29] The temple has been completed in 1472, and was built in rammed mud and wood. Cross-sections of 14 collected authentic pigment samples were analyzed. For the micro-Raman analyses paint fragments and cross-sectioned samples were placed on the microscope stage and illuminated with laser light (632.8 nm at a power ranging from 0.5 to 5 mW) through a ×50 objective. The scattered light was analyzed with a Labram dipersive Raman instrument equipped with a CCD detector cooled to 200° K.

The results showed that for the blue colors, *azurite* ($2CuCO_3 \cdot Cu(OH)_2$) was used, sometimes in combination with *lazurite* particles. Lazurite is a sodium aluminosilicate mineral, $Na_8[Al_6Si_6O_{24}]S_n$, (n varies), with a very deep blue color coming from sulfur radical anions residing in holes in the crystal lattice. It occurs naturally in semi-precious stones of lazurite (*Lapis Lasulae*) and probably was imported to Nepal from known sources in Badakhshan in northeastern Afghanistan. The Raman spectra of these blue pigments are shown in Fig. 12.

Malachite, a green, basic copper carbonate $Cu_2CO_3(OH)_2$, that also occurs as a natural mineral, was similarly found to have been used as a pigment to paint green temple decorations, and

27 M. Sánchez del Río, M. Picquart, E. Haro-Poniatowski, E. van Elslande and V. Hugo Uc, On the Raman spectrum of Maya blue, J. Raman Spectrosc. 2006; 37: 1046–1053.

28 R.G. Moreno, D. Strivay and B. Gilbert, Maya blue–green pigments found in Calakmul, Mexico: a study by Raman and UV-visible spectroscopy, J. Raman Spectrosc. 2008; 39: 1050–1056.

29 R. Mazzeo, P. Baraldi, R. Lujàn and C. Fagnano, Characterization of mural painting pigments from the Thubchen Lakhang temple in Lo Manthang, Nepal, J. Raman Spectrosc., 2004; 35: 678–685.

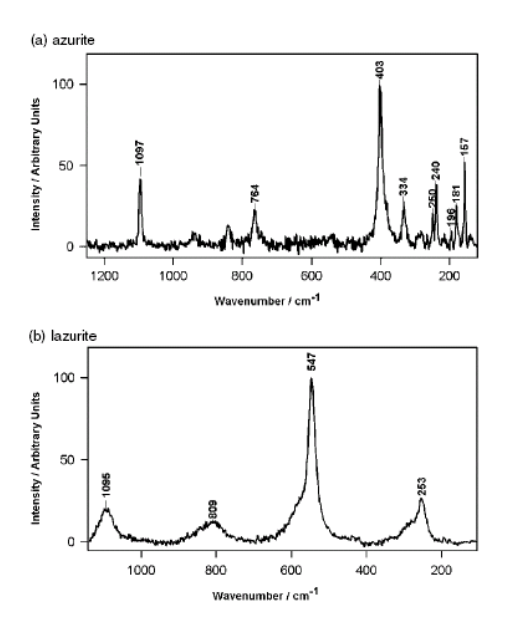

Fig. 12. Raman spectra obtained from the blue pigments layer samples from a Nepalese temple: (a) azurite ($2CuCO_3 \cdot Cu(OH)_2$) and (b) lazurite ($Na_8[Al_6Si_6O_{24}]S_n$, (n varies)). Cited from [29].

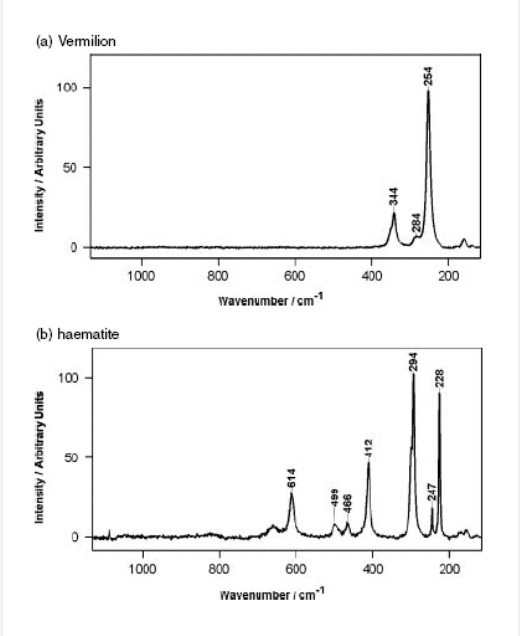

Fig. 13. Raman spectra obtained from pigments found in orange and red paint layers from a Nepalese temple: (a) *vermilion* and (b) *haematite*. Cited from [29].

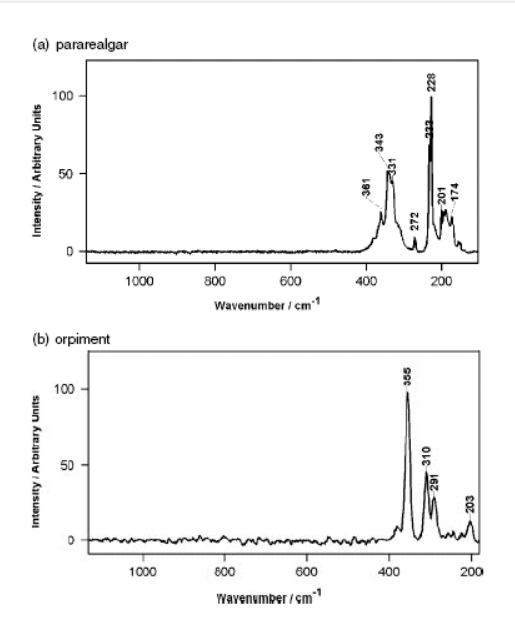

Fig. 14. Raman spectra obtained from the yellow layer underneath gold leaf of Buddha's face in a Nepalese temple: (a) *para-realgar* and (b) *orpiment*. Cited from [29].

also the copper sulfate hydrate *brochantite* was sometimes present, perhaps representing an alteration product of malachite.[29] Similarly red and orange painted layers were found to be constituted of *orpiment* (a yellow arsenic sulfide, As_2S_3) and *vermilion* (HgS, known from China since prehistoric times), both alone and in combination (see Fig. 13). A very interesting gilding technique has been used to produce Buddha's face: gold leaf was affixed to an underlying mixture containing orange-red particles of *para-realgar*, a polymorph of arsenic sulfide, *realgar* (As_4S_4), with traces of orpiment and vermilion. Red ochre (*haematite*) was present in the brown color decorations.[29] Some representative spectra are reproduced here in Fig. 13 and Fig. 14.

ROMAN FRESCOES

Certain 'green earth' pigments, mainly constituted of the clay mica minerals *celadonite* or *glauconite*, have been used since antiquity in the creation of artworks.[30] The green color comes from small celadonite micaceous scales, about 1–10 µm in length. The chemical composition of celadonite is approximately $K[(Al, Fe), (Fe, Mg)](AlSi_3, Si_4)O_{10}(OH)_2$ with substitutions varying inside the round parentheses. The micro-Raman procedure has been applied to some fragments of Roman frescoes from two archaeological sites in central Italy at Suasa (Ancona) and Pisaurum (Pesaro-Urbino) to test the green pigments. Raman spectra of celadonite (see an example in Fig. 15) shows features in the range 100–1200 cm^{-1}. The spectral region below 300 cm^{-1} is considered to show bands related to internal vibrations of MO_6 octahedra, where M stands for Si, Mg, Al, or Fe atoms. In the spectral range 300–800 cm^{-1}, bands are mainly due to vibrational modes of SiO_4 tetrahedra.

Most interesting for the analysis of celadonite pigments by Raman is the observation that the use of different lasers revealed resonance effects in the Raman spectra. With visible argon ion laser light excitation the bands at 459 and 960 cm^{-1} were found to be stronger, while for excitation with red and infrared longer wavelengths the band at 394 cm^{-1} is more evident. When the wavelength was increased, from 514.5 to 785 nm, an apparent shift towards lower wavenumbers of the band at about 545 cm^{-1} was observed (from 548 to 538 cm^{-1}), maybe due to intensity changes in an unresolved doublet.[30]

Thanks to the quality and spatial resolution of Raman microscopy it was possible to identify *celadonite* from *glauconite*, also employed in the Italian frescoes (see Fig. 16). Fine green grains of *glauconite* have an approximate chemical composition of $(K, Na)(Fe, Al, Mg)_2(Si, Al)_4O_{10}(OH)_2$, somewhat like celadonite, but with a larger content of Al due to a partial substitution of Al for Si (relative atomic % Si = 5.28, Al = 1.25; Mg = 0.70; Fe = 1.60). Common impurities, crystals of *pyrite* FeS_2, *haematite* α-Fe_2O_3, *goethite* FeOOH, and Fe_xO_y also occur. In Suasa and Pisaurum, the glauconite and celadonite pigments were found in different frescoes but never found mixed together, and celadonite was more diffuse than glauconite in both locations.[30]

Pigments labelled as 'green earth' are commercially available nowadays, but according to Raman examinations[30] only in some cases they are really based on celadonite or glauconite; often they contain mixtures of different minerals, from *aegirine* to *epidote*, from *lizardite* to *illite*, and in some cases an organic synthetic dye (*pigmosol green*) has been added as pigment to a combination of minerals, leading to a product with characteristics very different from that of the green earths.[30]

30 F. Ospitali, D. Bersani, G. Di Lonardo and P. Paolo Lottici, 'Green earths': Vibrational and elemental characterization of glauconites, celadonites and historical pigments, J. Raman Spectrosc. 2008; 39: 1066–1073.

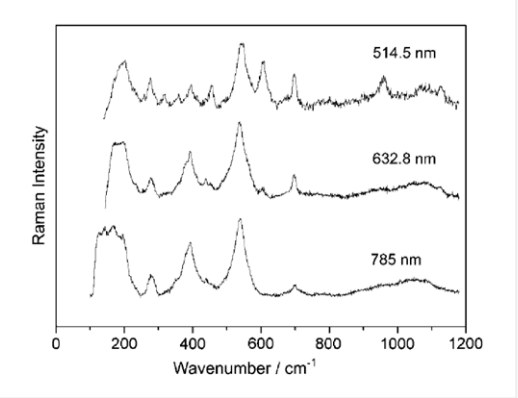

Fig. 15: Raman spectra of a *celadonite* sample (relative atomic% Si=4.54; Mg=0.80; Al=0.24; Fe=1.68) showing resonance Raman effects at shorter excitation wavelengths. Cited from [30].

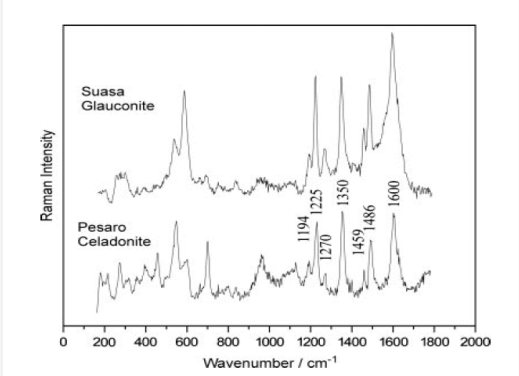

Fig. 16: Raman spectra of *glauconite* and *celadonite* found in Roman frescoe fragments coming from archaeological sites and showing extra bands at high wavenumbers. Cited from [30].

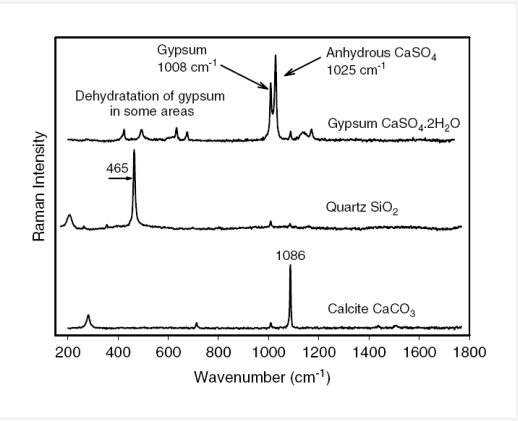

Fig. 17: Raman spectra of the components of the white coating render of the walls of the Tournai Notre-Dame Cathedral. Dehydration of the gypsum seems to have occurred with time resulting in spectra characteristic of the hemi hydrated or anhydrous forms of calcium sulfate. It is not originating from a too high laser power. Cited from [31].

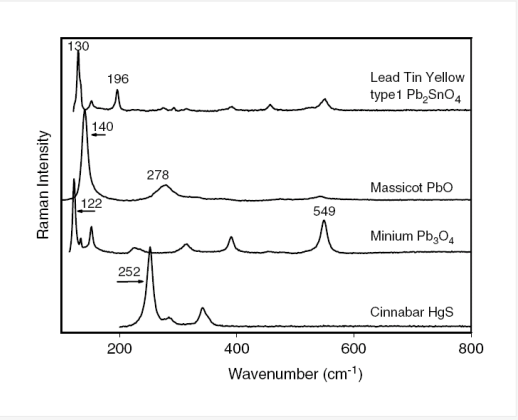

Fig. 18: Raman spectra of the yellow, orange and red pigments of the walls of the Tournai Notre-Dame Cathedral, cited from [31].

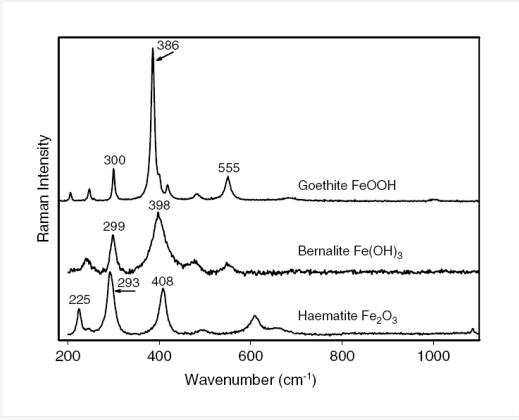

Fig. 19: Raman spectra of yellow, orange to red iron oxide pigments from the walls of the Tournai Notre-Dame Cathedral, cited from [31].

EUROPEAN CATHEDRAL MURAL PAINTINGS

Another study example has been concerned with pigments extracted from mural paintings from the Notre-Dame Cathedral of Tournai (Belgium). Samples from here have e.g. been analyzed by micro-Raman spectroscopy using visible light of wavelengths 488, 514.5 and 752.6 nm and low intensity, 0.1–10 mW.[31] The Raman method was preferred because of its non- or micro-destructive character (with some caution). A major problem encountered was, as in many other studies, local fluorescence originating from organic binders or fatty pollutants, which often masked the Raman bands to such an extent that useful spectra could not be obtained. However, various pigments of the Romanesque and Gothic palettes, in some instances dating back to perhaps 1250, could be conclusively identified from hundreds of micro-samples taken from walls.

The wall linings of the Tournai Cathedral have originally been covered with a render layer of limestone ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and quartz sand (SiO_2); the corresponding spectra are presented in Fig. 17.[31] The render has been applied to the masonry in order to fill in the depressions and the surface porosity of the wall stones. It was meant to play two different roles: protecting the natural stone from degradation as a sacrificial layer, and preparing wall surfaces before the mural paintings.

According to the study of the Raman spectra of the walls in the cathedral, the typical Middle Age palette pigments are shown in Fig. 18 and Fig. 19.[31] Oxides of lead, tin and iron were clearly identified by means of their characteristic spectra. Pigments used to obtain yellow, orange and red colors comprised *massicot* (yellow orthorhombic PbO), *lead tin yellow* (Pb_2SnO_4), yellow to red *ochres* ($Fe(OH)_3$–Fe_2O_3), *haematite* (red Fe_2O_3), *minium* (orange red Pb_3O_4) and *cinnabar* (deeply red HgS), suitably mixed to obtain the wanted hue, colors and brightness. The most common pigments seem to have been the red colored iron oxides. The yellow pigments might have an origin from old glass making techniques, according to new evidence on the existence of 'non-standardized' yellow Pb–Sn–Sb triple oxide pigments, very close in composition and structure to the Pb–Sn and Pb–Sb type oxides.[32]

Apparently, well crystallized α-Fe_2O_3, *haematite*, has been used for wall paintings since ancient times. As an example of this, one may compare the Medieval sample spectrum, Fig. 19, with e.g. results from prehistoric cave wall-paintings.[33] The Raman spectrum of the red *haematite* pigments always present a typical narrow peak at ca. 294 cm^{-1} (sometimes as an asymmetric doublet at 291–299cm^{-1}) combined with weaker-intensity bands at e.g. 226, 411 and 611 cm^{-1}, see e.g. Fig. 20. In particular, the 411 cm^{-1} band is sufficiently high in wavenumber to confirm the presence of well-crystallized *haematite*, since this band is known to occur at 400–407 cm^{-1} in structural states intermediate between goethite, FeOOH, and haematite, Fe_2O_3. Also the typical very wide band of haematite at ca. 1320 cm^{-1} is evident in the prehistoric sample.[33]

31 L. Lepot, S. Denoël and B. Gilbert, The technique of the mural paintings of the Tournai Cathedral, J. Raman Spectrosc. 2006, 37, 1098–1103.

32 C. Sandalinas, S. Ruiz-Moreno, A. López-Gil and J. Miralles, Experimental confirmation by Raman spectroscopy of a Pb–Sn–Sb triple oxide yellow pigment in sixteenth-century Italian pottery, J. Raman Spectrosc. 2006; 37: 1146–1153.

33 F. Ospitali, D.C. Smith and M. Lorblanchet, Preliminary investigations by Raman microscopy of prehistoric pigments in the wall-painted cave at Roucadour, Quercy, France, J. Raman Spectrosc. 2006; 37: 1063–1071.

Identified *blue* and *green* pigments spectra from the walls of the Tournai Notre-Dame cathedral are reproduced in Fig. 21. Pulverized *Lapis lazuli* and *azurite* ($2CuCO_3 \cdot Cu(OH)_2$) pigments were apparently much used in the blue zones from the 12th century. Lapis lazuli, ($Na_8[Al_6Si_6O_{24}]S_n$, also called *lazurite* or *ultramarine blue*) was introduced in Europe from Afghanistan. It was extensively used in the Middle Ages and during the Renaissance. The pigment was extremely expensive and unaffordable for many artists. Because of the price in old time Middle Age Europe, large blue surfaces of mural and other paintings contain *lazurite* only in exceptional cases. In the Tournai cathedral the rather extensive use of *lazurite* is an indication of the economical power of the church.[31]

Green areas were often found to contain *atacamite* and *posnjakite*. *Atacamite* is a pigment mentioned in old treatises such as the *De Diversis Artibus*. It consists of a green mineral ($CuCl_2 \cdot Cu(OH)_2$). *Posjnakite* is a copper sulfate ($CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$), although it may not originally have been present and could be formed during the time spent on the walls.

With respect to *white* and *black* color, respectively, lead white ($2PbCO_3 \cdot Pb(OH)_2$) and *carbon black* (soot etc.) were identified in certain areas in the Tournai Cathedral.[31] Some paint layers were found to show signs of *egg yolk* as the binding media on top of thin layers made of gypsum and chalk covering the stone, see Fig. 22. The application of egg yolk can be considered as a common way to apply pigments to a surface layer of certain mural paintings, or could also have been used as a way to grind the pigments before use of another binding medium. The egg yolk durability was found remarkable in combination with most pigments, except maybe the green copper ones. Furthermore, signs of *beeswax* were identified. Beeswax may be regarded as a protecting agent, applied in the past or by a modern conservation campaign to confer water repellence to the external surface – to protect from any water infiltration many times responsible of gypsum solubilization–crystallization processes that give rise to wall cracking. Since humidity is one of the main causes for the decay of mural paintings, it was not surprising for the expert people to find such beeswax organic traces.[31] Clear spectra of egg yolk and beeswax are shown in Fig. 22.

Finally, the presence of oxalates was seen (Fig. 22), related to aging due to degradation of chalk and organic substances applied during past restorations. *Calcium oxalate* can be attributed to metabolic processes by surface micro-organisms such as aggressive lichens. They produce oxalic acid which reacts with the $CaCO_3$, chalk, to form a thin calcium oxalate membrane. In the Palazzo Farnese, the Frescoes painted in 1560 by Zuccari have been found to be very significantly damaged by the invasion of aggressive lichen colonies. These organisms may produce up to 50% of their own biomass as *hydrated calcium oxalate*, especially near green copper based pigments and lead white, thereby destroying the platform on which the artwork is based.[34]

PIGMENTS RESTING ON PAINTED WOOD

There are many examples of studies on polychrome pigments on wooden historical items. As a recent example we shall only mention the case of a Raman spectroscopic study on a crucifix (from about 1400 AD) now in the National Museum in Gdansk, Poland.[35] Typically, characteristic spectral bands found were associated with different pigments on painted

34 H.G.M. Edwards, Probing history with Raman spectroscopy, Analyst 2004, 129, 870–879.

35 A. Kaminska, M. Sawczak, M. Oujja, C. Domingo, M. Castillejo and G. Sliwinski, Pigment identification of a XIV/XV c. wooden crucifix by means of the Raman spectroscopic technique, J. Raman Spectrosc. 2006; 37: 1125–1130.

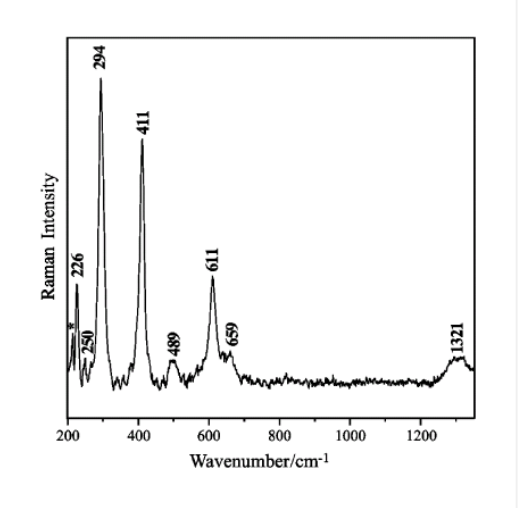

Fig. 20: Raman spectrum of a dark red crystal in a red pigment from a prehistoric wall-painted sample. Well-crystallised haematite, α-Fe_2O_3, is clearly recognized. The Raman spectrum obtained directly in the cave, excited by use of a diode laser, working at 780.0 nm with an intensity of 1.50 mW. Cited after [33].

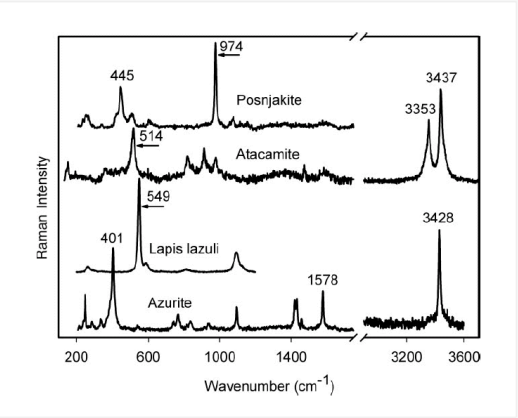

Fig. 21: Raman spectra of *blue* and *green* pigments from the walls of the Tournai Notre-Dame Cathedral, cited from [31].

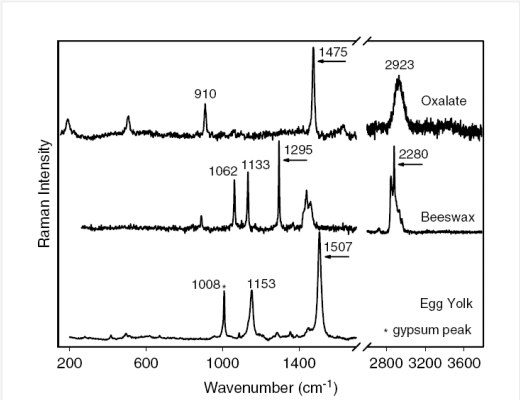

Fig. 22: Raman spectra of detected organic compounds: egg yolk, beeswax and oxalate from the walls of the Tournai Notre-Dame Cathedral, cited from [31].

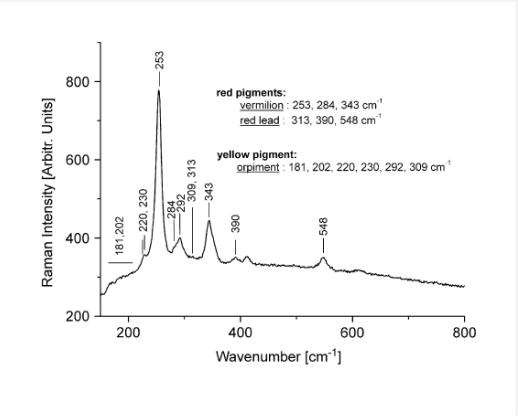

Fig. 23: Raman spectrum of a red pigment area with a rust-colored shade, depicting the side wound of Jesus, on a wooden crucifix from the National Museum in Gdansk Poland. Cited from [35].

areas of the object and also in cross sections. As seen in Fig. 23, a mixture of pigments must have been used by the artist to acquire the desired color of e.g. the side wound of Jesus: Bands corresponding to red pigments were identified: *vermilion* (253, 284, 343 cm^{-1}) and *red lead minium* (313, 390, 548 cm^{-1}). In other places numerous bands were ascribed to e.g. malachite and azurite. Bands corresponding to the pigments prussian blue, ($Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$) (282, 538 cm^{-1}), and *chrome yellow*, ($PbCrO_4$) (338, 360, 403 cm^{-1}), were also observed, but because these pigments are rather new inventions (known only since 1704 and 1803, respectively), partial retouching of some areas of the statue must have taken place.[35]

MODERN PIGMENTS

To complete this discussion it was considered of interest also to mention modern samples of art. Also here architectural paint analysis technique have become important for establishing the palette of historical paint colors, and reconstructing how a room or a facade might have looked at an earlier time.[36] As an illustrative example we may refer to mural paintings by the innovative Italian miniaturist Napoleone Verga (1833–1918). His art has recently been studied by a number of techniques including in situ non-destructive micro-Raman investigation.[37] The experimental results allowed identification of nineteenth century blue and green pigments, giving detailed information not only on Verga's palette and painting techniques but also on undocumented retouches. On the blue and green areas of the wall painting, 13 different pigments were identified by Raman-microscopy, viz. *ultramarine blue*, *cobalt blue* ($CoOAl_2O_3$), *prussian blue*, *emerald green* ($3Cu(AsO_2)2Cu(CH_3COO)_2$), *copper phthalocyanine*, *chrome yellow*, *massicot*, *cinnabar*, *carbon*, *lead white* ($2PbCO_3 \cdot Pb(OH)_2$), *white San Giovanni* ($CaCO_3$), *gypsum* ($CaSO_4 \cdot 2H_2O$) and *barite* ($BaSO_4$). Among these, only *copper phthalocyanine*, an organic dye invented in 1936, is thought to be not original.[37] The spectra were obtained using a JASCO Ventuno Raman spectrophotometer coupled to a microscope and equipped with a CCD detector, cooled to -50° C. The spectra were excited using green radiation from a doubled Nd:YAG laser. The laser power at the sample was always kept below 4 mW, and the exposure times went up to 400 s.[37] Other modern pigments are discussed in[38].

AN ALTERNATIVE TO RAMAN: THE VERY LOW FREQUENCY INFRARED RANGE

Provided that enough quantity of the sample is available, far infrared (FIR) spectroscopy may represent a useful analytical method, especially in the case of inorganic compounds some of which are not active in the mid infrared region and often, because of the fluorescent effect produced by organic media, not detectable by Raman spectroscopy.[39] Studies from the early 1970s have reported use of FIR spectroscopy in the field of characterization of inorganic pigments, using a polyethylene sampling method. Analyses can be and have been made with a moderate quantity of sample (0.5–1.5 mg).[39] The data obtained compare well with Raman results. An example of such results is shown in Fig. 24.

36 E. Kendix, O.F. Nielsen and M.C. Christensen, The use of micro-Raman spectroscopy in architectural paint analysis, J. Raman Spectrosc. 2004; 35: 796–799.

37 F. Rosi, C. Miliani, I. Borgia, B. Brunetti and A. Sgamellotti, Identification of nineteenth century blue and green pigments by in situ X-ray fluorescence and micro-Raman spectroscopy, J. Raman Spectrosc. 2004; 35: 610–615.

38 C.L. Aibéo, S. Goffin, O. Schalm, G. van der Snickt, N. Laquière, P. Eyskens and K. Janssens, Micro-Raman analysis for the identification of pigments from 19th and 20th century paintings, Raman Spectrosc. 2008; 39: 1091–1098.

39 E. Kendix, G. Moscardi, R. Mazzeo, P. Baraldi, S. Prati, E. Joseph, S. Capelli, Far infrared and Raman spectroscopy analysis of inorganic pigments J. Raman Spectrosc. 2008; 39: 1104–1112.

UV AS A MEANS TO AVOID FLUORESCENCE

As mentioned, fluorescence due to the binding media etc. is a main problem in Raman spectroscopy analysis of artistic pigments.[40] It has been proposed that one could use ultraviolet (UV) light to avoid the fluorescence.[41] The fluorescence problem in pigment identification can be brought down and minimized by application of local irradiation with controlled levels of pulsed UV laser light on the analyzed paint sample (pigment+binding media), followed by rather conventional Raman analysis with an IR source.[40] From a quantitative point of view, in some cases (chromium yellow and ultramarine blue) a signal to noise ratio improvement of 16 dB can be achieved by using pulsed UV irradiation and IR laser Raman analysis instead of direct Raman analysis with a visible laser.[40]

We have tried in an example to use continuous deep UV laser light (229 nm, with a power of a few mW) from a doubled Lexel Argon Laser. The sample consisted of only two microscopic fragments of a statue, IN 2830, from the Ny Carlsberg Glyptotek in Copenhagen, see Fig. 25. The light was analyzed with a Renishaw UV 2000 microscope spectrometer.[42] The samples were also analyzed with red light and green visible light in our laboratory, but in these cases the fluorescence was too strong to give usable spectra. Not even the strongest calcite band at 1086 cm^{-1} could be seen.

As is obvious from Fig. 25, the fluorescence has gone away when UV light is used for excitation. Unfortunately there is not any sign of the red pigment that was destroyed. So it is obvious that great care must be taken, at least when deep UV light is used. Weak light power levels must be used.

40 A. López-Gil, S. Ruiz-Moreno and J. Miralles, Optimum acquisition of Raman spectra in pigment analysis with IR laser diode and pulsed UV irradiation, J. Raman Spectrosc. 2006; 37: 966– 973.

41 S.A. Asher & C.R. Johnson, Raman spectroscopy of a coal liquid shows that fluorescence interference is minimized with ultraviolet excitation, Science N.S. vol. 225, No. 4659, 311–313, 1984.

42 B. Sharma, R.W. Berg and S.A. Asher, unpublished work.

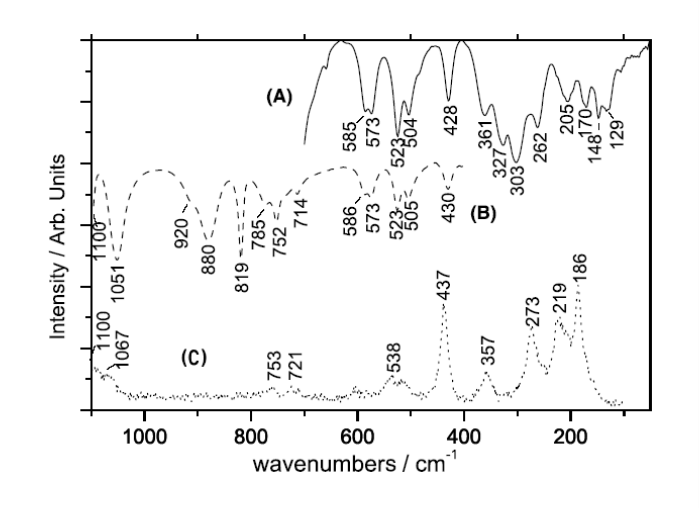

Fig. 24: Comparison of (A) a Far InfraRed (FIR) absorption spectrum, (B) a Middle InfraRed (MIR) absorption spectrum and (C) a Raman scattering spectrum of malachite, $Cu_2CO_3(OH)_2$. The sample was ground and dispersed in a matrix substance and pressed into a disc. The FIR spectrometer was a Thermo Nicolet 5700 with a Parker/Balston FT-IR PurgeGas Generator, preventing water and carbon dioxide in the atmosphere from interacting with the polyethylene matrix of the pellet and avoiding interference bands in the spectrum. The MIR spectrometer was a Perkin Elmer 1700 equipped with an MCT detector. In this case the sample was recorded in a KBr matrix pellet. Cited after [39].

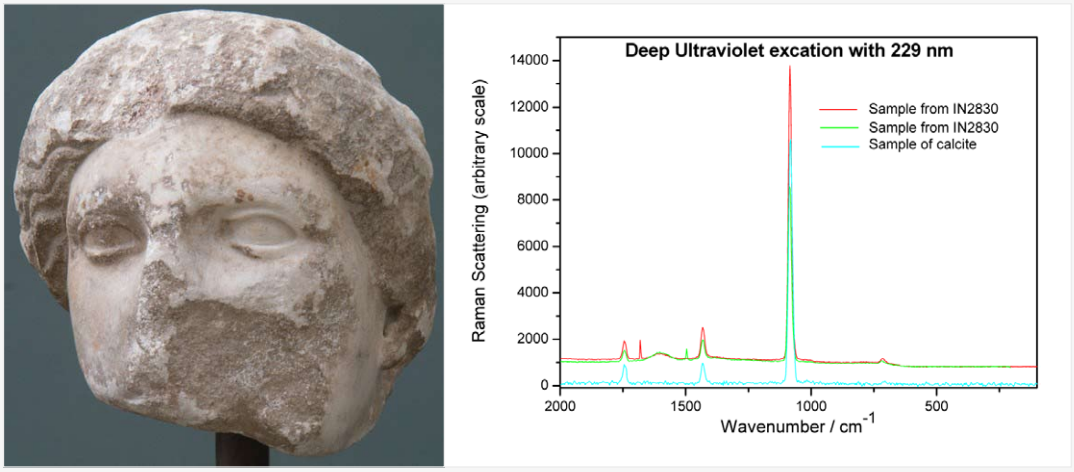

Fig. 25: Woman's head, statue IN 2830 from the Ny Carlsberg Glyptotek in Copenhagen. To the left the head is shown, to the right spectra of the fragments are shown and for reference the deep UV Raman spectrum of clear calcite.[42] Compare also with the calcite spectrum in Fig. 17.

CONCLUSIONS

From the above summary of results obtained by many researchers on many instruments, it can be stated that the use of Raman microscopy has been proven to be successful in many instances. Using Raman spectroscopy directly on spallated or scalpel-excised fragments of art and wall paintings, it has many times been possible to deduce information about the paint layers and thereby to provide information on the methodology used in the construction of the artwork. A major advantage of the technique is its semi-nondestructive nature and the ease of sampling, which requires little specimen preparation or treatment.

As one example, indigo blue, a color-fast pigment known in antiquity, has recently been identified on painted plaster from before the Bronze Age.[26] Raman worked for a range of pigments but not for all. Many blue, green and purple pigments could not be identified, possibly because the wavelength of the laser was not appropriate for these pigments, often causing an overload or fluorescence in the spectra.

Although there are now several databases published which assist the identification of art pigments, an integral part of the interpretation of the Raman spectra is the obtaining of related reference spectra. There have in the past been several attempts on the construction of databases of pigment material (including plasters and mortars), and on binding agents of organic origin used to increase the adhesion of the pigment to the substratum, but there is still a lack of complete data bases that are easy and cheap to use. This is so because information about inorganic and organic components in specimens is accessible only from commercial data bases or specialist reports.

It is the hope that this summary may serve to show that the use of Raman microscopy for the nondestructive analysis of archaeological specimens has a future.

ACKNOWLEDGMENTS

The author wishes to thank his collaborators in the area of Raman spectroscopy, archaeology and art; in particular, he is grateful to Jan Stubbe Østergaard, Susanne Brunsgaard Hansen, Ane Sælland, Kim Pilkjær Simonsen, Conny Hansen, Ole Faurskov Nielsen, and Lykke Ryelund. With respect to ultraviolet Raman spectroscopy, Bhavya Sharma and Sanford A. Asher from Pittsburgh University, Pennsylvania, USA, are thanked. The Danish Agency for Science, Technology and Innovation provided funding for this project.

The CPN Main Project 2008–2011: an outline

Jan Stubbe Østergaard[1]

The following is based on a text conceived at the outset of the Main Project in 2008. Where significant changes of plan have since taken place, a comment is added.

MOTIVATION

In launching the Main Project, the Ny Carlsberg Glyptotek (NCG) was motivated by the recognition that:

- it is a basic museum task to acquire knowledge of all aspects of the works in its care and to make this knowledge available to the general public as well as to scholarship. This task has not been fulfilled as regards traces of polychromy in its collection of Greek and Roman sculpture.
- information on the Greek and Roman sculpture collection is accessible to international scholarship. A documentation and research project focusing on traces of ancient polychromy may therefore contribute significantly to this dynamic field of study.
- polychromy studies are not only international in character but also necessarily interdisciplinary. The museum has established the Copenhagen Polychromy Network (CPN) and has international contacts with scholars and conservation scientist working in the field.
- to maintain and increase the present momentum of the study of ancient sculptural polychromy, one of the essential prerequisites is an increase in basic data acquired through interdisciplinary research activity and the publication thereof.

THE INTERNATIONAL DIMENSION

Status in ancient sculptural polychromy studies is characterized on the one hand by increasing activity, on the other by a lack of close collaboration and coordination. The aims and means of the field have not been the subject of any professional, international discussion;[2] a general written introduction to the field does not exist; research and publication are not subject to any common strategy, nor to any agreed sets of standards such as would seem necessary to ensure comparative studies.

It is therefore an essential element of the Main Project to keep relevant colleagues and institutions abroad informed about our work. As a first step, an International Advisory Panel was established to comment on our project program.

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1 Research curator, Ny Carlsberg Glyptotek.

2 Only few meetings devoted to ancient (and medieval) sculptural polychromy have so far been held: 'Die Farben der Antike – Neue Beobachtungen zur Polychromie und deren Wahrnehmung.' Glyptothek München, 4–5 June, 2005 (proceedings not published); 'La policromia su pietra naturale e ceramica dall' Antichità al Medioevo.' Giornata di Studio, Università degli Studi della Tuscia, Viterbo, 26.10.2007. (publication of proceedings planned); 'CIRCUMLITIO. Internationales Colloquium zur Polychromie der antiken und mittelalterlichen Skulptur.' Liebieghaus Skulpturensammlung, Frankfurt am Main, 10–12 December, 2008 (proceedings to be published); 'La policromia di marmi antichi: L'Ara Pacis e l'età augustea'. Giornata di studio 11.3.2009, L'Auditorium del Museo dell'Ara Pacis (proceedings to be published); 'International Round Table on ancient sculptural polychromy,' Ny Carlsberg Glyptotek, Copenhagen, 10–11 September, 2009 (proceedings not to be published).

The critical comments and suggestions received from the panel have been incorporated in the project planning.The panel members as well as others involved in the field internationally will be kept fully informed and consulted ad hoc as the project proceeds.

Our aim is to contribute to a discussion of such matters of common interests as documentation standards, research strategies and the desirability/possibility of forming professional fora for information sharing, publication and discussion (such as a website or other digital forum; electronic publication/e-journal; international meetings).

The issue of conservation documentation in digital form will be faced in the light of ongoing international initiatives on the subject.[3]

GENERAL PROJECT STRUCTURE

The project will develop along three parallel lines of investigation:

1 Visual examination and documentation of works following a predetermined strategy for their selection and sequence. The protocol includes macroscopic examination, tungsten light photography, UV-fluorescence and IR reflectography and microscopy. This is being conducted by the NCG project conservator and attached interns.

Comment: The predetermined sequence of sculptures for examination is likely to be revised. Rather than following a chronological order, it may be necessary to follow a strategy determined by what is of interest to potential funding parties. The protocol we developed remains relevant, but a shortened 'Survey protocol' has been introduced to increase volume of examined sculptures. Effectively then, visual examination will initially proceed according to the Survey protocol. The full protocol will be used when deemed profitable.[4]

2 In-depth instrumental analysis of works identified through visual examination as having particular potential. This involves conservation scientific and natural scientific analyses as relevant, by the range of instrumentation available to the CPN external network partners.

3 Ordering, evaluation, discussion and publication of acquired data, being conducted by NCG, CPN external partners and international network.

PROJECT STRATEGIES FOR SELECTION OF SCULPTURES FOR EXAMINATION

The collection in the Glyptotek comprises works in both stone, terracotta and bronze and all are in principle of interest to this project. In practise, priority is given to stone sculptures (limestone and marble), making up as they do the main body of the collection. It is also towards sculpture in this material that research in sculptural polychromy has mainly been directed. By focusing on stone sculpture the project is therefore most likely to make the best possible contribution to the field.

The collection consists of more than 1000 stone sculptures, dating from c. 600 BCE to c. 400 CE. The whole range of sculptural types, formats and genres are represented. The following major groupings may be identified: Archaic Greek originals (18); Classical Greek originals (80); Hellenistic Greek originals (71); Greek portraits (Roman copies 55, originals 12); Roman portraits (363); Roman ideal sculpture (353); Roman funerary monuments, altars, votive reliefs and varia (61).

3 The Andrew W. Mellon Foundation initiative, see: http://mac.mellon.org/issues-in-conservation-documentation

4 In this Report, the protocol is demonstrated as used in the article below on the sphinx Ny Carlsberg Glyptotek IN 1203. The Survey protocol will be presented in our 2010 report.

Of these sculptures, c. 120 have traces of polychromy visible to the naked eye. Closer examination is likely to reveal traces on other sculptures.

Faced with this large and heterogeneous body of works, the project has established a strategy for the selection of sculptures to be examined based on the following criteria, in order of importance: relevance to state of research; potential for acquisition of data; relation to particular strengths of the collection and museum research tradition; relation to research interests of CPN external partners

The selection of works for the first phase of visual examination (Spring 2009) was determined by the added criterion of representativity of formats (from statuettes to large scale statuary), since a main objective of this phase was the assessment of the time expenditure connected with the visual examination procedure.

Comment: Examination progress has been far slower than optimistically planned. Assessment of even approximate time expenditure is therefore not yet possible.

PROJECT PHASES

To provide a framework for observation of progress, evaluation and adjustments in the light of experiences won, the project has been divided into a number of phases. The phases are also a tool for budget control, as well as being conceived as 'milestones' to mark and report on project progress in the form of internal meetings and preliminary publications. Since there is no precedent for a project of this kind, it is hoped that the proposed phasing will offer a point of departure when organizing similar investigations elsewhere.

The phase content and objectives are subject to a considerable degree of uncertainty stemming in the main from three circumstances. Firstly, it is difficult to estimate the time and resources needed to reach the stated objectives. Existing publications on the investigation of traces of sculptural polychromy do not mention the time expenditure involved. Secondly, in continuation of this, it is for obvious reasons impossible to know the extent and character of the traces of polychromy which the project will reveal and how this will impact on each phase. Thirdly, at the time of writing, funding remains to be found for a number of key elements of the project – especially as concerns museum conservation staff, publications, website and database programming as well as planned scholarly meetings. The project program will be continually updated in the light of developments in this regard.

In a similar vein, it must also be remembered that the external partners will be making resources for instrumental analysis available to the project only to an extent that is compatible with the work programme at the various institutions.

Comment: It was originally planned that the first phase of visual examination should be completed by June 1, 2009. As it is, this phase has not yet been completed. Progress has been far slower than anticipated. The most important reason is undoubtedly that conservation staff resources are half of what was foreseen.

WORK SPACES

To facilitate the logistics involved in moving sculptures, and to improve communication of the project to the museum visitors, a work space for visual examination has been established in the corner of one of the sculpture galleries (Fig. 1–4). Having no precedents to follow, developing the space called for creative improvisation and a 'learning-by-doing' attitude.

The space measures 5 × 3 meters and is surrounded by a 2 meter high modular glass partition and a lockable door. Information material for visitors is mounted on the outside of the partition.

One half of the interior (Fig. 3) is taken up by a work desk and an equipment stowage area. The other half is designed for visual examination. Here, sculptures up to 300 kg may be set up on a turntable mounted on a wheeled platform whose height may be hydraulically regulated up to a height of 90 cm. For full scale statues, a heavy duty steel turntable for loads up to 1000 kg has been devised (Fig. 4). Both turntables have degree marking for control of photography angles.

The equipment needed for photography, including UV-FL and IR, using a Canon EOS 5D Mark II digital camera, is available. A commercially available collapsible pavilion has its black out roofing permanently mounted to neutralize natural light from the gallery skylights. For UV-photography, black out side panels are mounted. The four legs of the pavilion have been adapted to a height allowing statues up to 2.5 metres in the work space (Fig. 1–2).

Magnification tools for visual examination include a variety of magnifying glasses, a DinoLitePro video microscope and a Leica M651 operations microscope. Ideally, the work space should also be equipped with a high end video microscope (Keyence VHX-600 or similar), but this is beyond the present financial reach of the project.

The conservators working on the project have easy access to an (albeit improvised) office adjacent to the gallery where a Leica DM2500 dark field microscope is available for cross section microscopy. The office also provides what is necessary for processing and storing digital images.

VISUAL EXAMINATION PROTOCOL

The model for the protocol is the School of Conservation visual examination report form for polychrome sculpture. The report given above on the Pilot Project study of IN 2830 and below on the Main Project study of the Archaic Greek sphinx IN 1203 must for now serve as an indication of the protocol format. The new Survey protocol will be presented in our Preliminary Report 2.

FOR THE NEXT REPORT: COMPLETED AND ON-GOING VISUAL EXAMINATION

The second report will also contain the results of the work that has already been completed, but too late to be included here. Examination has been carried out of a Late Hellenistic/Roman Late Republican portrait, IN 1583 (Fig. 5), of the Late Archaic Greek head of a kouros ('The Rayet Head') IN 418 (Fig. 6) and of a portrait of the emperor Tiberius IN 1750 (Fig. 7). At the time of publication of this preliminary report, the first full-scale sculpture has been moved to the work space: the Late Hellenistic/Roman Early Imperial group of Artemis and Iphigeneia, IN 481–482a (Fig. 8). Our Preliminary Report 2 will contain much else beside. Publication is planned for the autumn of 2010.

Fig. 1: The CPN work space for visual examination and documentation in the Ny Carlsberg Glyptotek. Information for visitors is mounted on the outside. Museum photo.

Fig. 2: As Fig. 1, but with increased height to accommodate full-size statuary. Museum photo.

Fig. 3: The interior of the CPN workspace. Museum photo.

Fig. 4: Heavy duty steel turntable with degree markings. Height 50 cm. Museum photo.

Fig. 5: Late Hellenistic/Late Republican marble portrait, c. 100–50 BCE. Ny Carlsberg Glyptotek IN 1583. Museum photo.

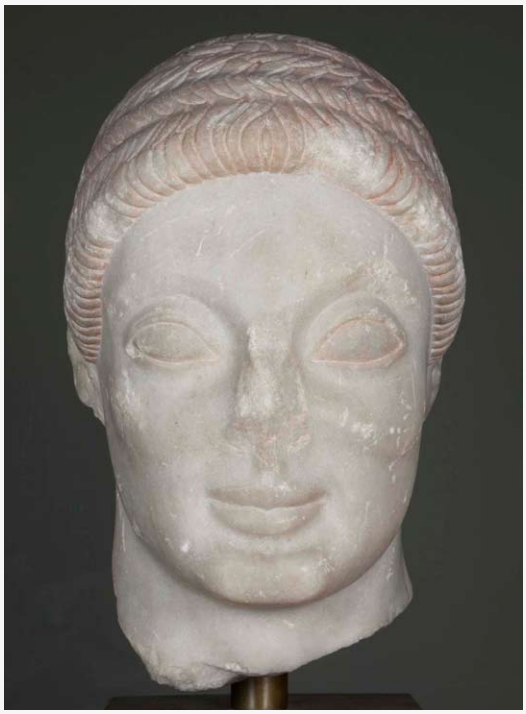

Fig. 6: Head of an Attic Kouros statue ('Rayet Head'), marble, c. 525 BCE. Ny Carlsberg Glyptotek IN 418. Museum photo.

Fig. 7: Marble portrait of the emperor Tiberius, c. 20–30 CE. Ny Carlsberg Glyptotek IN 1750. Museum photo.

Fig. 8: Artemis and Iphigeneia, marble, 1st century BCE–1st century CE. Ny Carlsberg Glyptotek IN 481–482a. Museum photo.

Documentation and investigation of traces of colour on the Archaic Sphinx NCG IN 1203

Maria Louise Sargent, Lin Rosa Spaabek, Mikkel Scharff, Jan Stubbe Østergaard[1]

ABSTRACT

The examination of traces of polychromy on an Archaic sphinx in the Ny Carlsberg Glyptotek was undertaken using a protocol developed for the purpose of co-ordinating the documentation and information concerning ancient polychrome sculptures. The Archaic sphinx was selected as the first of a number of sculptures from the collection of Greek and Roman sculpture, which will be examined for remains of their of original colours. The sphinx has clear traces of red on large areas, which can be observed with the naked eye. A sample of the red was studied by cross section analysis, micro-chemical analysis, scanning electron microscopy (SEM) combined with Energy dispersive X-ray (EDX) and X-ray fluorescence analysis (XRF). All the studies point in the same direction: the red colour is hematite(Fe_2O_3).

KEYWORDS

Polychromy. Archaic. Sphinx. limestone. Red. Hematite (Fe_2O_3). Ny Carlsberg Glyptotek.

INTRODUCTION

The Archaic sphinx[2] is the first of a number of sculptures from the Glyptotek's collection of Greek and Roman sculpture which has been examined and documented for traces of colour within the framework the CPN Main Project. The examination and documentation was undertaken following a protocol developed for the purpose of co-ordinating the documentation and information concerning ancient polychrome sculpture. The protocol provides standards for the methods which can be used for the examination of traces of colour on ancient sculpture.

Examination of the sphinx started in January 2009 in collaboration with conservator Lin Rosa Spaabæk and was carried out in a work space up in one of the galleries of ancient sculpture in the Glyptotek. While facilitating the logistics of moving sculpture to and from the work space, the location simultaneously gives the public an opportunity to follow the progress of the conservator's work.

ARCHAIC SPHINX IN 1203

The following section details the examinations of the Archaic sphinx IN 1203 and the results obtained.

1 Maria Louise Sargent, Project conservator, Ny Carlsberg Glyptotek; Lin Rosa Spaabæk, Conservator, Copenhagen; Mikkel Scharff, conservator, Head of the Departments of Painting and of Monumental Art, Royal Danish Academy of Fine Arts, The School of Conservation; Jan Stubbe Østergaard, research curator, Ancient art, Ny Carlsberg Glyptotek, Copenhagen (archaeological comment).

2 Johansen 1994, 40 no. 4 (with earlier literature, to which add: Floren 1987, 283; Boardman 1991, Fig. 225 w. text); Kreikenbom 2002, 159–160; Brinkmann 2003, no. 234, Fig. 234.1–5.

BASIC DATA

IN 1203
Motif: Sphinx
Dimensions: 84 × 70 cm
Date: c. 570 BCE[3]
Type of work: Sculpture in the round, tomb marker
Place of manufacture: Attica, Sparta (?)
Material: Poros limestone
Acquisition: 1895
Period: Archaic, 700–500 BCE

METHODOLOGY

Examination of the sphinx was divided up into the following categories: Visual examination, photographic documentation, ultraviolet fluorescence (UV-FL), raking light examination, video microscopy, microscopy, the taking of samples and examination of cross sections, micro-chemical analysis, Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray (EDX), X-Ray Fluorescence analysis (XRF), FT-IR and Gas Chromatography–Mass Spectrometry (GC-MS).

VISUAL EXAMINATION

Initially the sphinx was systematically examined with the naked eye and with a binocular magnifier with ×3 magnification. The examinations took place in the light from two tungsten light sources which were located at a 45 degree angle to the centre of the sculpture.

PHOTOGRAPHIC DOCUMENTATION AND EXAMINATION

The photographic documentation was made with a digital camera Canon EOS 5D Mark II. The sculpture was rotated about its axis with an interval of 45 degrees, and thus photographed with eight exposures. The top and bottom of the sculpture were likewise photographed (Fig. 1–8) In addition, detailed photos were taken of various selected areas of the sculpture. In order to subsequently make possible orientation in relation to the taking of samples and microscope images an alphanumerical grid was imposed on each of the detailed pictures with given coordinates.

ULTRAVIOLET FLUORESCENCE (UV-FL)

In addition to being photographed in the tungsten light, the sphinx was also examined and photographed under ultraviolet radiation, by means of which pigments, dyes and binding media in some cases fluoresce: in this way they are emphasised, appear more clearly and exhibit greater contrast (Fig. 9 & 10).[4] The precondition for UV-FL photography is the use of long wave UV-radiation and a filter which prevents the UV-radiation from being reproduced in the photograph. UV-fluorescence which, on the other hand is transmitted in the range of visible light, passes unhindered through the filter and can therefore be reproduced in

3 Johansen 1994, loc. cit.; Richter 1961, 10–11, no. 3 dates the sphinx to c. 590 BCE; Floren 1987, 283 '580–570'; Boardman 1991, Fig. 225 'c. 580', Kreikenbom 2002, 159–160 '580–570'.

4 Bjerre 1980, 22.

Fig. 1: Sphinx. Archaic Greek original c. 570 BCE, Poros limestone Ny Carlsberg Glyptotek (NCG) IN 1203, tungsten light.

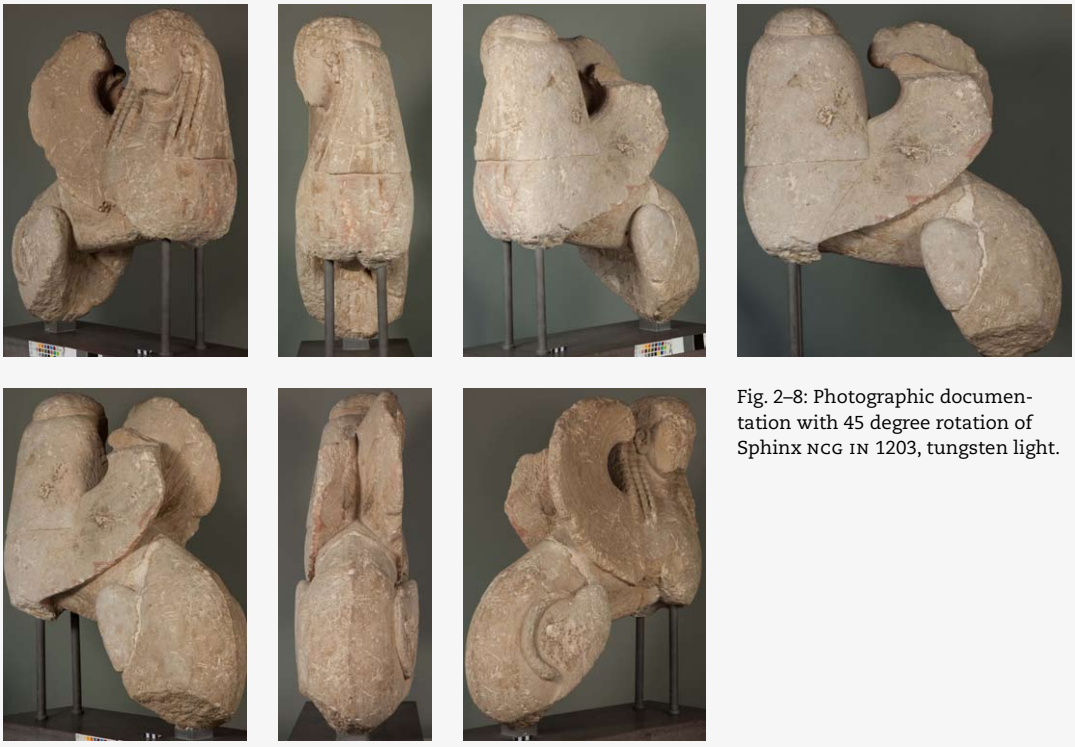

Fig. 2–8: Photographic documentation with 45 degree rotation of Sphinx NCG IN 1203, tungsten light.

Fig. 9: NCG IN 1203, UV fluorescence photo, right side.

Fig. 10: NCG IN1203, UV fluorescence photo, left side.

Fig. 11: NCG IN 1203, detail photo of chest, location of sample 1.

Fig. 12: NCG IN 1203, detail photo of right shoulder, location of sample 6 and sample 2–2b.

Fig. 13: NCG IN 1203, detail photo of back of wings, location of sample 3–3b and sample 4 and 4b.

Fig. 14: NCG IN 1203, detail photo of left wing, location of sample 9.

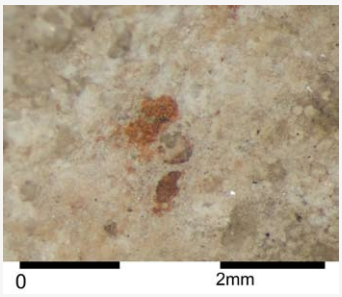

Fig. 15: NCG IN 1203
Microscope image in situ. 26×
Red above left eye.

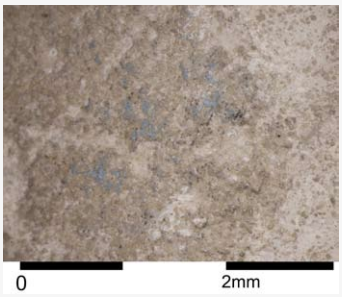

Fig. 16: NCG IN 1203, Sample 5
Microscope image in situ. 26×
Modern blue from left shoulder.

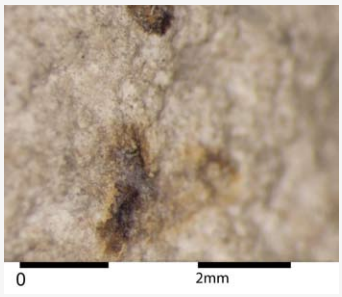

Fig. 17: NCG IN 1203
Microscope image in situ. 26×
Yellow ochre from the back hair.

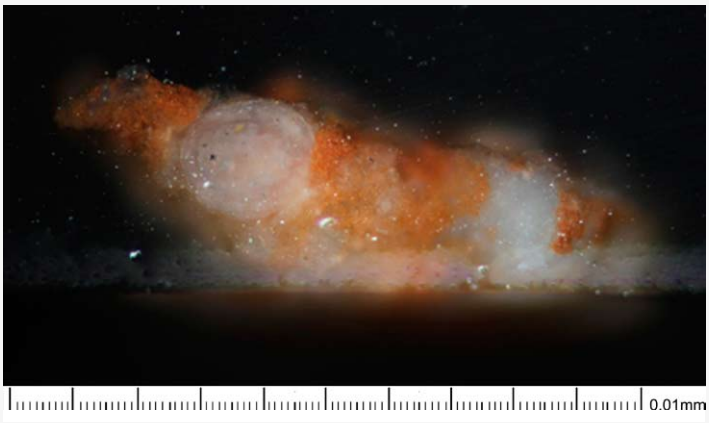

Fig. 18: NCG IN 1203, Sample 3a,
cross section, 100× tungsten light.

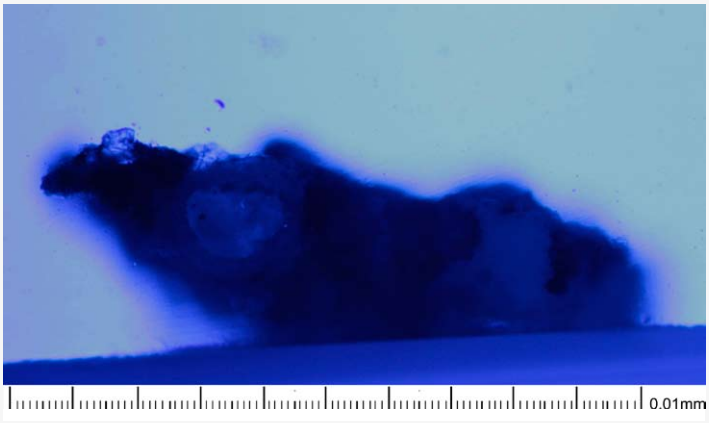

Fig. 19: NCG IN 1203, Sample 3a,
cross section, 100× UV light.

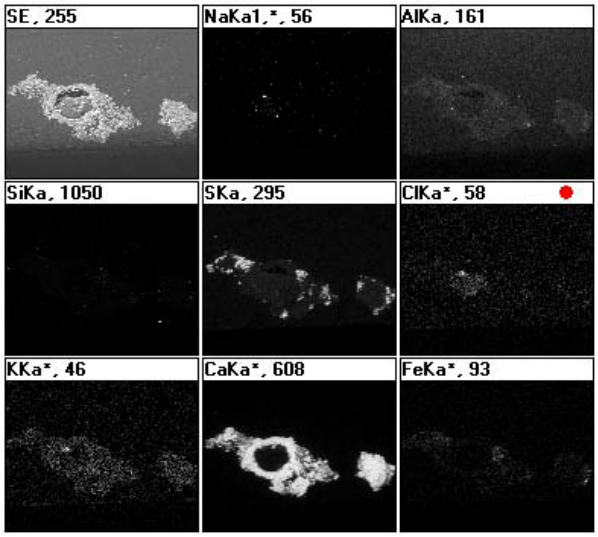

Fig. 20: NCG IN 1203, Sample 3a SEM/EDX backscatter picture. 200×.

Fig. 21: NCG IN 1203 location of XRF-08 (yellow area).

Fig. 22: NCG IN 1203 location of XRF-03,07.

Fig. 23: NCG IN 1203 location of XRF 01,02 and 04–06.

the photograph. For this purpose a Tiffen 2A filter was used (cutting at around approx. 400 mm).

RAKING TUNGSTEN LIGHT

In addition, the sphinx was examined and photographed in raking light, which implies the use of a mono-directional light source, the purpose of which is the revealing and emphasising of the differences in the level in the surface, e.g. tool marks, incised preliminary work and marked guidelines. Raking light examination was particularly employed to show up any contour incisions of scale-shaped feathers on the chest and the shoulder. The earrings were examined for any possible pattern, such as rosettes. In addition the flat back hair was examined with regard to finding incisions for painted locks of hair, which are known from contemporary sphinxes (Sphinx, Athens Acropolis 632).

Both UV-FL and the raking light exposures demand a total blackout of the immediate surroundings. Therefore the public will also notice a blackout tent being raised in the work space when this form of examination and documentation is to be carried out.

MICROSCOPIC EXAMINATIONS

For microscopic examinations three different types of microscope were used:

- Leica M651 operations microscope, which makes it possible to examine the sculpture in situ at up to ×26 magnification with a 150 mm objective (lens) at a working distance of 15 cm.
- DinoLitePro video microscope, a small hand-held microscope which can be connected to a computer which makes it possible to record both still and video images.
- Leica DM2500 M stereo microscope which is used to examine cross sections.

The entire sphinx was systematically examined with the aid of the operations microscope, supported by the video microscope. In addition microscopic pictures were taken of selected areas by connecting a camera attached to the operations microscope.

THE TAKING OF SAMPLES

It was necessary to take samples of various pigments. The samples can be used for the cross section examinations, micro-chemical analyses as well as element analyses with SEM/DEX. The samples do not need to be larger than a very few pigment grains, i.e. with a surface area as small as 0.25–1 mm^2. The following samples were taken:

1 Red from the chest (Fig. 11)
2 Red from the damaged patch on the chest (Fig. 11)
3 Red from the area between the flight feathers on the back of the left wing (Fig. 13)
4 Black from the flight feathers on the back of the left wing (Fig. 13)
5 Light blue from the left shoulder
6 Blue from the right shoulder (Fig. 12)
7 Black dots from the right wing
8 Black from the left shoulder
9 Yellow/brown from the flight feathers on the back of the right wing (Fig. 14)
10 Yellow from the left shoulder

CROSS SECTION EXAMINATION

For the preparation of cross sections the colour samples and individual grains of pigment were placed in a Serifex® polyester resin with styrene as solvent and hardener (methyl ethyl

ketone peroxide) from Struers. The cross section was sanded with wet-grinding paper 240, 400, 800, 1000, 1200 and dry-polished paper 4000 with odour-free paraffin.

A cross section may reveal something about the grain size of the pigment. The capacity of a colour layer to cover can be defined from e.g. whether the pigments of the paint layer are fine or coarse grained. At the same time one can also tell from a cross section whether there is a build-up of layers of pigments.

Cross section of sample 1–4 were prepared. Each of the various cross sections was assigned an inventory number and a sample number as well as being photographed with a camera connected to the Leica DM2500 M stereo microscope, in both halogen light and under UV-radiation. Finally the photographs were given a scale (Fig. 18–19).

MICRO-CHEMICAL ANALYSIS

Micro-chemical analysis is a rapid, straightforward and economical method of identifying pigments, in which chemical reactions are used to identify which elements the pigments consist of. The method should be compared with other examinations, since it is neither quantitative, nor can it provide information on the composition of the individual pigment. In addition the micro-chemical analysis method is regarded as a destructive analytical method – even if on a minute scale: the sample used is destroyed in the analysis.
Micro-chemical analyses were carried out on Sample 1, taken from the chest of the sphinx. It was tested for cinnabar (HgS), red lead (Pb_3O_4) and hematite (Fe_2O_3).

SEM/EDX (SCANNING ELECTRON MICROSCOPY/ENERGY DISPERSIVE X-RAY)

All samples were tested with the aid of SEM/EDX. For this, the apparatus (Jeol JMS 5310-LV low vacuum) of the Royal Danish Academy of Fine Arts, School of Conservation, was used with assistance from Jettie van Lanschot (conservator, cand.scient.cons) and Jørn Bredal Jørgensen (geologist, cand.scient.). In order to observe how the various elements were distributed, a mapping (X-ray map) was made which indicates the X-ray intensity of the selected elements and their mutual disposition in the surface of the cross section (Fig. 20).

X-RAY FLUORESCENCE ANALYSIS (XRF)

Several different areas of the sphinx were examined, and results interpreted, by professor Minik Rosing of the Museum of Geology/Natural History Museum of Denmark using a hand-held X-ray fluorescence device (XRF) (Fig. 21–23).

In order to determine which elements were present in the stone itself, without the pigment remains, a break surface was examined. In addition, the red and blue pigments from the right shoulder were examined. Also black from the back of the left wing was examined in order to establish whether it was remains of a pigment. On the examination of the red pigment, Minik Rosing writes:

'The second sculpture investigated for its red pigment was an Archaic Greek limestone Sphinx from Attica with traces of red colour. Here we used a hand-held XRF (X-ray fluorescence spectrometer).[5] This instrument has a c. 1 cm^2 area of analysis. The analysis of a faint red pigmentation of the Sphinx showed higher levels of Fe in these areas compared to background, and there were no traces of Pb or other heavy elements in the fluorescence spectra from the pigmented areas, which lead to the conclusion that the red pigment on

5 Innov-X Alpha Series 8000 LZX/R

this sculpture was a Fe-oxide based pigment such as red ochre, which is abundantly present throughout the Mediterranean region.'

BINDING MEDIUM ANALYSIS

In Antiquity, use was often made of organic binding media such as animal glue, wax, egg or drying oil, which is often not – or only to a limited extent – preserved.

Sample 1 of the red pigment from the chest was examined for binding medium by means of FT-IR spectroscopy, the results of which may indicate the presence of organic or inorganic compounds. The sample has also been sent to the Department of Chemistry and Industrial Chemistry at the University of Pisa where Dr Ilaria Bonaduce will undertake a GC-MS analysis for binding medium.

RESULTS

The following results and discussion are based on the examinations and analyses of the sphinx IN 1203 as described above. Samples removed from the sculpture were very small, which made some of the analyses very difficult to perform. A certain margin of error or uncertainty is partly due to this fact.

VISUAL EXAMINATIONS

The visual examinations, including the microscopic examinations carried out in situ, indicate that there is red paint in many areas of the sphinx:

1 On a large area of the chest (Fig. 11).
2 On the front edge of both wings.
3 Along the entire underside of both wings.
4 Many areas along the edge between the flight feathers (Fig. 14).
5 Along the head band around the head.
6 On the right area of the hair.
7 On four of the triangular ornaments decorating the (dress?) border at the neck, corresponding to every other of these ornaments (Fig. 12).
8 Along the bottom edge of the border which marks off the chest from the plumage.
9 In an individual triangular ornament which extends as far as the locks of hair on the left side (Fig. 12).
10 Between each of the locks of hair (Fig. 12).
11 On the right side, under the wing.
12 On the underside of the body between the forelegs.

Other pigments:

1 A yellow ochre has been detected on the hair at the back (Fig. 17).
2 Ochre has also been found on one of the flight feathers on the back of the right wing.
3 Several small traces of ochre on the left side of the abdomen.
4 Traces of ochre above and below the right eye (Fig. 15).
5 Minute traces of blue on the right shoulder.
6 Light blue on the left shoulders which is believed to be modern (Fig. 16).
7 Black, corresponding to every other wing feather on the back of both wings, leaving the question open whether it is pigment or not (Fig. 14).

ULTRAVIOLET FLUORESCENCE (UV-FL)

The sphinx fluoresced bright orange, in uneven layers over most of the sculpture, most powerfully on the wing feathers and under the eyes. To what this fluorescence is due has yet to be determined. The result can be due both to originally applied material, possibly a combination of a pigment or dye and a binding medium which, together fluoresce orange, and/or a later surface treatment of the sculpture. These possibilities should be further examined. Areas with red paint visible to the naked eye absorbed the UV-radiation and appeared dark.

RAKING LIGHT

Raking light examination was particularly used to explore whether there actually were incisions of shell-shaped contour feathers on the chest and shoulder. The examination produced no result. In addition, the flat back hair was examined in the hope of finding incised lines indicating the contours of locks of hair, but without result. On the other hand raking light highlighted the grooves outlining the musculature on the right and left hind legs and this was documented photographically.

CROSS SECTION EXAMINATION

Examination of the cross section with the red pigment from Samples 1–3 indicates only one layer, as no trace has been found of a 'primer' under the red pigment. The pigment was exceedingly fine-grained which indicates careful preparation and a high degree of covering capacity. Common to all three samples is the additional characteristic that the red pigment grains are found located between white, semi-transparent grains from the stone. Small black grains, which may be the result of pollution, lie sporadically between the pigment and the white grains. Examination with UV-radiation revealed that the red pigment absorbed more than the surrounding white grains.

MICRO-CHEMICAL ANALYSIS

Micro-chemical analysis was carried out on samples from the layer of red pigment on the chest. The analysis of cinnabar (HgS) and red lead (Pb_3O_4) was negative, while the analysis of hematite was positive, which indicates that the red pigment contains iron.

SEM/EDX (SCANNING ELECTRON MICROSCOPY/ENERGY DISPERSIVE X-RAY)

Common to all the samples: Large quantities of Ca (calcium) covering most of the samples, which may be assumed to be part of the stone. Sporadic presence of Si (silicate) which may either come from clay particles from the ground or from the abrasive used in the manufacture of the sample.

Sporadic appearance of sulphur in all the samples, and may possibly be a component of plaster, which, again, may be a component of the stone.

Samples 1–3: Examination of Samples 1–3 of the red pigment failed to indicate the presence of mercury or lead, as a component of cinnabar and red lead respectively. On the other hand it was apparent that iron was present, which supported the result of the micro-chemical analyses. Iron has a weak contrast and therefore only appears rarely with any clarity on an SEM analysis. By letting the SEM run for a longer time a clearer picture is obtained. The faint appearance of iron in the sample indicates that there has only been relatively little pigment, that this has been very fine-grained and possibly mixed in an extender, a conclusion that would be supported by the cross section examinations (Fig. 20).

Sample 4: Examination of Sample 4 (the black from the back of the left wing) produced no clear result. In Antiquity carbon was often used for the preparation of black pigment. Carbon is a very light element and its presence is therefore difficult to establish with a SEM/EDX analysis. However, no elements were found which were contained in the other black pigments used in Antiquity, such as phosphorus (bone black?) or manganese (manganese black?). On the other hand, a high content of titanium (Ti) indicates that the black might be pollution.

Sample 5: The results of the examination of Sample 5 showed that the blue pigment from the left shoulder was modern, based on the high content of titanium (Ti). The result was reinforced by microscopic examination in situ, which shows a uniform orientation of the pigment. The colour was added to the sculpture by accident and is, in all probability, the same paint which formerly covered the walls in Room 6 where the sphinx has been exhibited since the early 1950s.

Sample 6: Blue from the right shoulder. Had a fairly small content of copper (Cu), though this was not persuasive. The sample should be more closely examined to achieve a less ambiguous result.

Sample 7 & 8: Sample 7 had a character of a number of uniform round balls localised within a limited area. The results of the examination suggest a contamination from cinders. The results from Sample 8 show a high content of sulphur and indicate pollution embedded in plaster.

Sample 9: Contained iron, which indicates a yellow ochre.

Sample 10: The results of Sample 10 (yellow from the left shoulder) are still awaited.

X-RAY FLUORESCENCE ANALYSIS (XRF)

Examination of the damaged area revealed a large quantity of sulphur and calcium, but also a small amount of iron (3000 ppm), which must be regarded as a natural occurrence in this type of stone. Areas with red pigment exhibited a twice as high iron content, which, additionally, testifies to the presence of ochre. It was not possible to define the blue from the right shoulder. The explanation may be the limited presence of pigment. The black form the back of the left wing did not answer the question whether the black was pigment or not.

BINDING MEDIUM ANALYSIS

The results of the FT-IR did not show the presence of any binding medium containing protein (egg). However, it did produce a picture of another organic compound which might turn out to be a wax or an oil, probably of recent character, which was judged by the tops around 2923 and 2854 cm^{-1}. Similar results were observed from the examination of the woman's head IN 2830 in the Ny Carlsberg Glyptotek (see the Pilot Project report on this sculpture). The results of an additional binding medium analysis with GC-MS are still awaited.

CONCLUSION

Examination and documentation of the sphinx IN 1203 were carried out using a protocol developed for the purpose of coordinating documentation and information about antique polychrome sculpture. The protocol made it easy to begin the examination of the sphinx. Hopefully the result of the sphinx as well as similar examinations will create a better knowledge basis concerning the original state and visual appearance of the sculptures as well as a better understanding of the deterioration. Some uncertainties may be related to the fact

that most sculptures in older collections are without any information about excavation and treatment until acquisition by the museum.

The result of the UV-FL examination showed a bright orange fluorescence, divided into an even layer over most of the sculpture: it was at its strongest on the wing feathers and under the eyes. The reason for the fluorescence has yet to be clearly established but can be due both to originally applied material and/or a later surface treatment of the sculpture.

Raking light examination failed to indicate any tool marks, neither on the neck-hair, the shoulders or the chest.

Clear, visible traces of red pigment were found on large areas of the sphinx. The red paint was analysed with the aid of a microscope, cross section analysis, micro-chemical analysis, SEM/EDX and XRF. The results of all the analysis pointed in the same direction: the red paint is an iron-containing compound and thus an ochre colour. Examination also showed there was a very fine-grained pigment with a high covering capacity and a single-layer structure.

The general pigment composition has been affirmed of most of the samples while the binding media is yet not confirmed.

OUR THANKS TO

Jettie van Lanschot, Conservator, cand.scient.cons., The Danish School of Conservation
Jørn Bredal-Jørgensen, Geologist, cand.scient., The Danish School of Conservation
Mogens S. Koch, Photographer and Conservator,The Danish School of Conservation
Prof. Minik Rosing, dr.phil, the Museum of Geology/Natural History Museum of Denmark
Dr. Ilaria Bonaduce, Department of Chemistry and Industrial Chemistry, University of Pisa.

ARCHAEOLOGICAL COMMENT[6]

Among the stone sculptures of the Greek Archaic period that have by chance come down to us, sphinxes form a small but distinct and thoroughly interesting group. It is the more surprising that to my knowledge no in-depth study of them has so far been published – nor of archaic representations of sphinxes as such, for that matter.

Stone sphinxes were set up as votives in sanctuaries[7] and as gravestones[8]. The latter, the funerary sphinxes, are almost all from Attica and generally have the head turned at right angles to the body, towards passers-by. IN 1203 clearly belongs to this class.

What is known of the polychromy of this particular group of monuments is found only as disiecta membra. The membra may however be assembled without too much trouble thanks to monographs devoted on the one hand to Attic funerary monuments of the Archaic period, and on the other, to Archaic sculptural polychromy, respectively by G.M.A. Richter in 1961 and V. Brinkmann in 2003, the latter supplementing Richter because it is not restricted to funerary monuments.[9]

To provide an up to date archaeological comment on the polychromy of our sphinx IN 1203 would therefore require as a point of departure a combined use of Richter and Brinkmann, with the addition of monuments and literature that are either more recent or have been

6 By Jan Stubbe Østergaard. Abbreviations according to the guidelines of the Deutsches Archäologisches Institut (www.dainst.org)

7 Billot 1977

8 Holzmann 1991

9 Richter 1961; Brinkmann 2003.

missed by both of them. The whole range of iconographically relevant winged parallels on monuments of the Archaic period must of course also be taken into account: Gorgons, Sirens, Griffons, Pegasi and the like.[10] Such a study cannot however be undertaken within the compass of a Preliminary Report on our project.

In available literature, pigments on Archaic sphinxes have to date not been identified, but rather macroscopically described. The only exception known to me is the sample of red colour taken from the head of a funerary sphinx found in Athens in 1994 in the area of the Acharnian Gate on Odos Aiolou. (Fig. 24) It is dated ca. 540 BCE and is now kept in the magazines of the 3rd Ephoria in Athens.[11] The sample was analyzed in the Laboratory of the National Archaeological Museum by Dr. Eleni Magou; the pigment was identified as haematite.[12] The red colorant on our somewhat earlier sphinx is of the same character.

The proposed dating of our sphinx[13] places in the company of three other sphinxes of the first quarter of the 6th century BCE. Colours remain on all of them, but no published visual documentation exists. The sculptures in question are:

1 A marble sphinx in the Metropolitan Museum of Art in New York, MMA 24.97.87, dated c. 600 BCE. Traces of red was observed on the fillet and on feathers, black is seen between the wings.[14]
2 A limestone sphinx fragment, also in the Metropolitan, MMA 26.13, dated c. 600 BCE. White was reported on the face, the neck, the left foreleg, the belly and on the raised borders; black on the hair and on the left wing; red on the breast, the left wing covert and some feathers on the right wing.[15]
3 Finally, there is the limestone sphinx from Vari, in the National Archaeological Museum in Athens NAM 4476,[16] dated c. 590 BCE. There are remains of the white stucco which coated the piece and some red colour on the stucco[17] (Fig. 25).

In this group, 2 and 3 have a stylization of the flight feathers in two registers and a use of raised borders similar to ours. We also find parallels to the use of a red colour found on the Copenhagen sphinx: on the fillet, on the chest, on the wing coverts, and on the flight feathers. The black found on the wings of 1 and 2 would at least support the identification of the black on IN 1203 as being ancient. But we found no trace of a stucco coating as on 3.

10 Cf. Richter 1961, 50–51 on the feathers of birds and creatures of myth.

11 Inv. no. M 4518 (head) and 4519 (wing fragment). Karagiorga-Stathakopoulou 1996/1997 (2000) 2–3. pl. 1 a–c, 4a–c, 5a–b

12 Karagiorga-Stathakopulou 1996/1997 (2000) 3 no. 9. The method of analysis used is not described.

13 Cf. note 3 above. The dating of these sculptures is difficult, cf. Kreikenbom 2002, 159.

14 Richter 1961, 10 no. 1

15 Richter 1961, 10 no. 2

16 The inventory given by Richter seems to be incorrect, cf. Kaltsas 2003, 322. no. 676. inv. no. 4476 'Youth with chlamys'. The Vari sphinx is not included in the catalogue. Following the two references given by Kaltsas shows that the number he gives is not a misprint. I have not been able to establish the correct inv. no. for the sphinx.

17 Richter 1961, 11 no. 4

Fig. 24: Head of an archaic marble sphinx, c. 540 BCE. Athens, 3 Ephorate, inv. no. M 4518. From ADelt 51–52, 1996/1997 (2000) 2–3. pl. 1 a–b.

Fig. 25: Fragmentary limestone sphinx, c. 600–575 BCE. Athens, National Archaeological Museum inv. no. 4476? (cf. note 16). From Richter 1961, fig. 19.

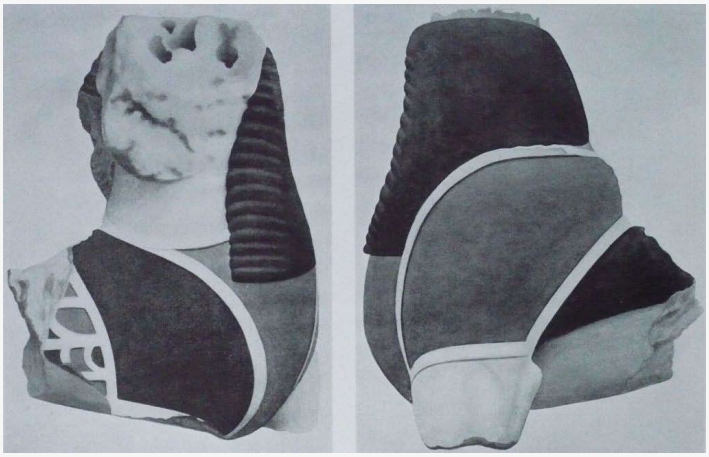

Fig. 26: Reconstruction in b/w of an archaic limestone sphinx fragment, c. 600 BCE. New York, Metropolitan Museum of Art, inv. no. 26.13. From Hall 1944, 332 figs. 9 and 10.

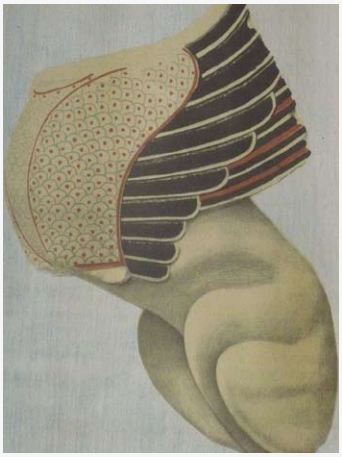

Fig. 27: Reconstruction of an archaic limestone sphinx fragment, c. 575–550 BCE. New York, Metropolitan Museum of Art, inv. no. 43.11.16. From Hall 1944, pl. X.

Fig. 28: Reconstruction of an archaic marble sphinx, c. 540 BCE. New York, Metropolitan Museum of Art, inv. no. 11.185. From Hall 1944, pl. VII.

Fig. 29: Reconstruction of an archaic marble sphinx, c. 550 BCE. Athens, Acropolis Museum inv. no. Acr. 632. From Schuchhardt – Neusser 1940, colour plate after p. 76.

Four published reconstructions of the polychromy of archaic Attic sphinxes are known to me and are shown here (Figs. 26–29).[18] Closest in style to IN 1203 is the New York limestone sphinx fragment, Fig. 23, but the hairstyle is different in having horizontal rather than vertical stylization of the locks – a feature found preserved on 3 (Fig. 25).

IN 1203 was chosen as our working-up, trial piece in visual examination because it is one of the oldest sculptures in the collection, because colour was clearly visible and because it is quite complex in form, despite the high degree of stylization. It served its purpose well. As regards its polychromy, the results gained cannot claim to be spectacular. Their importance lies in the fact that they are the first won from an archaic Greek sculpture to be published in such a completely documented manner. Our hope is that this will encourage future close examination of similar monuments already identified – not least by Richter and Brinkmann – as being rich in preserved remains of their original polychromy.

18 New York, MMA 26.13: Hall 1944, 332 figs. 9 and 10 in b/w. 336. New York, MMA 43.11.16: Hall 1944, 335 pl. X; New York, MMA 11.185: Hall 1944, 334 pl. VII. Athens, Akropolis Museum 632: Schuchhardt–Neusser 1940, colour plate after p. 76; Brinkmann 2003, no. 70, fig. 70.7.

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Other CPN activities

In the course of these projects, the CPN has presented papers at a number of scholarly meetings and has organized a couple of meetings itself.

PAPERS PRESENTED AT SCHOLARLY MEETINGS

J.S. Østergaard
"Primary research on ancient Greek and Roman sculptural polychromy; a Pilot Project in Copenhagen"
At: Die Farben der Antike – Neue Beobachtungen zur Polychromie und deren Wahrnehmung". Staatliche Antikensammlungen und Glyptothek, München, 4–5 June, 2005 (proceedings not published).

M. Scharff – R. Hast – J.S. Østergaard
"Remains of Polychromy on Ancient Greek and Roman Sculpture" (poster; published in D. Saunders – J.H. Townsend – S. Woodcock (eds.), The Object in Context: Crossing Conservation Boundaries. Contributions to the Munich Congress, 329).
At: The Object in Context: Crossing Conservation Boundaries. IIC congress, Munich, 28 August–1 September, 2006.

J.S. Østergaard
"The Copenhagen Polychromy Network: A primary research project on ancient Greek and Roman sculptural polychromy in the Ny Carlsberg Glyptotek"
At: La policromia su pietra naturale e ceramica dall' Antichità al Medioevo. Giornata di Studio, Università degli Studi della Tuscia, Viterbo, 26 October, 2007. (proceedings to be published);

And, updated, at: "CIRCUMLITIO". Internationales Colloquium zur Polychromie der antiken und mittelalterlichen Skulptur. Liebieghaus Skulpturensammlung, Frankfurt a/M, 10–12 December, 2008 (proceedings to be published).

M. Scharff – J.S. Østergaard
"Investigating the Polychromy of Greek and Roman stone sculpture: The Copenhagen Polychromy Network Main Project"
At: The 2. International Symposium of Conservation and Research on the Terracotta Army and Polychrome Cultural Relics, Xi'an, P.R. China, 23–25 March, 2009 (proceedings to be published).

J.S. Østergaard
"Research on ancient sculptural polychromy in the Ny Carlsberg Glyptotek, Copenhagen: introduction and first results"
At: Les Arts de la couleur en Grèce ancienne – et ailleurs". École Française d'Athènes, 23–26 April 2009 (proceedings to be published).

SCHOLARLY MEETINGS

Ny Carlsberg Glyptotek, Copenhagen, 10–11 September, 2009
(proceedings not to be published).

SPEAKERS

Mark Benford Abbe
(Advanced Certificate in Conservation, MA, Ph.D. Candidate, Institute of Fine Arts, New York University; Research Scholar, Metropolitan Museum of Art, New York)
Project: The polychromy of Roman sculpture; Aphrodisias.
"Some Recent Investigations into the Polychromy of Roman Marble Statuary"

Clarissa Blume
(MPhil, PhD student, University of Bochum/University of Heidelberg)
Project: The Polychromy of Hellenistic Sculpture.
"Portraits of the Ptolemies – Greek-style portraits and their polychrome finish"

Dr. Vinzenz Brinkmann
(Head of the collection of ancient art, Liebieghaus Skulpturensammlung; professor, Ruhr-Universität Bochum)
Project: Ancient sculptural polychromy.
"Latest Research on the Polychromy of Early Greek Marble Sculpture" (with U. Koch-Brinkmann)

Dr. Ulrike Koch-Brinkmann
(Classical archaeologist and reconstruction expert, München)
Project: The techniques of ancient sculptural polychromy; experimental reconstruction.
"Latest Research on the Polychromy of Early Greek Marble Sculpture" (with V. Brinkmann)

Prof. dr. Philippe Jockey
(Professeur d'Histoire et Civilisation grecques Université de Provence (Aix-Marseille 1))
Project: The surface treatment of Hellenistic sculpture from Delos.
"Theoretical and methodological issues raised by the study of the surface treatment of the Hellenistic Sculpture from Delos"

Prof. dr. Paolo Liverani
(Professore Associato, Dipartimento di Scienze dell'Antichità, Facoltà di Lettere e Filosofia, Università di Firenze)
Project: Sculptural polychromy of the Roman imperial age.
"Observations on the colour in Roman imperial sculpture: technique and meaning"

Alexander Nagel
(MA, PhD candidate, University of Michigan, Ann Arbor, Kelsey Museum of Archaeology; Freer and Sackler Galleries, Smithsonian Institution, Washington DC)
Project: The Persepolis Polychromy Project; Polychromy of Achaemenid Sculpture; Near Eastern sculptural polychromy.
"Approaching the Polychromies of the Ancient Near East:
The Persepolis Polychromy Project"

Dr. Thorsten Opper
(Curator, Department of Greece and Rome, The British Museum)
Project: Polychromy of classical sculpture in the British Museum (pilot study).
"The Polychromy of Ancient Sculpture:
Current work and future plans at the British Museum"

FROM THE COPENHAGEN POLYCHROMY NETWORK:

Jan Stubbe Østergaard
(Research curator, ancient art, NCG/CPN)
"Main Project Summary"

Maria Louise Sargent
(Conservator NCG/CPN)
"The CPN protocol in practise"

Mikkel Scharff
(Conservator, Head of Department, School of Conservation)
"Establishing the CPN protocol for visual examination"

Prof. dr. Minik Rosing
(Geologist, Natural History Museum of Denmark)
"Geochemical analyses of ancient pigments"

COLOUR ON FORM, FORM UNDER COLOUR – THE AESTHETIC DIMENSION IN EUROPEAN POLYCHROME SCULPTURE

Seminar at the Carlsberg Academy, Copenhagen, 30 October, 2009

SPEAKERS AND ABSTRACTS

- Jan Stubbe Østergaard
  (MA, research curator, ancient art, Ny Carlsberg Glyptotek)
  "Introduction to the matter at hand"

  Abstract
  I will introduce the subject of ancient sculptural polychromy and outline status in this field of research. The aesthetic dimensions of ancient polychrome sculpture are as of self evident research interest as they are difficult to explore on the basis of the meagre evidence provided by the traces remaining on the originals. A useful spin-off of the experimental archaeological effort put into research based reconstructions of the polychromy of ancient sculptures has been the at times vehement criticism of their aesthetic and technical quality. Though based on a misunderstanding of the rationale of the reconstructions, such criticism has served to highlight the necessity of a dialogue with art historians and conservators conversant with the techniques and aesthetics of the closest analogies to ancient polychrome sculpture that we have available, namely the far better preserved early modern European polychrome sculpture. From the point of view of the study of ancient sculptural polychromy, such a dialogue would serve as platform for hypotheses about the aesthetic dimension of colour on form in ancient times.

  The paradox is that for reasons rooted in the historiography of art history and the reception of Greek and Roman sculpture, the aesthetic dimension of European polychrome sculpture has received only modest scholarly attention. This aspect will be briefly explored.

- Dr. Susie Nash
  (Senior Researcher, the Courtauld Institute of Art, London)
  "The Great Cross at Chartreuse de Champmol:
  Claus Sluter, sculptor, and Jean Malouel, painter"

  Abstract
  The construction and decoration of the Chartreuse de Champmol for Philip the Bold in the late 14th century is remarkably well documented. We have detailed payment accounts for materials and labour, including pigments and gold leaf, and with them we can follow the processes of creating and polychroming large scale stone monuments like the Great Cross made for the central cloister of the monastery, and known today as the 'Well of Moses' (1395–1404). Analysis of these documents in combination with recent technical analysis allows us insights into how a sculptural workshop, headed by Claus Sluter, and a painting workshop, headed by Jean Malouel, co-ordinated work and collaborated, on the conception of the colour on this work as well as on its practical undertaking. What is also important to consider, and harder to define, is why this work was painted at all, given its exposed location (which required remedial measures early on) and given that different choices concerning the surface treatment of imagery in stone were made for other monuments within the complex. These differences allow us to explore how sculptural colour might hold meaning.

- Dr. Maria Fabricius Hansen
  (Art historian, Assistant professor, Department of Art History, University of Århus)
  "Colour blind: The optics of Classicism as a problem in art historical accounts of the Mediaeval Period and the Renaissance"

  Abstract
  A reluctance to recognize the importance of colour for sculpture and architecture is not limited to accounts dealing with classical antiquity. The wide spread tendency to overlook the role of colour in relation to form has also affected art historical presentations of Medieval and Renaissance sculpture and architecture. In his book Fra Angelico (1990), the art historian Georges Didi-Huberman writes vividly about our ability not to see; about the art historians propensity for not seeing, or to disregard that which does not fit into the scheme of things in the way we expect.

  The pronounced colour blindness found among classical archaeologists and historians of art has to do with the cult of classicism which has dominated those subjects from Winckelmann onwards. This also goes to explain the lack of interest in the question of what the effect of a sculpture is when polychrome and when seen in its monochrome material. Drawing on examples from Medieval and Renaissance sculpture and architecture, my paper discusses the apparent conflict between classical, monochrome form, and the un-classical, coloured surface. We will be looking at colour as found in the reused Roman architecture of Medieval times, as well in the sculpture and architecture in the Italian renaissance of the Quattrocento. In this way I hope to throw light on some of the conventional assumptions which colour (or rather 'decolorize') our view of the past.

- Jørgen Hein
  (Art historian, Curator, De Danske Kongers Kronologiske Samlinger, Rosenborg Slot)
  "Polychrome wax sculpture of the 17th and 18th century"

  Abstract
  The point of departure for this paper is the series of portrait busts of members of the Danish royal house, kept in the Royal Collections at Rosenborg Castle and the Museum of National History at the Castle of Frederiksborg. These busts date from the period 1669–1772. The majority are taken from death or life masks, while a few are modelled. Most are dressed in clothes belonging to the person portrayed. The busts were set up either in the private royal apartments or exhibited in the Collection of Treasures at Rosenborg. From 1690s onwards they were all on show in the so-called 'Hall of Heroes' of the Royal Cabinet of Curiosities.

  The busts point both forward and back in time. Looking back in time, they lead to the cult of the dead in classical antiquity, a cult inherited by the Medieval Period, as in the figures in effigie known from royal tombs in France, England and Spain, as well as in the votive gifts, the portraits of patrons and the representations of saints in the catholic Church. The way forward in time leads from the Cabinets of Curiosities of royals and aristocrats, to the travelling Wax Cabinets which from the end of the 17th century showed the populace in and around London and Paris depictions of both the powerful and the misshapen; the precursors of the Madame Tussaud's of our own time.

  Wax is a cheap and easily available material which may be dyed and/or painted on. It is extremely well-suited to the depiction of human skin, musculature and veins. The effect may be heightened with by the addition in natural or synthetic materials of such features as beard stubble, eyebrows, hair and glass eyes. Artistically, the end result is a polychrome sculpture of great realism, apt to fool the senses and invite thoughts on the Magic – especially in a time before the advent of photography.

Wax is however also a brittle and easily perishable material; as a consequence only few works survive. It is therefore difficult to judge the extent to which the polychromy of the preserved pieces is representative and whether such works influenced polychrome sculpture in other materials. To shed some light on such issues, I present some selected 17th and 18th century polychrome sculptures in small formats, of stone, alabaster and ivory.

- Anna Schram Vejlby
  (Art historian, Copenhagen)
  "Red Cheeks. Colour and sculpture 1750–1860"

Abstract
The period 1750–1860 is in many respects a transitional one, both as regards polychrome sculpture and its reception.

In my paper I describe the process of development in sculpture, from the glaring whiteness of neoclassicism to discreetly red cheeked godesses and on to a complete polychromy – which by the mid 19th century led some critics to describe as timid those sculptors who did not employ a full range of colours.

Sensual, life imbuing colour, changing with the light and the time of day, was definitely not appreciated by neoclassical sculptors, architects and philosophers of art. They were bent on depicting Eternity and Truth, subjects incommensurate with ever changing colour, especially in such a reprehensible combination of art forms as that seen in polychrome sculpture. For artists who admired the perfect forms of the ancient masterpieces, clad in noble white marble, the dawning knowledge of ancient polychromy was not welcome.

By and large Winckelmann ignored the instances of polychromy which he came across, and seems only to have found polychrome works of a kind not Greek of the best period. Herder praised sculpture as being pure form, unfettered by the scintillating illusionism of colour. And even Quatremére de Quincy, author of the first work on ancient sculptural polychromy, seems to have preferred the chryselephantine statues, untainted by applied colour.

I will be presenting works representative of the cult of white marble – but more especially those exceptions (such as works by Canova and Gibson) which at one and the same time confirm the rule and point forward towards an art devoted to other ends than the representation of the Eternally True. My point of departure will be the art theoretical tradition which from the Renaissance passed judgement on colour as being sensual and temporal, as opposed to the timelessness of line and form. A tradition which thrived in the rarefied airs of neoclassical art and art theory. But which experienced a change of circumstances in the mid-19th century, a time when polychrome sculpture was hailed by some for the very reason that it placed the works in question close to life as lived, here and now.

- Flemming Friborg
  (Art historian, Director, Ny Carlsberg Glyptotek)
  "Colourful, repressed – and tempting? Colour in European sculpture of the 19th century"

Abstract
My contribution deals with European sculpture in the period from c. 1800–1910. Through discussion and interpretation of works from that period, I attempt to focus on, and describe

- Colour as problematic in sculpture from c. 1800 on
- Romanticist attitudes to colour and sensual perception, in sculpture and in general
- The impact of art history and the history of ideas on the development of modern sculpture 'in colour'

- The beginnings of a modernistic upending of the mimetic relation of sculpture to 'reality'
- Colour as an exponent of 'The New' in the visual arts, especially in the art of Gauguin and the Fauvistes /the Expressionist, including the reception of this approach by Picasso and Braque

By way of introduction, I will outline the main elements of theory and practise with which the art of sculpture had to deal at the opening of the 19th century in regard to the use of colour. Romanticist fascination (combined with moral dread) of sensual perception is set up against classicistic ideals of whiteness and spiritual as well as formal purity; following on this, I offer an analysis of two particularly relevant works (Gibson's 'Tinted Venus' (1851) and Cordier's 'Jewess of Algiers' (1862).

'Naturalism vs. Idealism' is discussed in the light of a nascent shift of aesthetical values. A shift closely connected with the advent of major, modern national states and colonial powers, involving changed conditions for the world of art and its representational framework. On this background, I examine the relations of sculpture to the human being, in body and in mind, as revealed by predominantly French works of art between 1870 and 1900 such as Degas' 'Ballet Dancer, 14 years' (1879–81). Novel choices of materials and techniques as well as the application of industrial means of shaping (also in the decorative arts) serve to com of shaping serve to combine colour more strongly with form in the period at hand. This expansion in the handling forms and materials by 'classic' art forms is then followed in works by Braque, Picasso and Duchamp.

- Dr. Mikael Wivel
  (Art historian, Copenhagen)
  "Modernism and the return of polychromy"

Abstract
At the end of the 19th century, Danish sculptors were still pinned under the weight of the Bertel Thorvaldsen tradition. It was just as much a case of in-breeding as of apathy. Only when a group of amateurs in the field got together in the mid 1880s did a weather change occur. Their forum was the workshop of Johan Wallmann at Utterslev near Copenhagen. Here, experiments in ceramics were under way. The initiative was taken by the architect Thorvald Bindesbøll, but the people to let their talents loose and reintroduce colour into Danish sculpture were paint ers such as Theodor Philipsen, Elise Konstantin-Hansen and, not least, Niels, Joakim and Suzette Skovgaard. J.F. Willumsen belonged as well, though he never came to Utterslev..

Polychrome sculpture is thus an integrated part of the break through of Modernism in Denmark. It is significant that that painters, not sculptors, were the ones to recognize its rejuvenating potential. Neoclassicism had relegated polychrome sculpture to, at best, the rear ranks of the visual arts, for common people. Its rediscovery and acceptance is one of the earliest instances in the 20th century of the inspiration unorthodox artists might fid in the so-called trivial arts.

As a result, polychromy has been present in Danish sculpture ever since, and that with such force that it has near driven marble and bronze off the field. Modernists such as Jais Nielsen and Adam Fischer were among the first to take up the challenge from Utterslev, but since then independent sculptors like Mogens Bøggild, Henrik Starcke, Jørgen Haugen-Sørensen, Bjørn Nørgaard, Kurt Trampedach and Christian Lemmerz have each in their own way explored the artistic potential of polychromy with astounding originality.

- Bjørn Nørgaard
  (Visual artist)
  "Is colour an optimizer of form – or does it reduce form?"

- Mikkel Scharff
  (Head of Department)
  The Royal Danish Academy of Fine Arts, The School of Conservation
  "Polychrome sculpture in Antiquity and in European Middle Ages:
  A view from conservation science"

Abstract
Knowledge of the structure, the materials and their deterioration in polychrome sculpture is achieved by systematic and detailed examination and documentation., accompanied by relevant chemical and physical analyses. In connection with this it is – as always in heritage preservation – of the first importance to collaborate closely with all relevant stakeholders and specialists, in order to ensure the integration of results from the fields of conservation science, archaeology, chemistry and physics. In the sphere of conservation of visual art, the term 'technical art history' is used to describe the coordination of data from humanistics and the technical sciences.

The School of Conservation in Copenhagen is interested in the further development of aspects of conservation scientific research. It has therefore joined the Copenhagen Polychromy Network with enthusiasm. Our aim is to obtain increased knowledge of pigment remains on ancient sculpture, to understand the structure, the materials and their deterioration. We also aim to test a number of methods of examination and analysis on ancient sculpture. Knowledge of the polychromy of Greek and Roman sculpture may increase our understanding of the technological background for medieval use of colours on buildings, interiors and a variety of objects. It is our hope that we may at the same time contribute new data to a field of research now in its formative phase. Finally, it is hoped that increased knowledge will help in planning preventive measures designed to preserve the remains of polychromy still found on ancient sculptures.