From Molecules to Medieval Manuscripts

Team-Pigment
Durham University
Northumbria University
Great Britain – Key places

- Iona
- Glasgow
- Wearmouth/Jarrow
- Lindisfarne
- Durham
- Cambridge
- Oxford
- Winchester
- Canterbury
Sept. 2012: - asked ‘would I be interested in using spectroscopy to analyse inks in medieval manuscripts?’

‘Team-Pigment’ formed
Richard Gameson
Kate Nicholson

May 2013: First campaign – Insular Gospels and local MSS

May 2014: Mobile instrumentation - first trips outside Durham

May 2018: Most recent trip, Hunter Library, Glasgow

To date: over 250 British books studied + many other objects
Could we analyse the manuscript pigments? The Challenge

• Our analysis must be non-destructive, non-contact

• Can we use Raman and diffuse reflectance spectroscopy to identify pigments in medieval manuscripts?

• They have NEVER been examined this way before!

• The books are simply priceless – cannot be moved to Chemistry Dept.

• We would have to move equipment to the books – not a trivial undertaking.
Chemists Analysing Pigments

Some Experiments and Observations on the Colours Used in Painting by the Ancients
Humphry Davy
*Phil. Trans. R. Soc. Lond.* 1815 *105*, 97-124, published 1 January 1815

Analyse non-destructive des pigments par microsonde Raman laser: exemples de l’azurite et de la malchite
Bernard Guineau
*Studies in Conservation*, 1984 *29*, 35-41

La Microsonde Raman Laser: un nouvel instrument d’analyse des pigments dans les enluminures
Jean Vezin
*Scriptorium*, 1984 *38*, 325-326
Raman Spectroscopy

- Molecules are always moving or vibrating
  - the vibrational spectrum is characteristic - ‘fingerprint’
  - shine laser onto page and look at the scattered light
  - difference between $\lambda_{\text{in}}$ and $\lambda_{\text{Raman}}$ gives the vib. spec.
Diffuse Reflectance

incident light

scattered & reflected light
Multi-spectral Imaging

Filter

450 nm
500 nm
650 nm
850 nm
Moving the Mountain....
How not to damage the books...
.... use very low power

Laser power < 0.5 mW over ca. 5 µm²

  - 50 x lens, 2.25 mW

  - 10 - 100x  3 - 10 mW

  - 50 -100x  min power 17 - 0.17 mW
Mobile Raman: Specification

• Easily portable by train/car/plane and 2-persons, 2 cases, < 20 kg ea.
• Kit will contain diffuse reflectance, optical imaging and Raman instrumentation – easy to set up & calibrate
• All have to be non-contact measurements
• Mounted on rugged frame to allow use over open, and part-open books

• Raman
  • Ideally two wavelengths, 633 nm and 532 nm
  • Low wavenumber capability - < 80 cm\(^{-1}\)
  • Moderate resolution, \(\sim 10\) cm\(^{-1}\) is good enough for most materials
  • Sensitivity – work employs low laser powers, < 0.5 mW
  • Free-space microscope – ability to move the light to the sample

• Imaging
  • Ability to image across range 350 – 1100 nm achromatically
  • Moderate resolution > 1 Mpixel across pages up to A3 in size.
  • As many wavelengths as possible!

• Diffuse Reflectance
  • Reflectance spectra in range 350 – 1100 nm minimum
  • Sample area of \(\sim 1\) mm\(^2\) to allow specific areas to be analysed
  • Ideally would like to extend to NIR – 1100 - > 2500 nm…
A Word of Warming

Commercial Raman system, 785 nm, ‘adjustable power’, (100 mW min)
Raman Spectroscopy

Horiba LabRAM-HR

Team-Pigment mobile Raman
Raman Spectroscopy

Horiba LabRAM-HR

< 0.5 mW over ca. 5 µm²

Team-Pigment mobile Raman

< 0.4 mW over ca. 600 µm²
Continual Development - New Raman Probe

Much smaller than currently available
- better access to margins

Can operate at low wavenumber (> 70 cm\(^{-1}\))
When lux can kill
Current FORS practice

250 mW cm\(^{-2}\), 400 – 2500 nm
ca. 100,000 Lux
FORS – novel design

350 – 1100 nm range

Low light intensity on sample
(< 0.02 mW/mm²)

Unique ‘Lancaster’ design

Large stand-off (~ 8cm) for safety of book

Frame mounting – stability

Small region of analysis, φ~2 mm

Reflectance (*100)

Wavelength (nm)

Smalt
Indigo
Lapis lazuli
Azurite
Full-spectrum FORS

UV-SWIR: 350 – 2500 nm

Low light intensity on sample
(< 0.1 mW/mm²), φ = 2mm

No temp rise, < 1°C

Same ‘Lancaster’ design
- Large stand-off (< 4 cm)
Multispectral Imaging

LED illuminators for UV-NIR

Mono-1.3 MP CCD camera images through a set of 9 interference filters

No refocussing during spectral acquisition provides multi-spectral data set for PCA etc.

Scattered light imaging and fluorescence imaging possible.
Raman in a Suitcase
A-II-10 Part of a 7th Century Gospel Book
A-II-10 Part of a 7\textsuperscript{th} Century Gospel Book

© Dean & Chapter of Durham Cathedral
Revealing subtle differences: A-II-16

Scribal marks—different composition pigment

PbO (massicott)

Pb$_3$O$_4$ (red lead)

© Dean & Chapter of Durham Cathedral
Sources of Pigments in the 7/8th Century

**Red lead (minium)**
\[ \text{Pb}_3\text{O}_4 \]
Does occur naturally - but not in UK
Weardale was source of lead-ore (PbS) in Roman times..

\[ \text{PbS} \rightarrow \text{Pb} \rightarrow 2\text{PbCO}_3.\text{Pb(OH)}_2 \rightarrow \text{Pb}_3\text{O}_4 (\rightarrow \text{PbO}) \]

**Orpiment**
\[ \text{As}_2\text{S}_3 \]
Not found in UK
Commonly found near volcanic areas in Italy (Vesuvius and Tuscany)

**Verdigris**
Corrosion product of copper metal with e.g. urine

**Indigo (woad)**
Extracted from woad plant - grows like a weed
A book containing the daily orders of service, a well used, and rather damaged book

Originally written in black ink (Latin), old English translation was written in red by Aldred (Chester le Street, ca. 970)

What inks were used?

Collectar – DCL A.IV-19
c.f. Lindisfarne Gospels, f. 220v, (John)
Interesting – NOT red-lead or vermilion!

This is red-ochre – iron oxide/clay

‘Low-cost’ – readily available?

Raman and diff. ref. show it is the same pigment used in the Lindisfarne Gospels

Did Aldred discover red is easier to read?
The Normans are coming - or “1066 and all that”
• Symeon was thought to have trained in Normandy – did he bring his methods to Durham?
Libellus de Exordius - Pigments

- orpiment
- vermilion
- lapis lazuli
Libellus de Exordius - Pigments

- Copper salt
- Lapis lazuli
- Red lead
- Vermilion
- Oak gall
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<th>Lapis</th>
<th>Egyptian Blue</th>
<th>Azurite</th>
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A Surprising Discovery

Note - lapis spectrum showed additional strong emission at ca. 900 nm…
A Surprising Discovery

Note - lapis spectrum showed additional strong luminescence emission at ca. 900 nm…
NIR Imaging

Area illuminated with red laser

CCCC MS-411, *fol. 40r*

Reproduced by kind permission of the Master and Fellows of Corpus Christi College, Cambridge

Image recorded at > 850 nm
Egyptian Blue: CaCuSi$_4$O$_{10}$

VIII. Some experiments and observations on the colours used in painting by the Ancients. By Sir Humphry Davy, LL. D. F.R.S.

Read February 23, 1815.

I. Introduction.

The importance the Greeks attached to pictures, the estimation in which their great painters were held, the high prices paid for their most celebrated productions, and the emulation and competition which arose from the various efforts to excel each other, are strong proofs of the infinite value which they placed upon pictures. But what had been the case in Greece must have been the same in Egypt, where the most celebrated of the ancient artists resided, and where the colours which they used may probably have been Egyptian Blue. For this colour is still known under the name of Egyptian Blue, and it is not improbable that it was the same which the ancients used, and which they called ocreus.

IV. Of the blue colours of the Ancients.

Different shades of blue are used in the different apartments of the baths of Titus, and several very fine blues exist in the mixtures of colours to which I have referred in the last two sections.

These blues are pale or darker, according as they contain larger or smaller quantities of carbonate of lime, but when this carbonate of lime is dissolved by acids, they present the same body colour, a very fine blue powder similar to the best smalt or to ultramarine, rough to the touch, and which does not lose its colour by being heated to redness; but which becomes agglutinated and semifused at a white heat.

This blue I found was very little acted on by acids. Nitromuriatic acid by being long boiled upon it gained, however, a slight tint of yellow, and afforded proofs of the presence of oxide of copper.

There is every reason to believe, that this is the colour described by Theophrastus as discovered by an Egyptian king,* and of which the manufactory is said to have been anciently established at Alexandria.
Egyptian Blue is known to have a long-lived excited state, $\tau_f = 100$ $\mu$s

Excite with short pulse of red light (650 nm, 1 $\mu$s) and detect emission at $> 850$ nm with time.
Pigments of the 10th Century

**Lapis Lazuli**
From Afghanistan, blue colour derived from sulfur radical anions in matrix Reflective in NIR

**Vermilion (cinnabar) HgS**
Synthetic and naturally occurring ore, Material in manuscripts likely to be finely ground cinnabar

**Egyptian Blue CaCuSi₄O₁₀**
Synthetic blue pigment based on Cu. Luminesces in NIR!

**Azurite Cu₃(CO₃)₂(OH)₂**
From weathered copper ores, mined from C.12 in Saxony Absorbs in NIR
Bodleian Douce-319 An ‘Encyclopedia from ca. 1270

A book produced in Spain, but with ‘Arabic’ influence

Similar to Fra Mauro map of 1450?

Reproduced by kind permission of the Bodleian Library, Oxford
Bodleian Douce-319 fol 8v

Vermilion, HgS

Lapis lazuli

Orpiment, As$_2$S$_3$
5 Images, recorded at 5 different wavelengths
Principal component analysis of multi-spectral images allows us to map pigments on the page – clusters of data are presented as false-colour images.
The Challenge of Maps

Bodleian Library, ‘Gough Map’ ca. 1320?

Verdigris, indigo, vermilion
Raman in a Suitcase – we really can work anywhere…

Gough Map ©Bodleian Library
The Challenge of Maps

CCCC MS-161, Matthew Paris,
*Chronica Majora* 1230-1240
Verdigris, lapis lazuli, vermilion, azurite?
Hereford, Mappa Mundi

Hereford Cathedral
Mappa Mundi
ca. 1300
Hereford, Mappa Mundi, (1300)

Vermilion – text & Red Sea

Azurite - blue rivers
(mostly flaked off)

Oceans and seas  ???
Very degraded, no Raman

Some gold leaf lettering –
mostly flaked off
Conclusions

• Instrumentation for work needs to be mobile – books are not easily moved – to allow studies of coherent series of MSS

• Raman gives detailed information on small areas – other methods – FORS, imaging, XRF… are also required to corroborate findings

• Team Pigment now have portable Raman, UV-SWIR reflectance, pXRF and UV-NIR imaging instrumentation

• Now where?
  New instrumentation.
  Future campaigns.
    Very old books, e.g. St Augustine Gospel, c.6
    Complete the Canterbury-Winchester study, c.10-c.12
    Extend the map-work?
“We owe huge debt of gratitude to the people who made this work possible – and for the librarians who trusted our team of scientists with a set of priceless books.”

**Team Pigment**
- Prof Richard Gameson
- Dr Kate Nicholson
- Dr Andy Duckworth
- David Howell
- Dr Sheila Hingley / Judy Burg
- Gabriel Sewell / Lisa di Tommaso
- Dr Andrew Millard

**Libraries**
- Durham University & Cathedral Bodleian Library
- University College Oxford
- Trinity College Oxford
- Keble College, Oxford
- Corpus Christi College Cambridge
- Trinity College Cambridge
- Fitzwilliam Museum
- York Minster
- Aberdeen University
- Glasgow University Library
- Edinburgh University Library
- Hereford Cathedral Library
- British Library
- Royal College of Arms

**Cash and help…**
- Rob and Felicity Shepherd
- Horiba (UK)
- Ocean Optics (UK)
- Andor (UK)
- AHRC