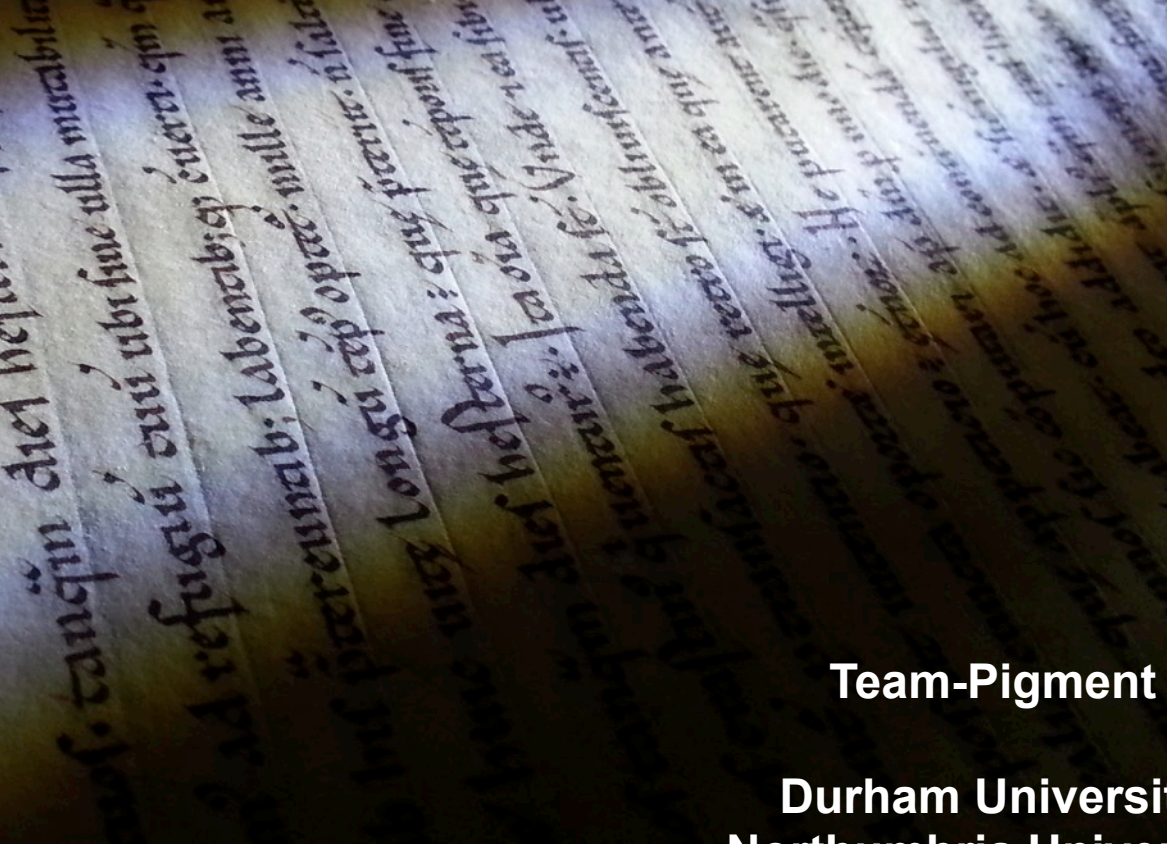


From Molecules to Medieval Manuscripts



diei hesterni
refugium
longum tempus

Team-Pigment

Durham University
Northumbria University

Team-Pigment

Durham University
Northumbria University

Great Britain – Key places







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

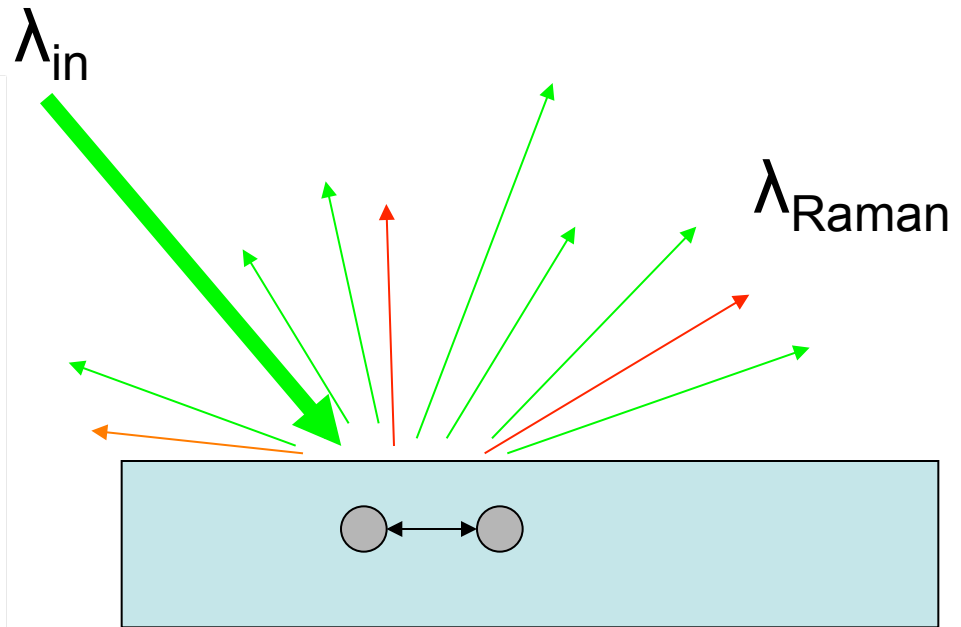
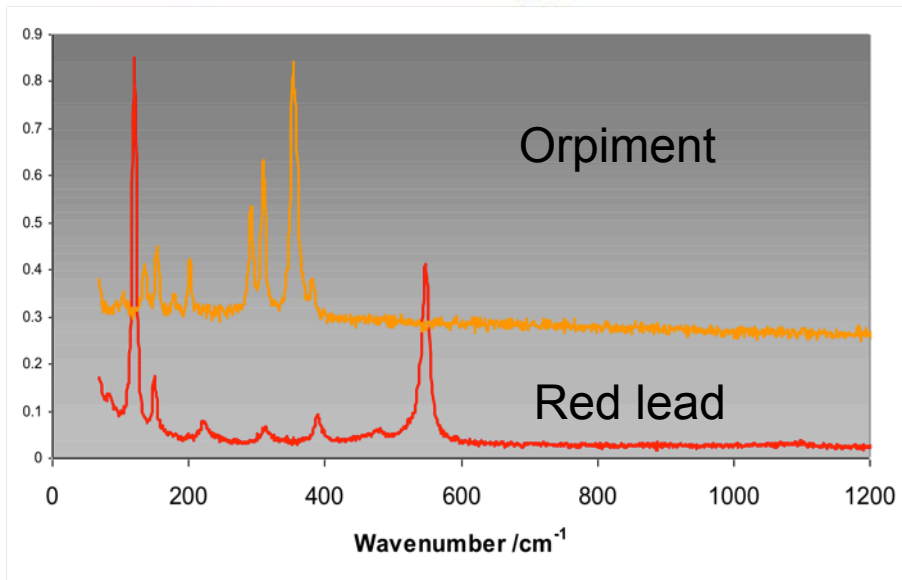
La Microsonde Raman Laser: un nouvel instrument d'analyse des pigments dans les enluminures

Jean Vezin

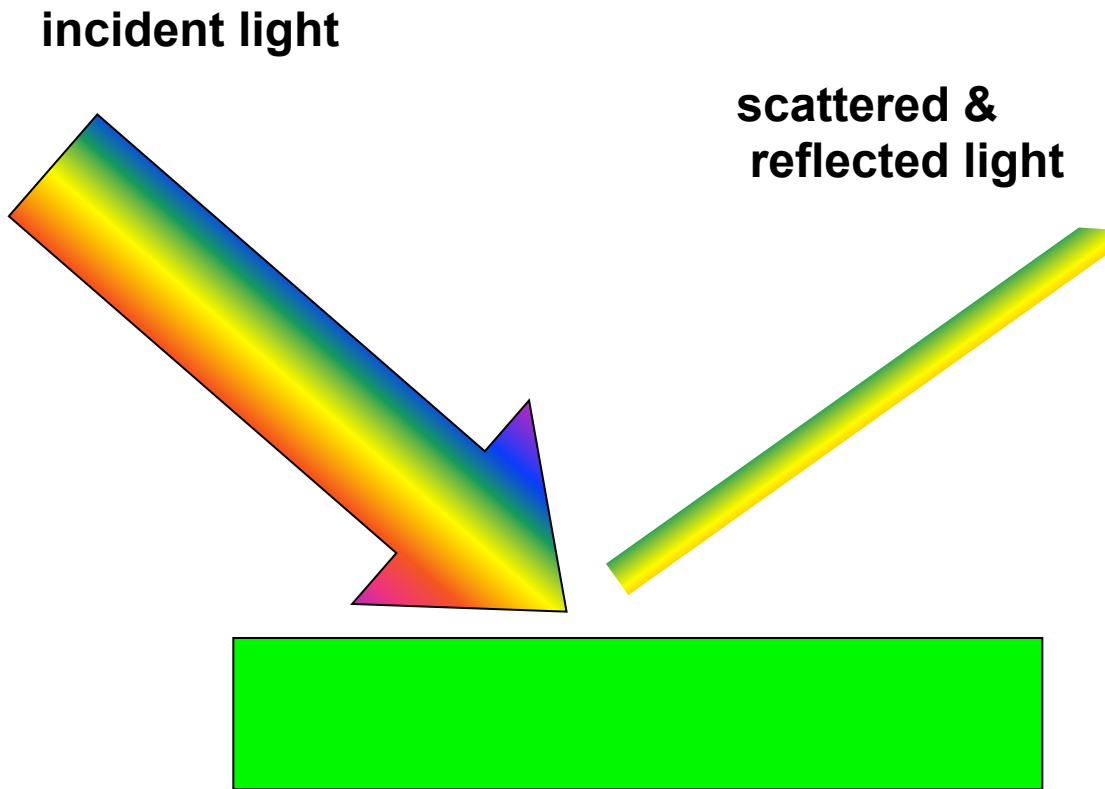
Scriptorium, 1984 **38**, 325-326

Raman Spectroscopy

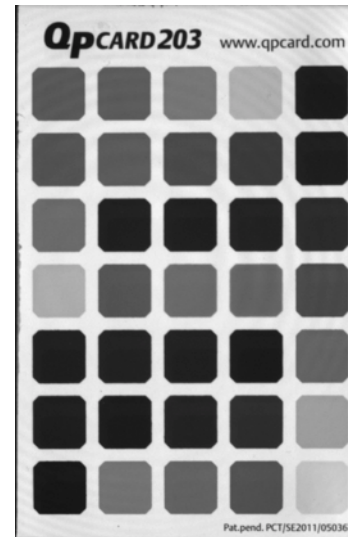
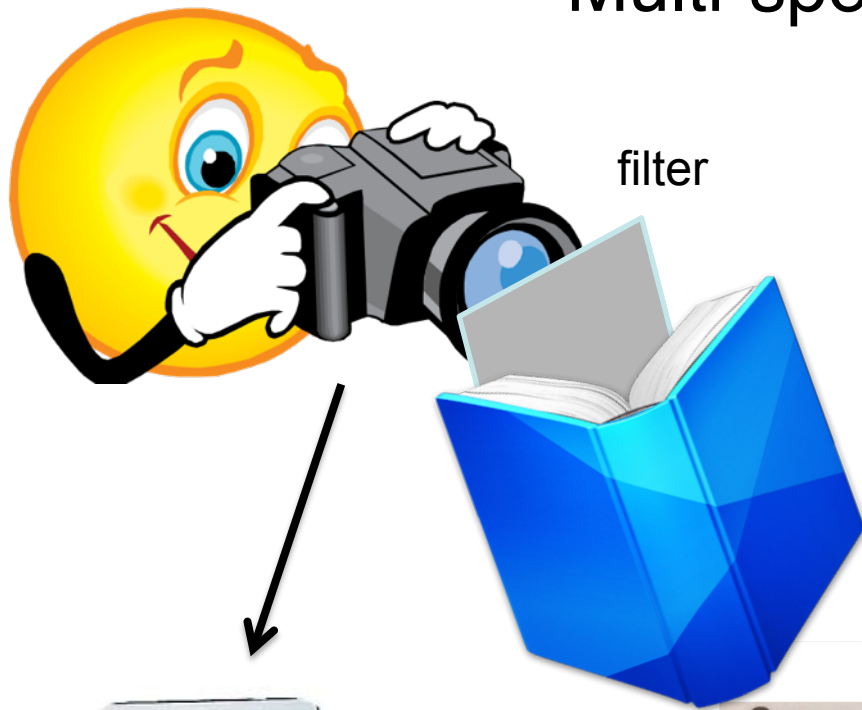
- Molecules are always moving or vibrating
 - the vibrational spectrum is characteristic - 'fingerprint'
 - shine laser onto page and look at the scattered light
 - difference between λ_{in} and λ_{Raman} gives the vib. spec.



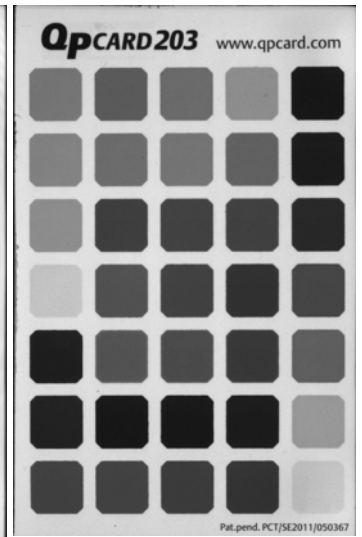
Diffuse Reflectance



Multi-spectral Imaging



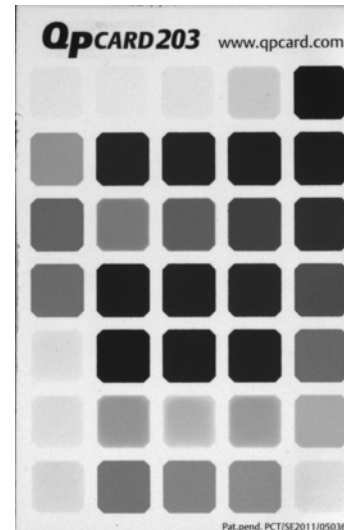
450 nm



500 nm

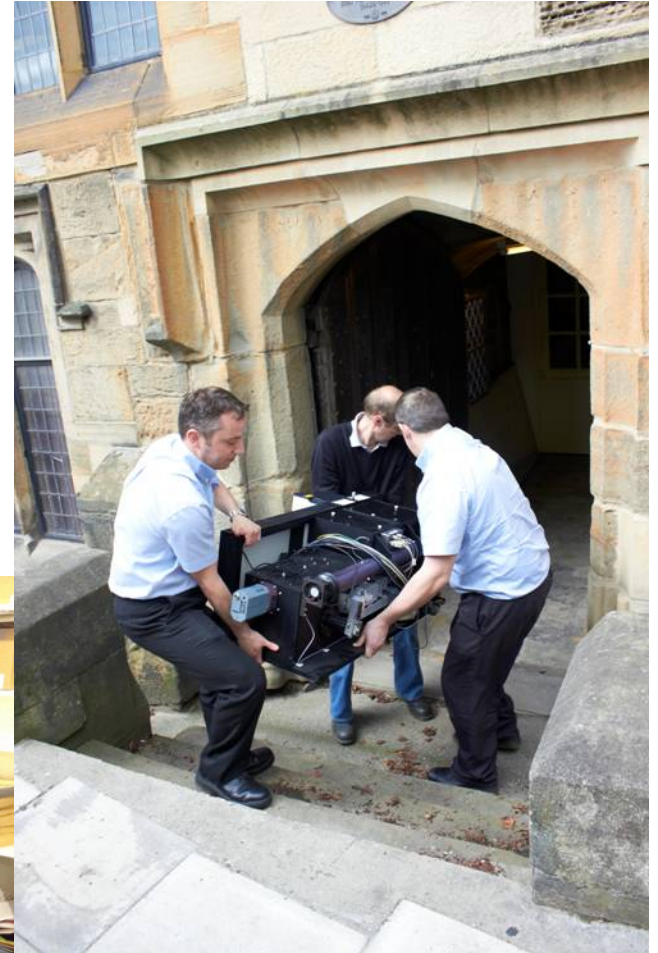


650 nm

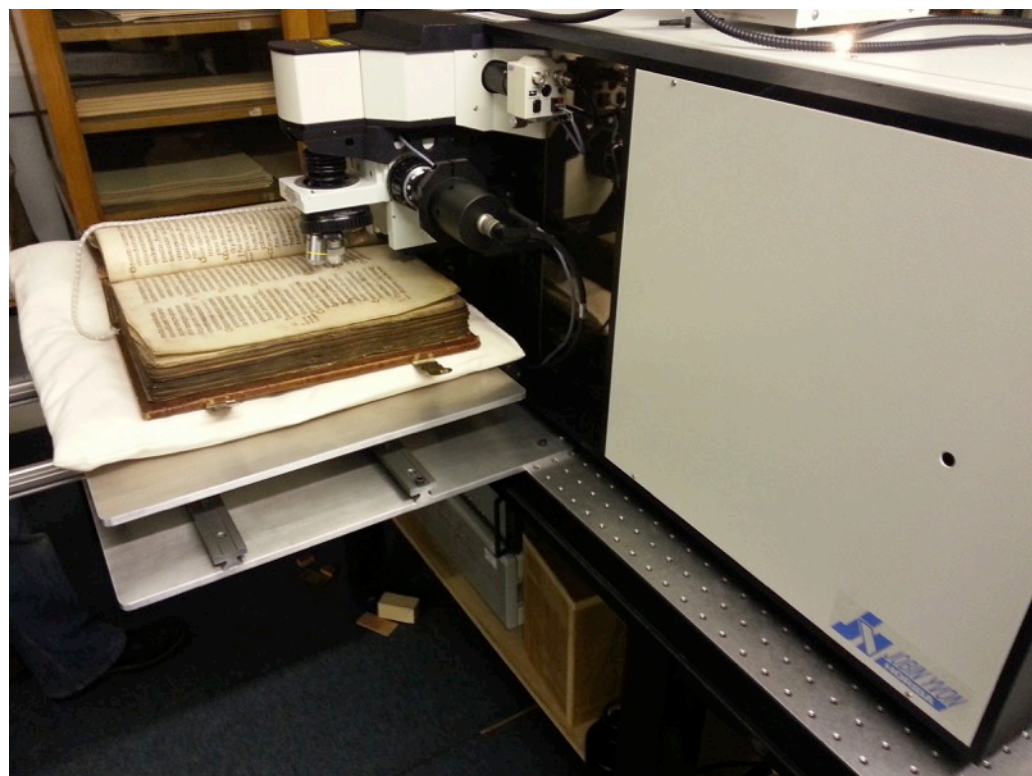
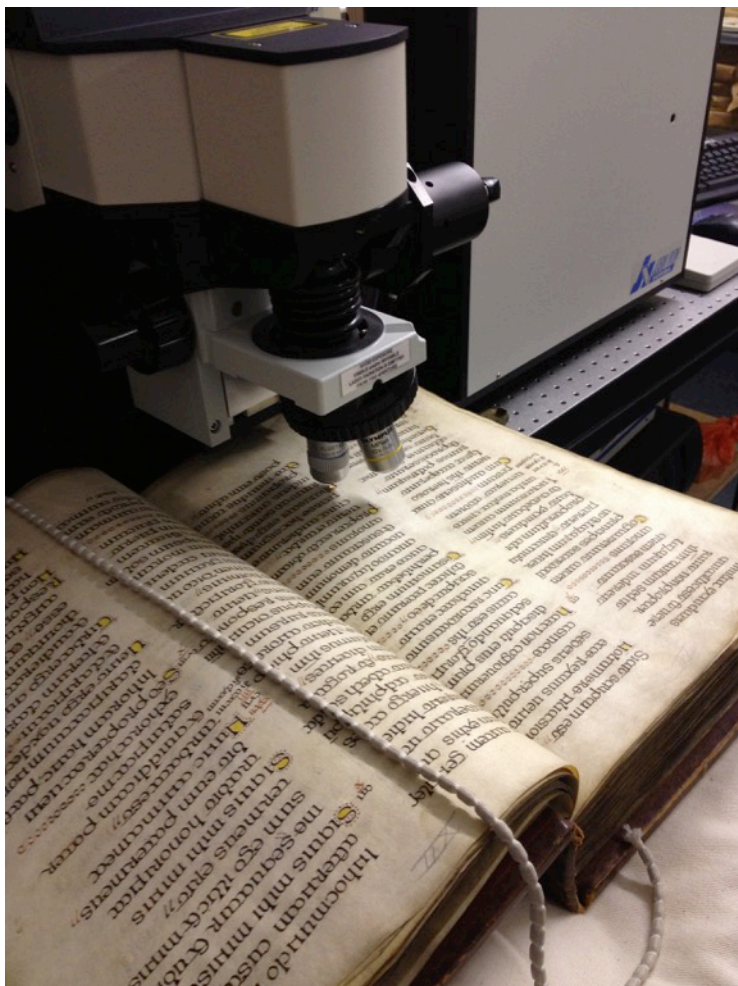


850 nm

Moving the Mountain....



How not to damage the books...
.... use very low power



Laser power < 0.5 mW over ca. 5 μm^2

J. Raman Spec. (2009) **40** 1043-1049

J. Mol. Structure (1997) **405** 1-11

J. Raman Spec. (2009) **40** 1966-1973

50 x lens, 2.25 mW

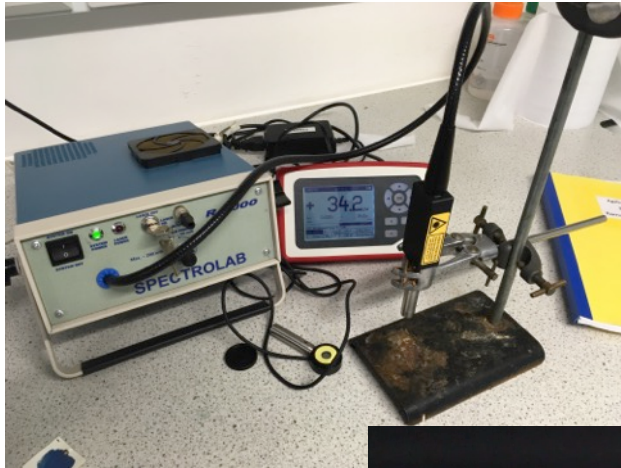
10 - 100x 3 - 10 mW

50 -100x min power 17 - 0.17 mW

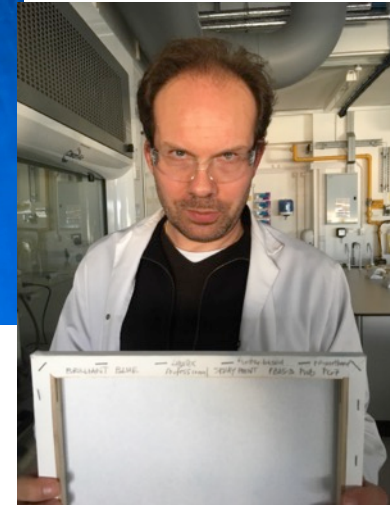
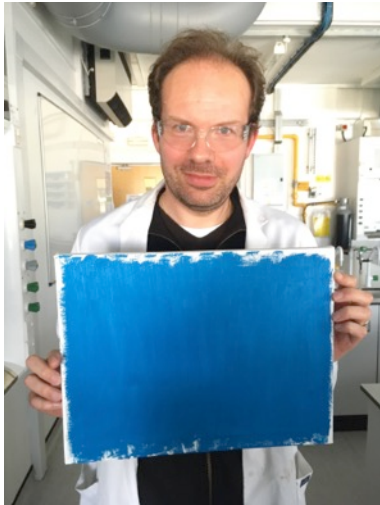
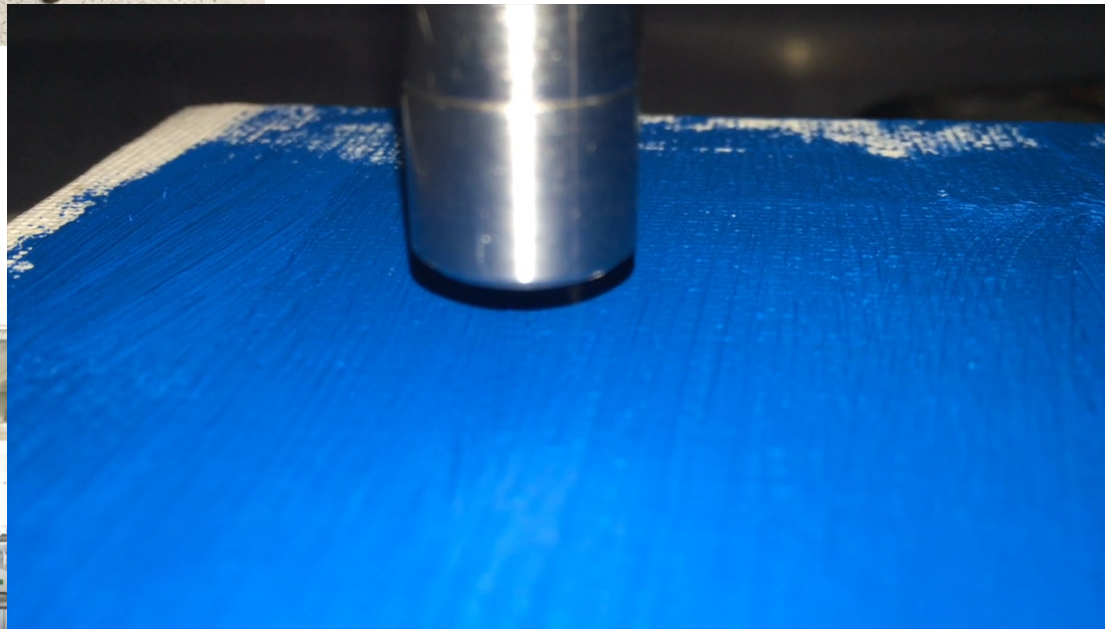
Mobile Raman: Specification

- 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, $\sim 10 \text{ cm}^{-1}$ 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 $\sim 1 \text{ mm}^2$ 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

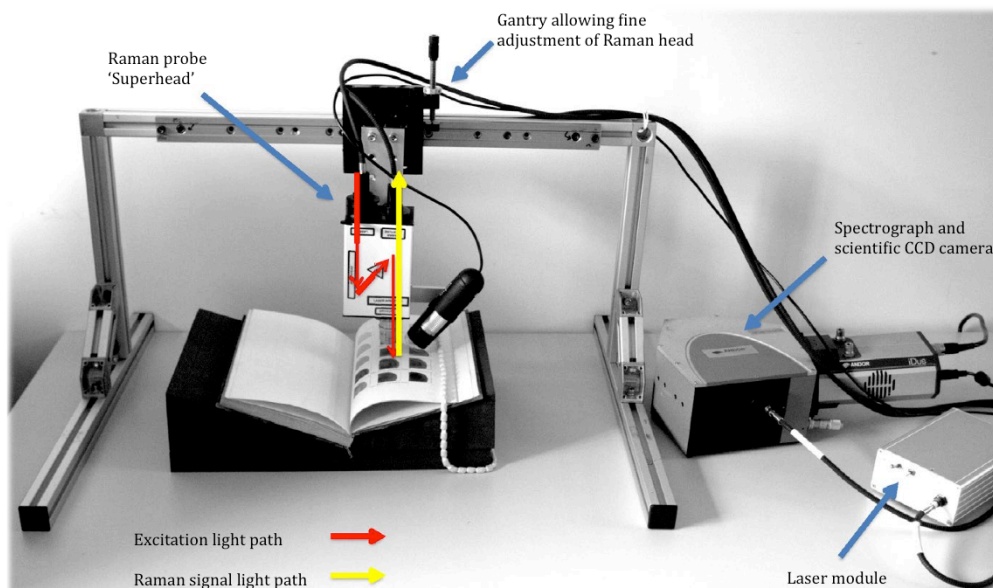


Horiba LabRAM-HR



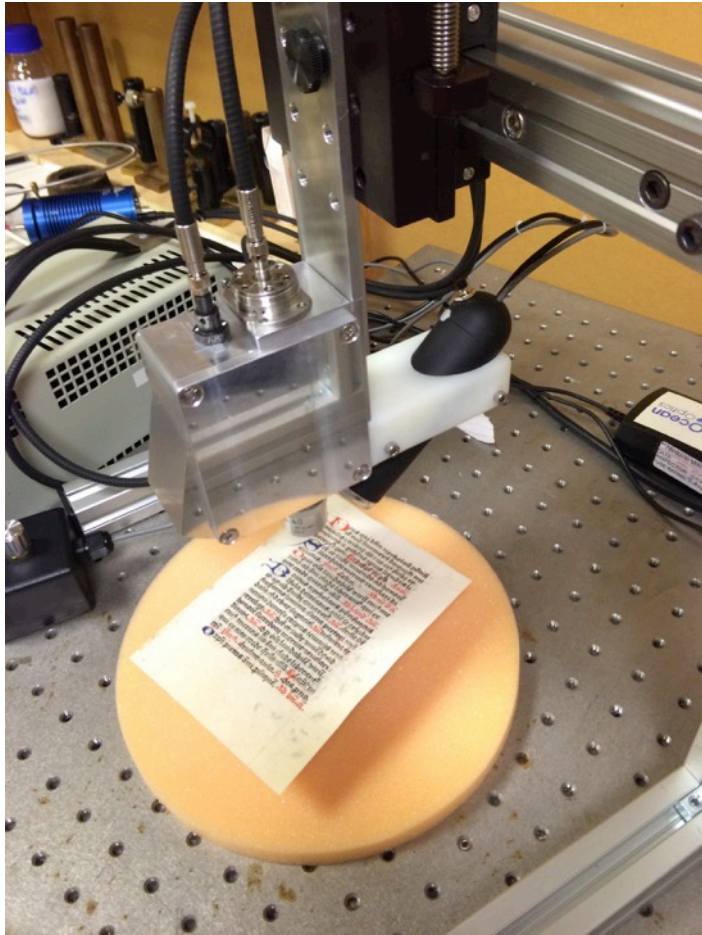
$< 0.5 \text{ mW}$ over ca. $5 \mu\text{m}^2$

Team-Pigment mobile Raman



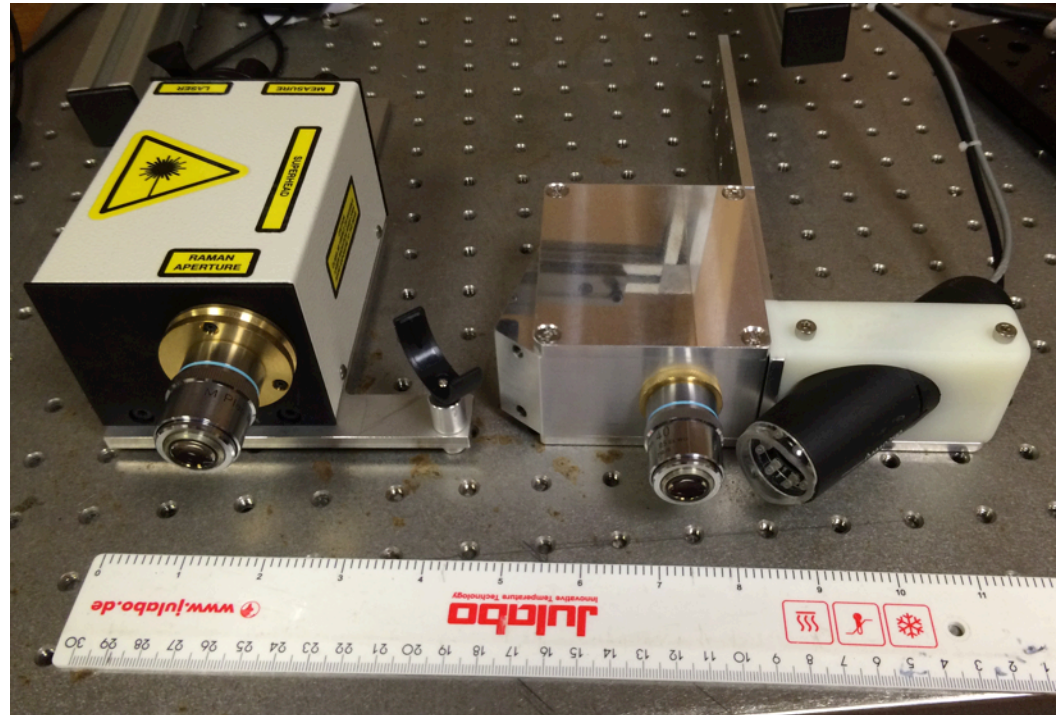
$< 0.4 \text{ mW}$ over ca. $600 \mu\text{m}^2$

Continual Development - New Raman Probe



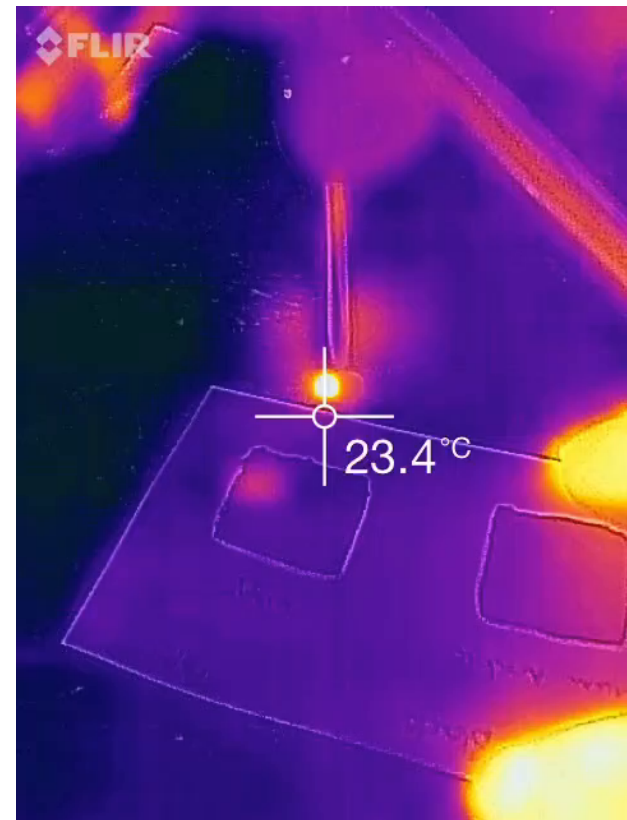
Much smaller than currently available
- better access to margins

Can operate at low wavenumber ($> 70 \text{ cm}^{-1}$)



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

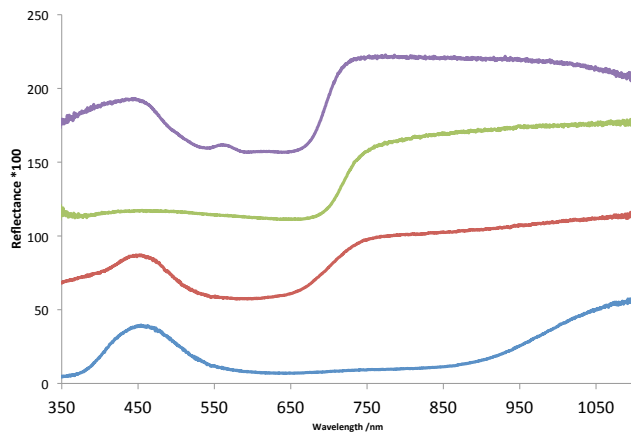
Low light intensity on sample
($< 0.02 \text{ mW/mm}^2$)

Unique ‘Lancaster’ design

Large stand-off ($\sim 8\text{cm}$) for safety of book

Frame mounting – stability

Small region of analysis, $\phi \sim 2 \text{ mm}$



Smalt
Indigo
Lapis
lazuli
Azurite



Full-spectrum FORS

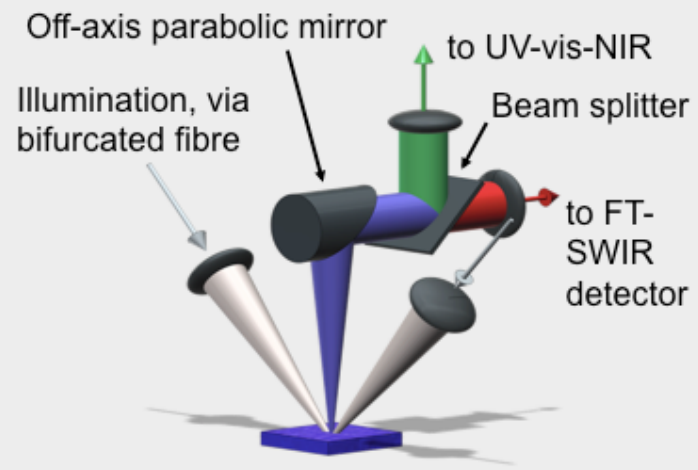
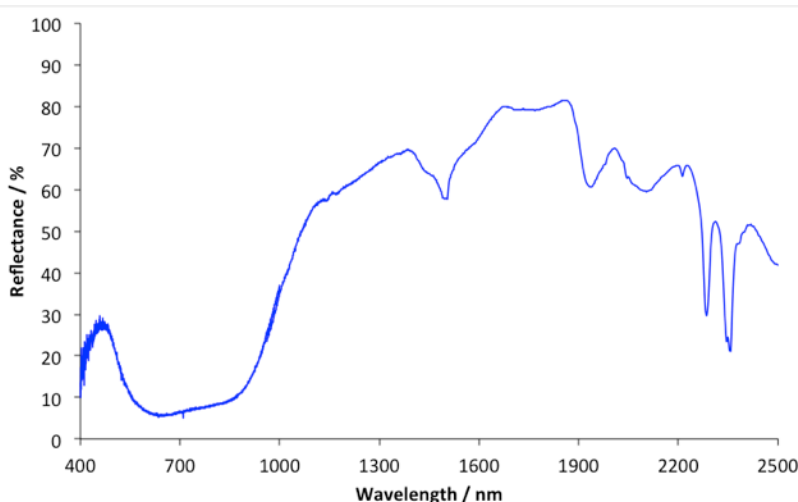
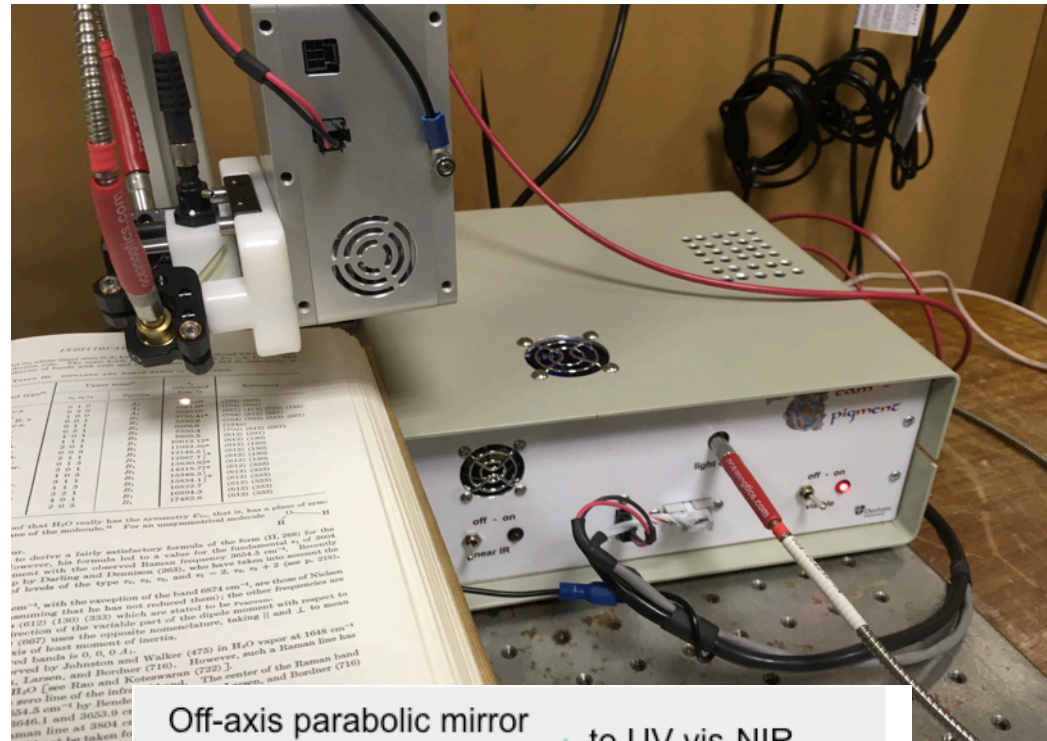


UV-SWIR: 350 – 2500 nm

Low light intensity on sample
($< 0.1 \text{ mW/mm}^2$), $\phi = 2\text{mm}$

No temp rise, $< 1^\circ\text{C}$

Same 'Lancaster' design
- Large stand-off ($< 4 \text{ cm}$)



Multispectral Imaging

LED illuminators for UV-NIR

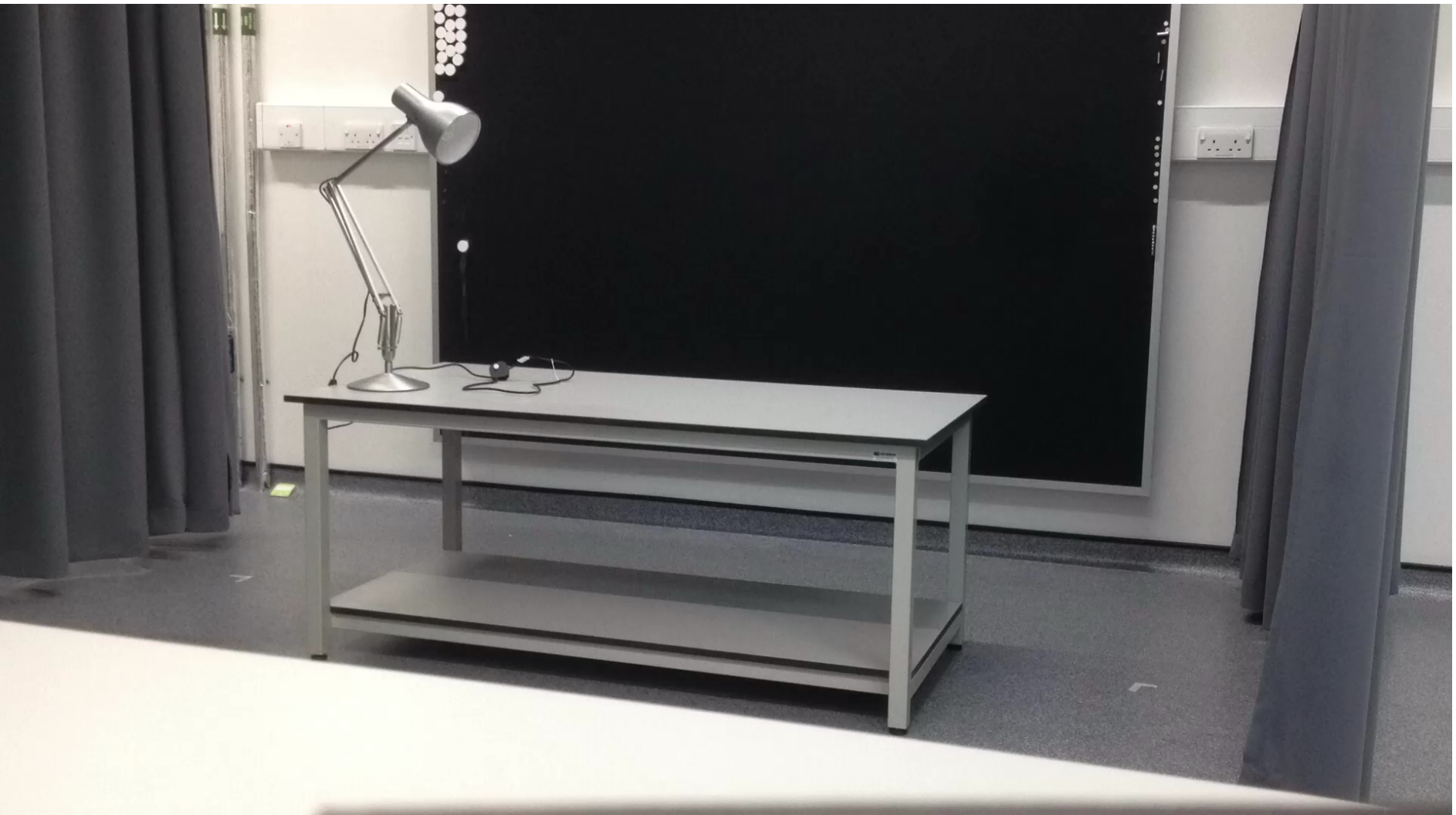
Mono-1.3 MP CCD camera
images through a set of 9
interference filters

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

Scattered light imaging and
fluorescence imaging possible.



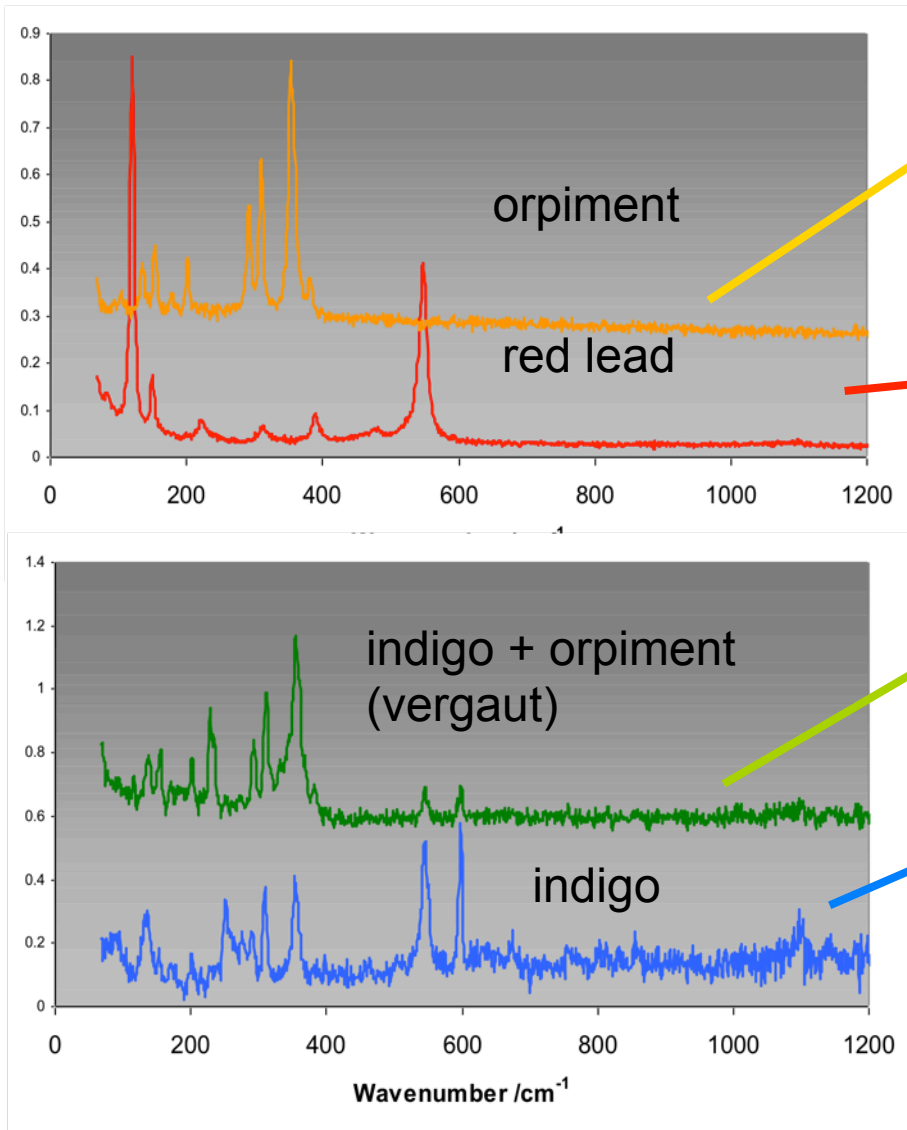
Raman in a Suitcase



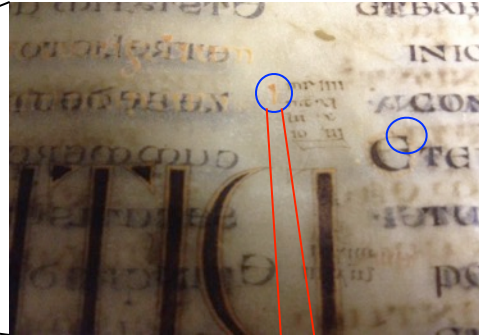
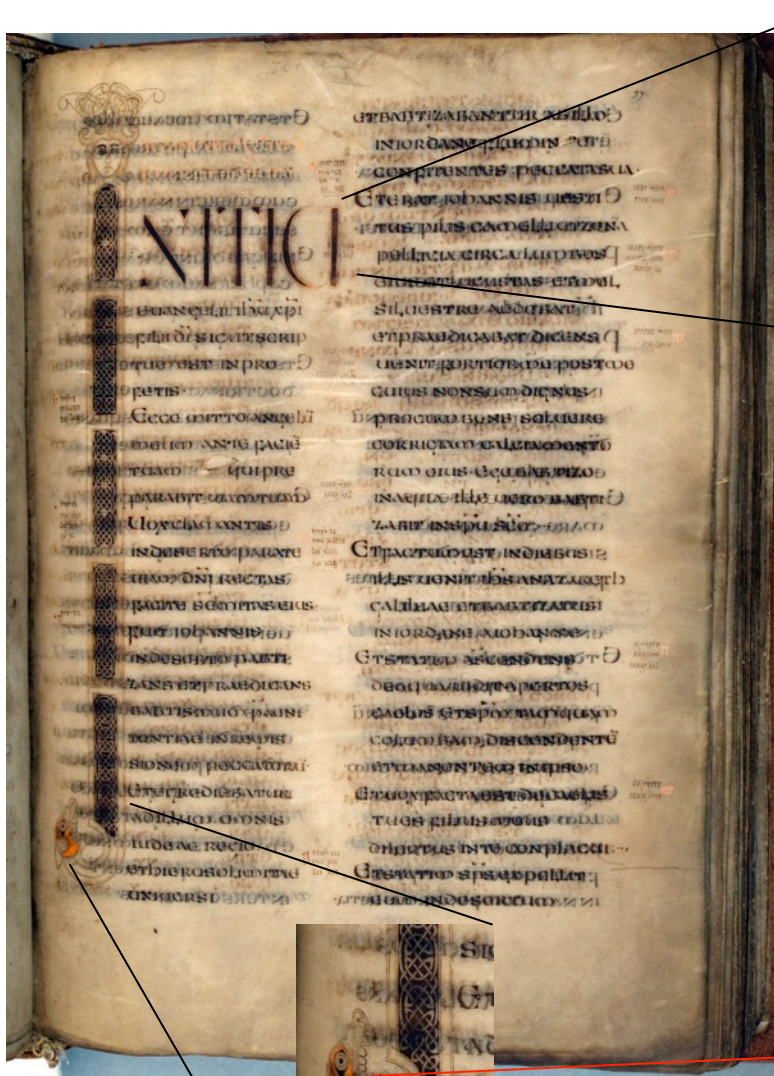
[illegible]

A 11.10

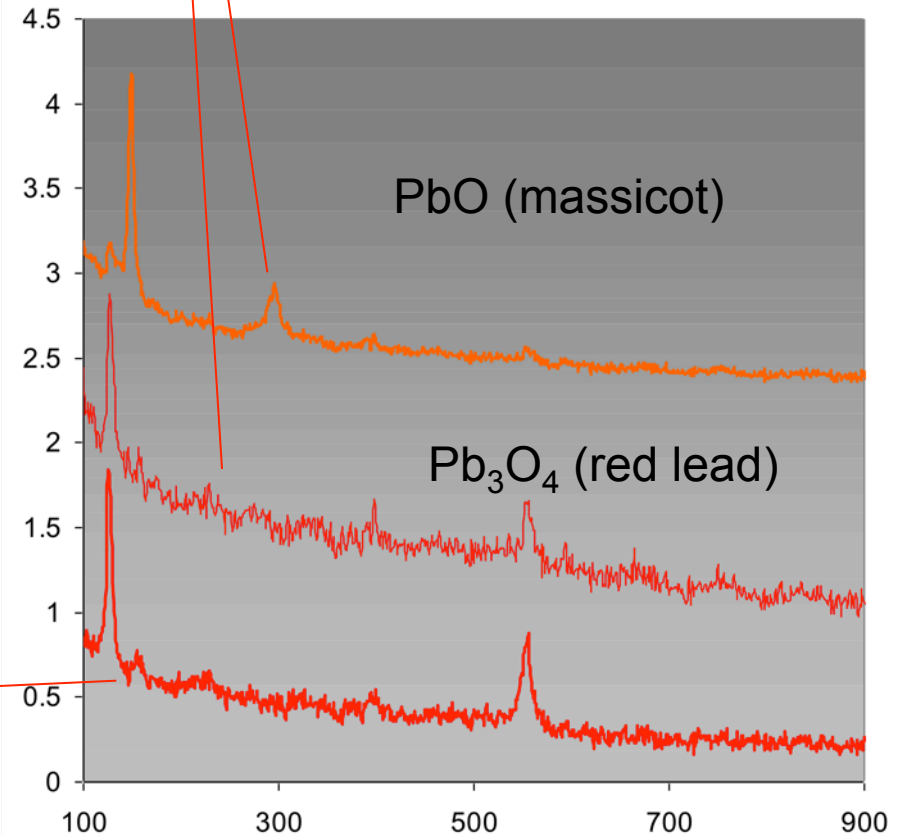
A-II-10 Part of a 7th Century Gospel Book



Revealing subtle differences: A-II-16



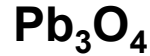
Scribal marks-
different composition
pigment



Sources of Pigments in the 7/8th Century



Red lead (minium)



Does occur naturally - but not in UK
Weardale was source of lead-ore
(PbS) in Roman times..



Orpiment



Not found in UK
Commonly found near
to volcanic areas in Italy
(Vesuvius and Tuscany)

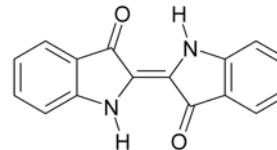
Verdigris

Corrosion product of copper
metal with e.g. urine



Indigo (woad)

Extracted from woad plant
- grows like a weed

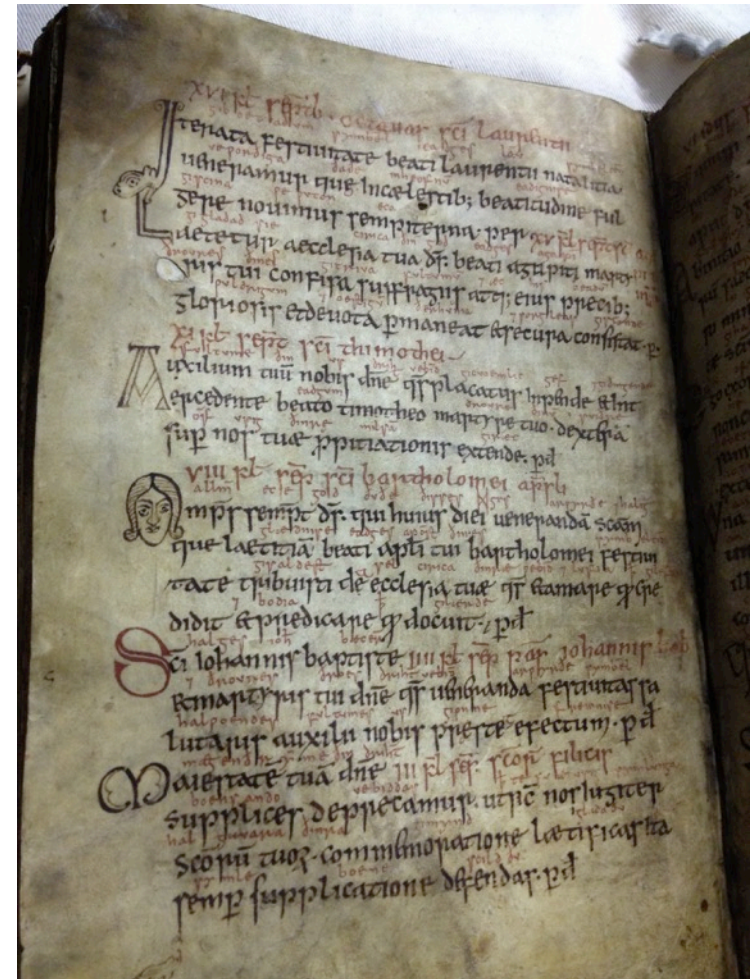


Collectar – DCL A.IV-19

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?



c.f. Lindisfarne Gospels, f. 220v, (John)

^{rimbel dæg} ^u ^{newgeleped t}
sabbatum est nomen

^{de þar genoma t}
ut tollere

^{been} ^{din}
tributum tuum

^{xxxviii} ^{dr de t} ^{hal}
Respondit eis quine-

^{he me} ^{voed} ^{genim}
fecit sanum

^{been} ^{din}
ille mihi dixit tolle

^{ga}
tributum tuum

^{t rælar}
^{þe ne pr nre}

ne dea
^{had hvogv}

quid co
^{poende}

adit u
⁷ ^{maðe}

amun
^{þe de hæl}

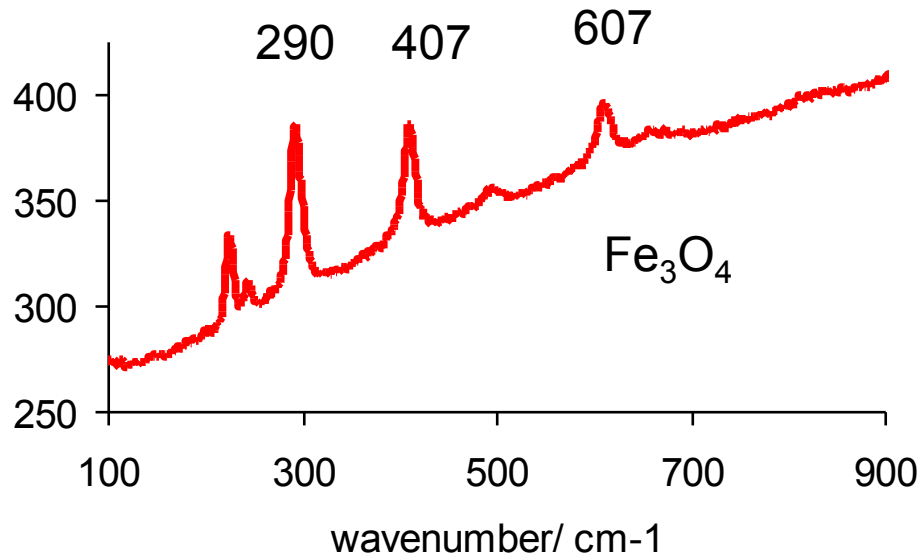
quia ih
^{hine} ^{ha}

eum so
^{feðem t}

propt
^t

Collectar – DCL A.IV-19

Interesting – NOT red-lead or vermilion !

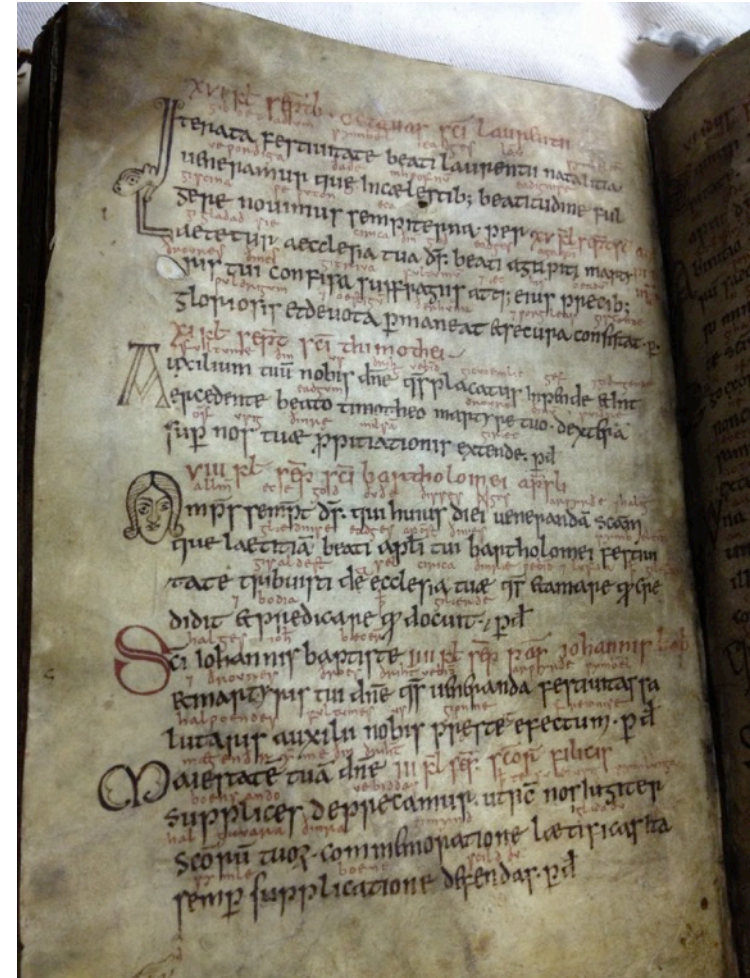


This is red-ochre – iron oxide/clay

‘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?

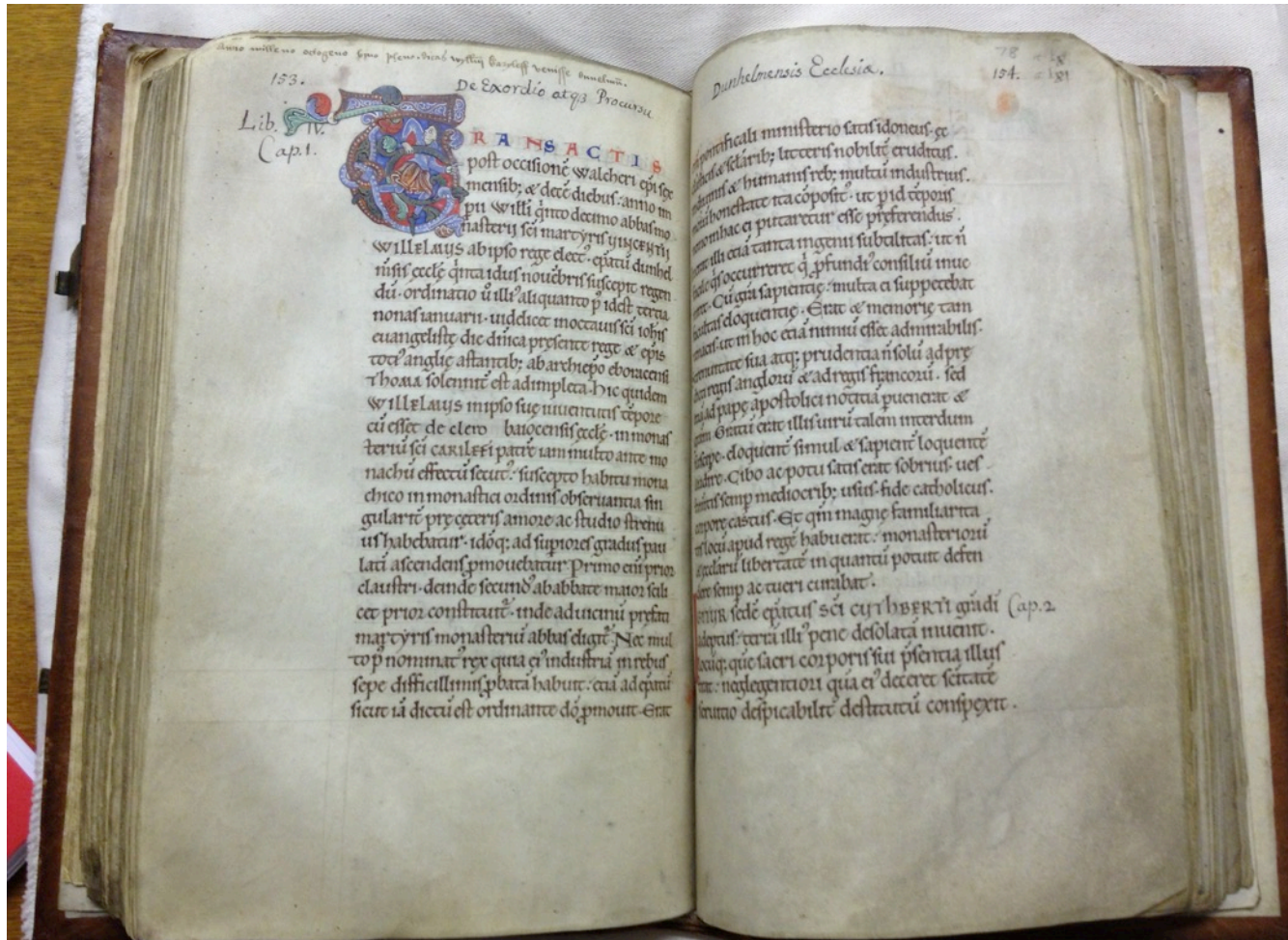


The Normans are coming - or “1066 and all that”

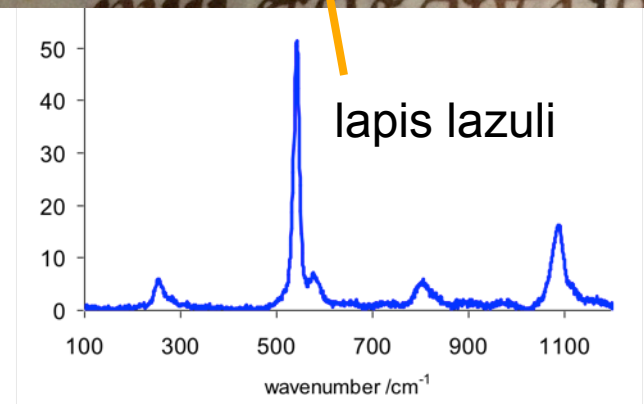
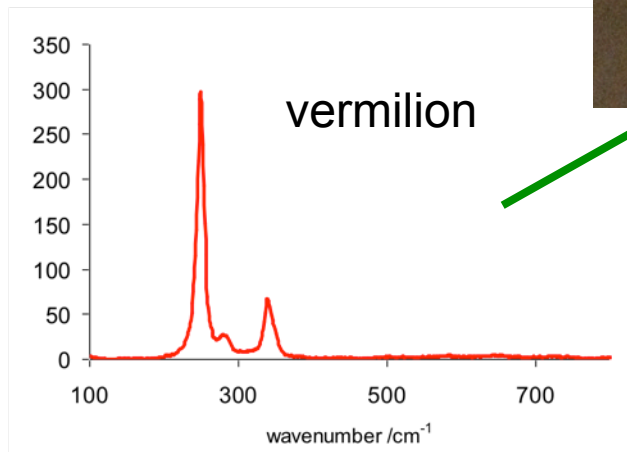
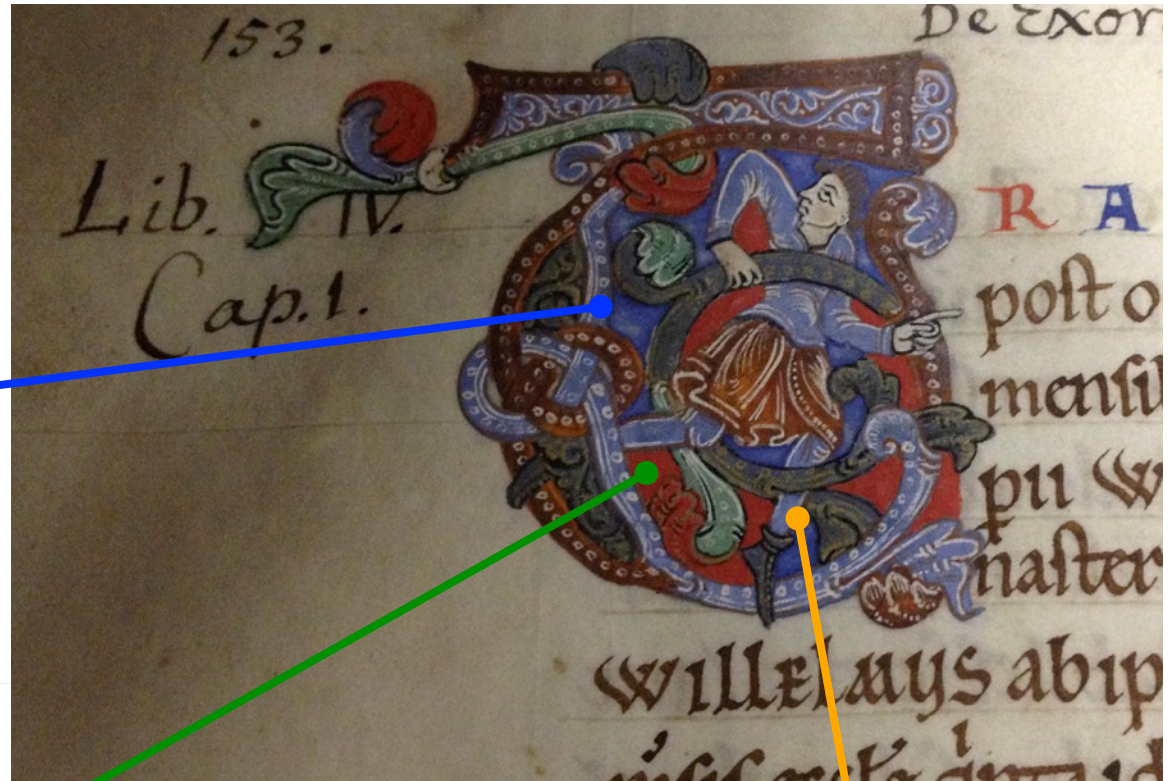
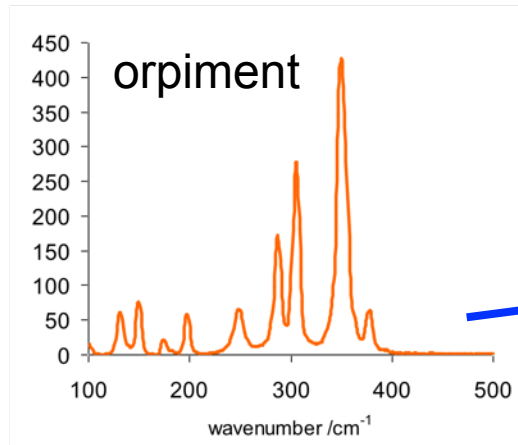


Libellus de Exordius DUL Cosin V-II-6

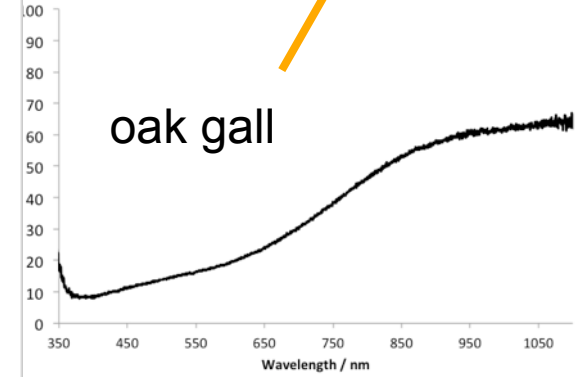
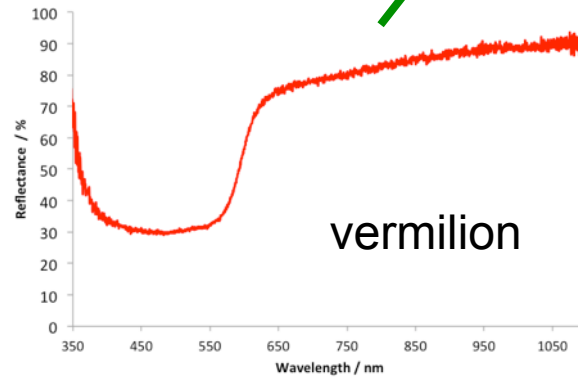
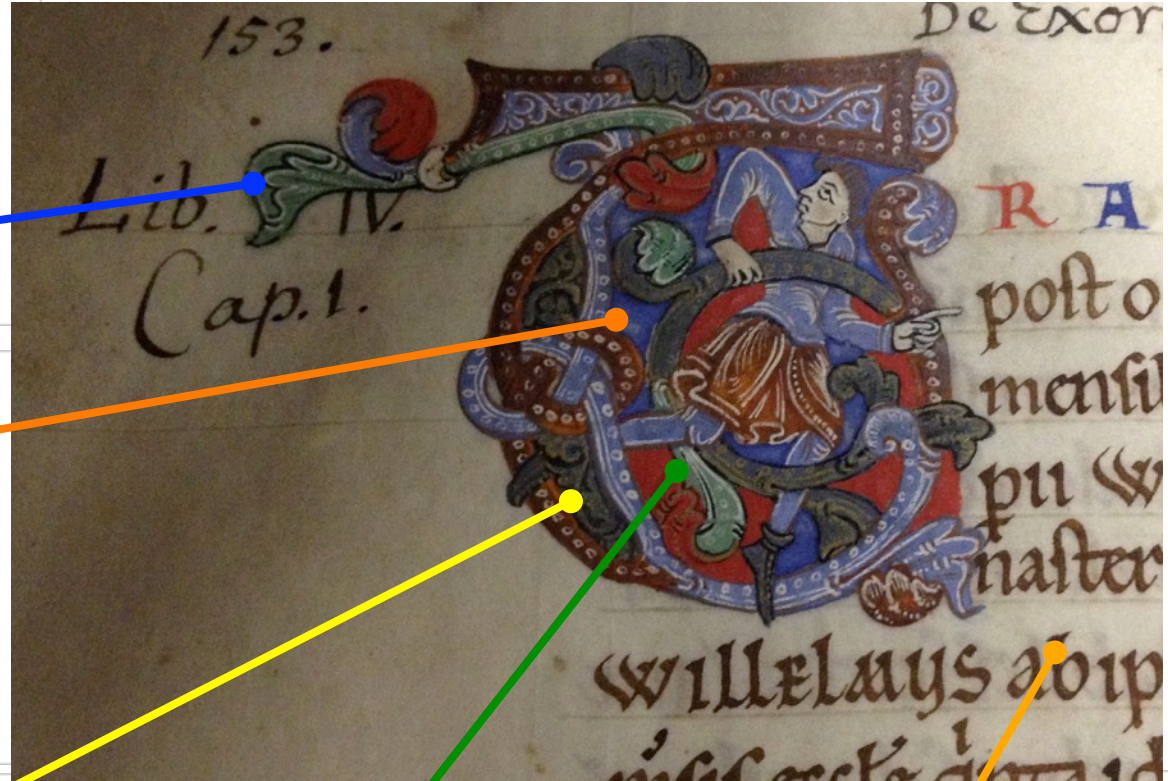
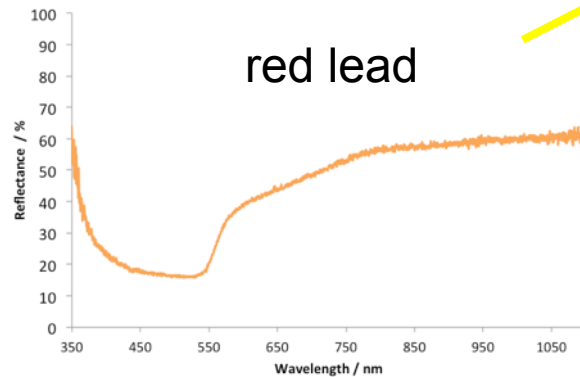
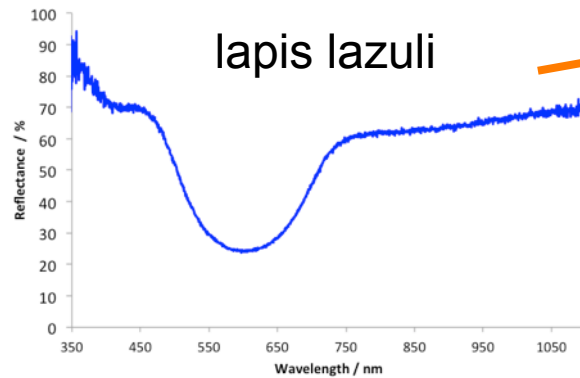
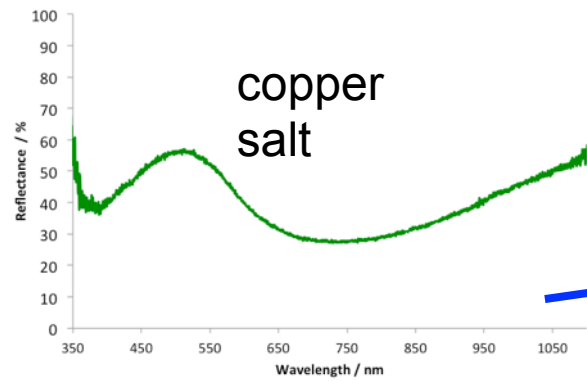
- Symeon was thought to have trained in Normandy – did he bring his methods to Durham?



Libellus de Exordius - Pigments



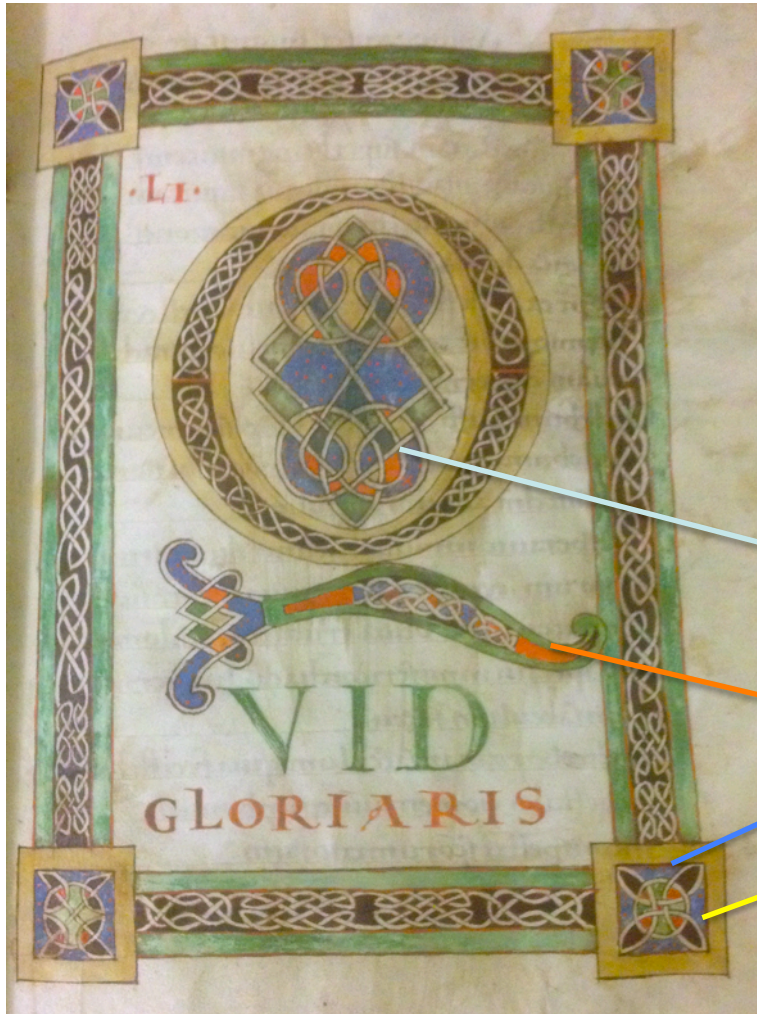
Libellus de Exordius - Pigments



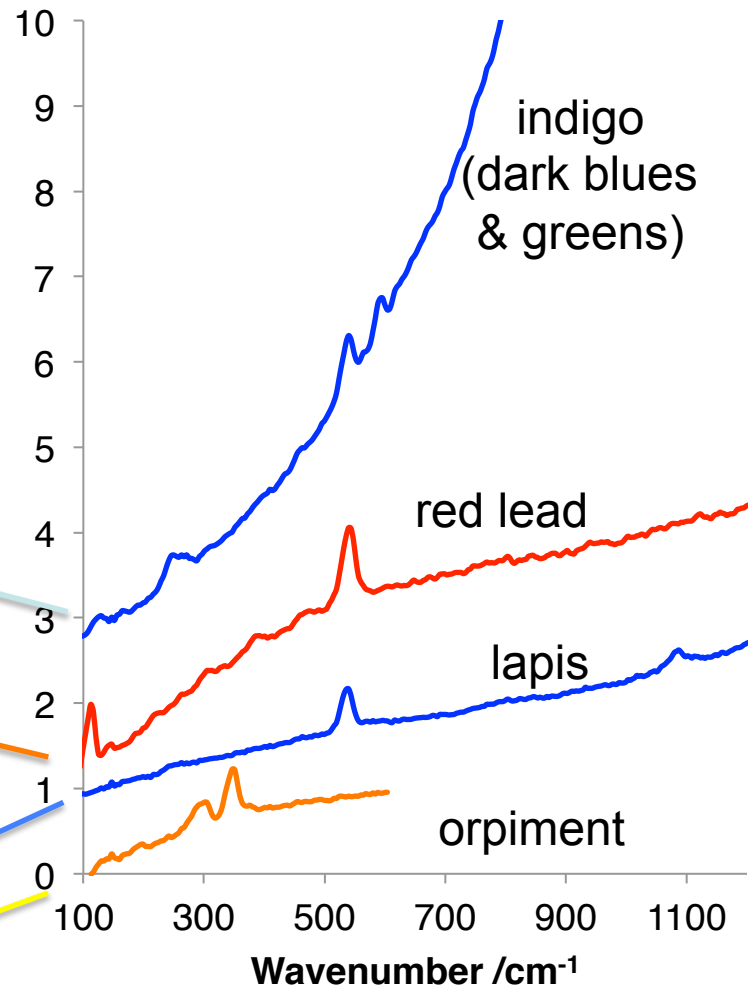
Tales of Canterbury Books

Manuscript	Lapis	Egyptian Blue	Azurite	Indigo	Lead white	Red lead	Iron Ochre	Vermilion	Orpiment	Vergaut	Verdigris	Orcien
TCC MS-B.11.2 (Amalarius), St Aug. x(1)	✓	✓		✓	✓	✓	✓		✓	✓		
BOD MS-579/1 (Leofric Missal additions), XtCh x(2)	✓					✓*	✓					
TCC MS-O.3.7 (Boethius), St Aug. x(2)						✓	✓	*	✓			
CCCC MS-389 (Vitae), St Aug. x(ex)	✓					✓					✓	
CCCC MS-23 (Prudentius), XtCh x(4/4)	✓					✓					✓	
TCC MS-O.2.31 (Prosper), XtCh x/xi						✓	✓	*			✓	
CCCC MS-411 (Psalter), ? x/xi	✓	✓		✓		✓		*	✓	✓	✓	
TCC MS-B.10.4 (Trinity Gospels), ? xi(1/4)	✓	✓		✓	✓	✓	✓		✓	✓	✓	✓
BL MS-Cott. Cleop. C.viii (Prudentius), XtCh x/xi	✓					✓	✓				✓	
BL MS-603 (Psalter Artist A-D), XtCh xi(in)	✓					✓		✓				*
BL MS-Arundel 155 (Psalter), XtCh xi(1/4)	✓			✓	✓	✓					✓	
BL MS-Add. 34890 (Gospels), XtCh xi(1/4)	✓				✓	✓			✓		✓	✓
DCL MS-B.iii.32(ii) (Aelfric's grammar), XtCh xi(med)	✓					✓					✓	
BL MS-603 (Harley Psalter Art. F), XtCh xi(1-med)	✓		✓			✓		✓				
DCL MS-B.iii.32(i) (Hymnal), XtCh xi(1-med)	✓					✓	✓	✓			✓	
CCCC MS-389 f1v (Vitae), St Aug. xi(2)								✓				✓
TCC MS-O.2.51 (Priscian), St Aug. xi(ex)	✓							✓			✓	✓
DUL MS-Cosin V.v.6 (Gradual), XtCh XI(4/4)	✓							✓	✓		✓	✓
CCCC MS-270 (Sacramentary), St Aug. xi(ex)	✓					✓		✓				✓
CCCC MS-291 (Bede), St Aug. xi/xii	✓		✓					✓	✓	✓	✓	✓
TCC MS-B.3.9 (Ambrose), XtCh xi/xii	✓	✓						✓	✓		✓	✓
DCL MS-B.ii.16 (Augustine), St Aug. xi/xii	✓	✓						✓	✓	✓	✓	✓
TCC MS-B.2.36 (Chrysostom), XtCh xii(1)	✓							✓	✓		✓	✓
CUL MS-Dd.1.4 (Josephus), XtCh xii(1)	✓				✓	✓		✓	✓		✓	✓
BOD MS-Bodley 271 (Anselm), XtCh xii(1)	✓							✓	✓			✓
TCC MS-R.17.1 (Eadwine Psalter), XtCh xii(med)	✓				✓	✓		✓				
CCCC MS-4 (Bible), XtCh xii(med)	✓				✓	✓		✓			✓	✓

A Surprising Discovery

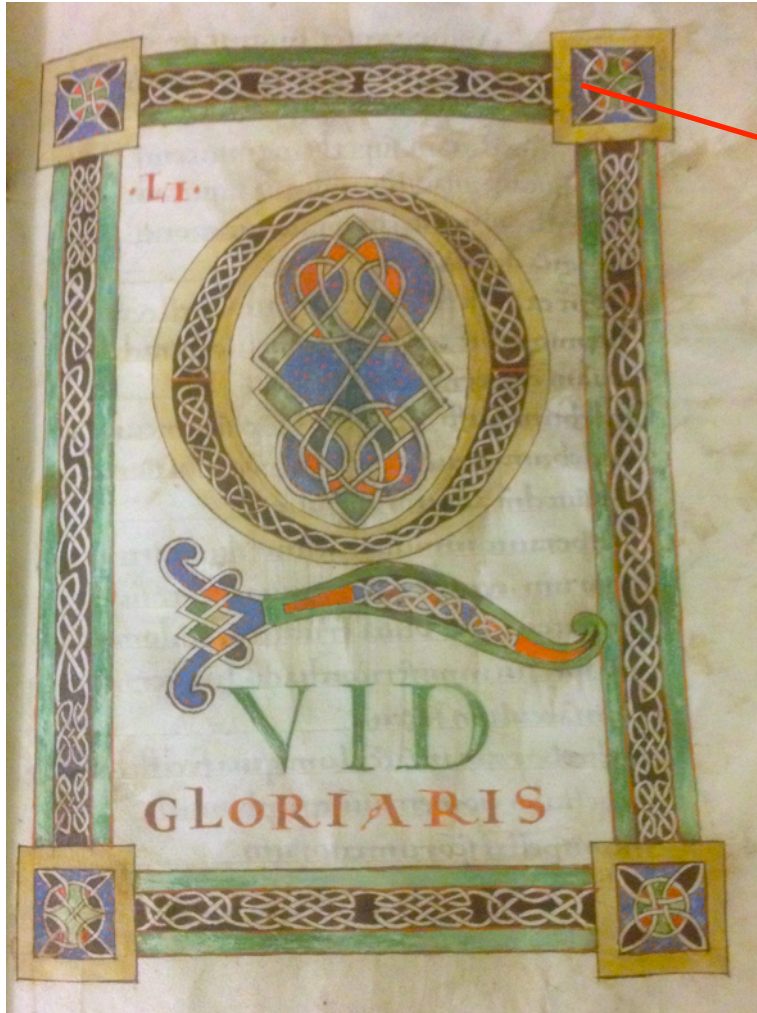


CCCC MS-411, fol. 40r



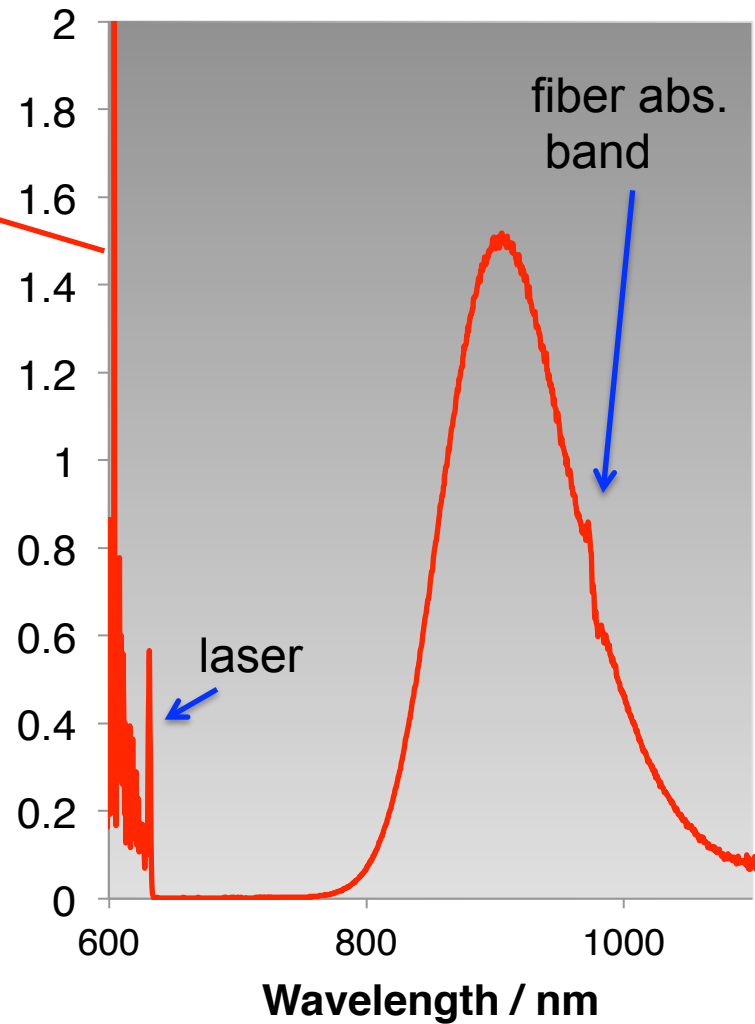
Note - lapis spectrum showed additional strong emission at ca. 900 nm...

A Surprising Discovery



CCCC MS-411, *fol.* 40r

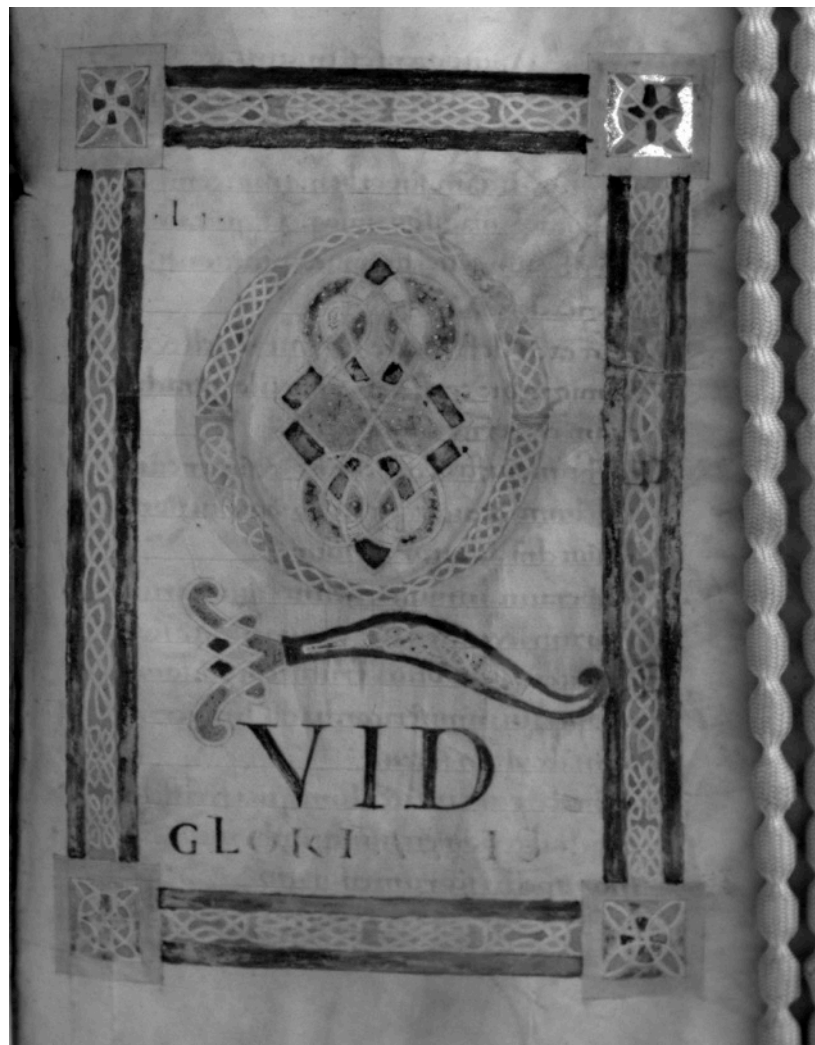
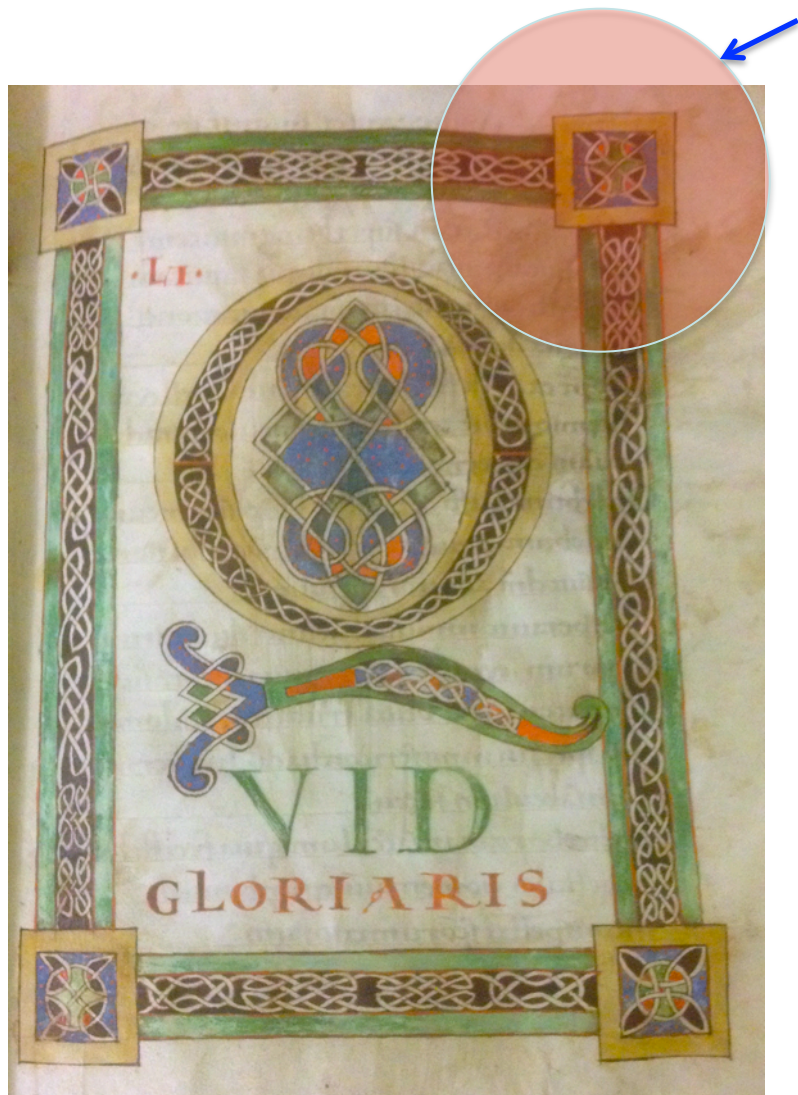
Reproduced by kind permission of the Master and Fellows of Corpus Christi College, Cambridge



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

NIR Imaging

Area illuminated with red laser



CCCC MS-411, *fol.* 40r

Image recorded at > 850 nm

Egyptian Blue: $\text{CaCuSi}_4\text{O}_{10}$

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

IV. *Of the blue colours of the Ancients.*

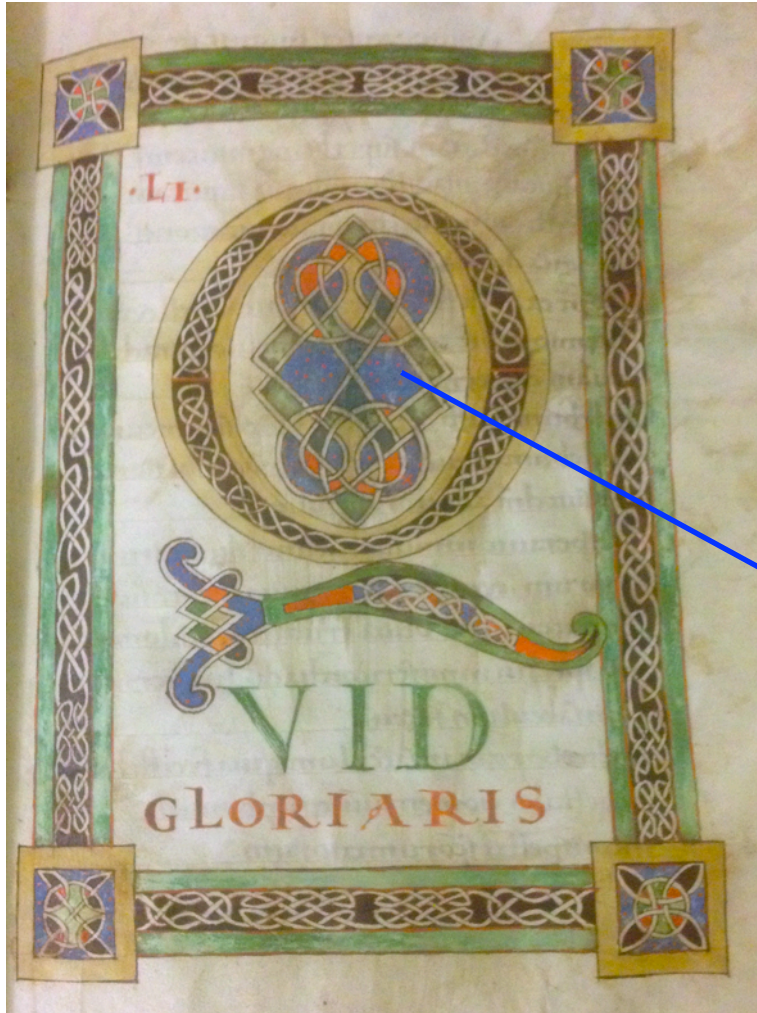
Different shades of blue are used in the different apartments of the baths of Titus, and several very fine blues exist in the mixtures of colours to which I have referred in the last two sections.

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.

Time-resolved measurement

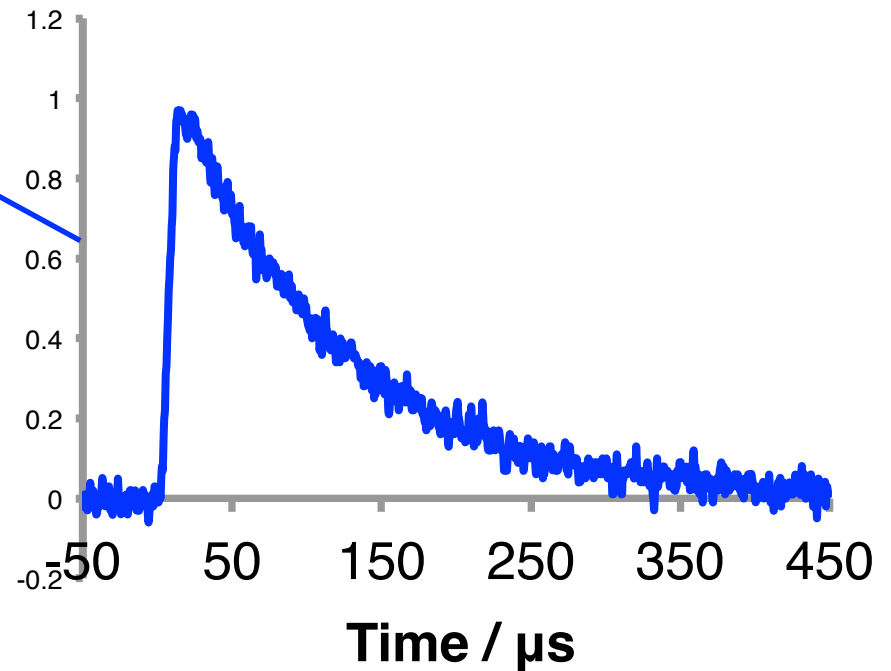


CCCC MS-411, *fol.* 40r

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Egyptian Blue is known to have a long-lived excited state, $\tau_f = 100 \mu\text{s}$

Excite with short pulse of red light (650 nm, 1 μs) and detect emission at $> 850 \text{ nm}$ with time.



Pigments of the 10th Century



Lapis Lazuli

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

Egyptian Blue



Synthetic blue pigment based on Cu.
Luminesces in NIR !

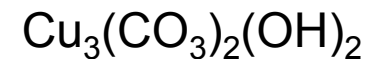


Vermilion (cinnabar) HgS

Synthetic and naturally occurring ore,
Material in manuscripts likely to
be finely ground cinnabar



Azurite



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

fol 2r

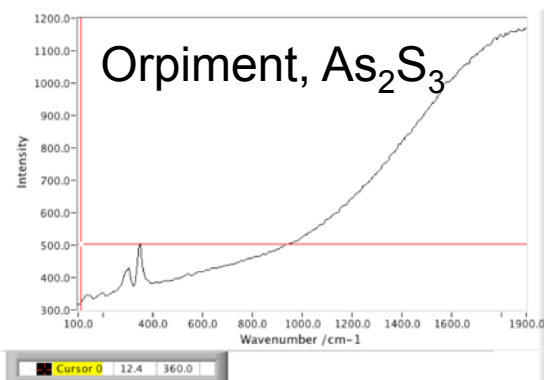
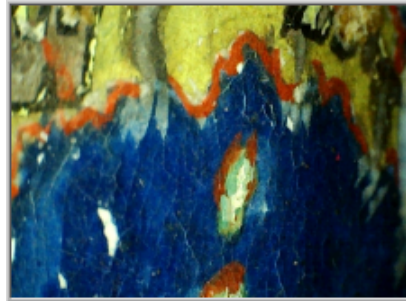
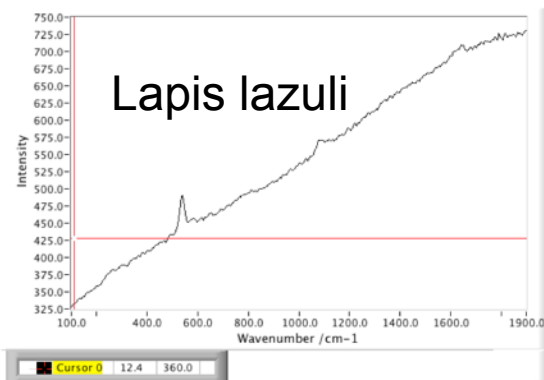
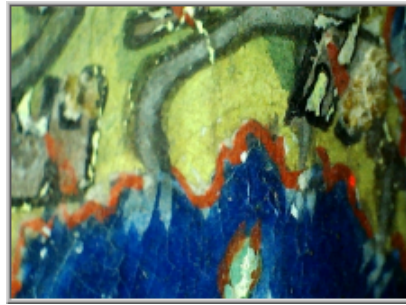
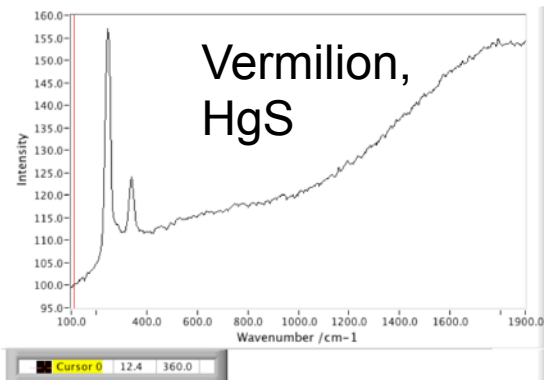


fol 8v

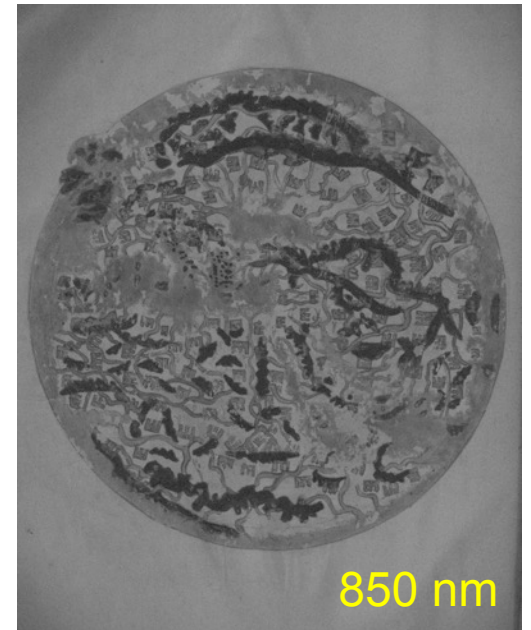
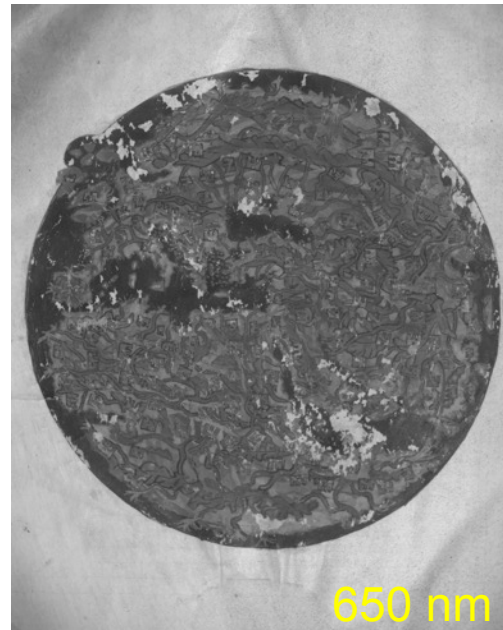
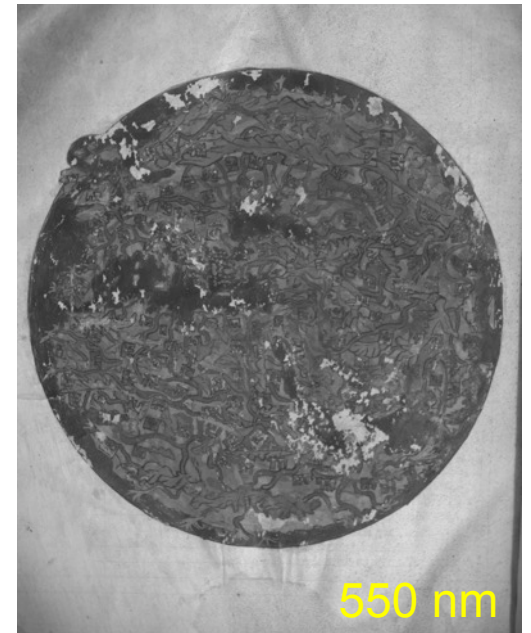
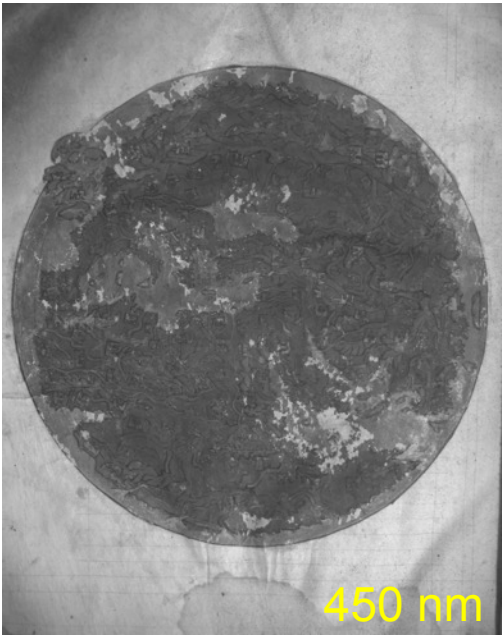


Similar to Fra Mauro map of 1450?

Bodleian Douce-319 fol 8v

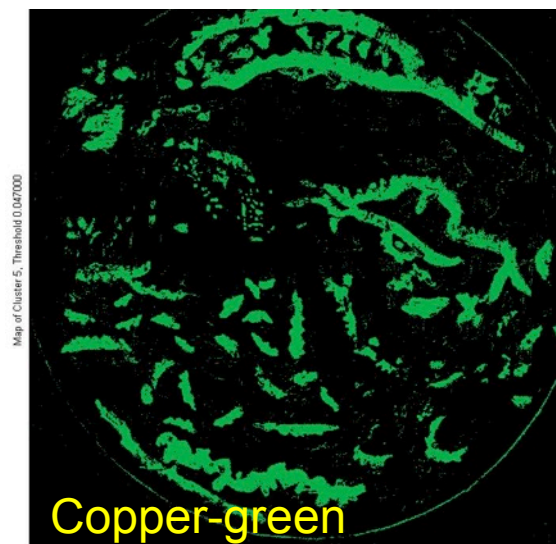
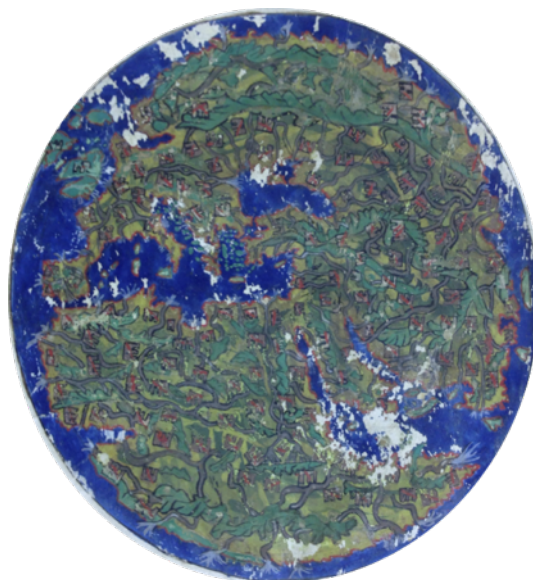
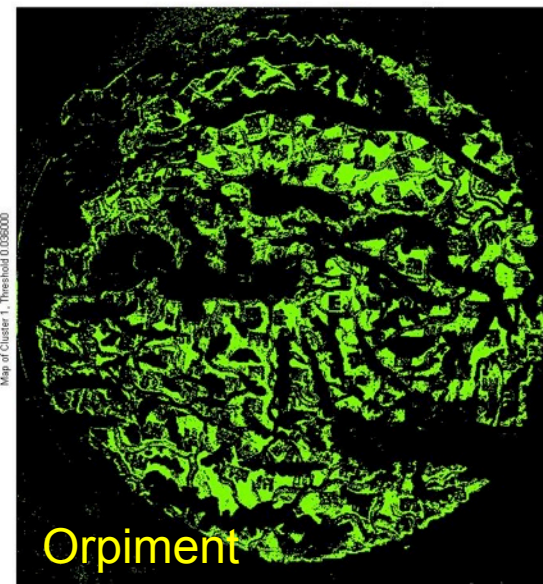
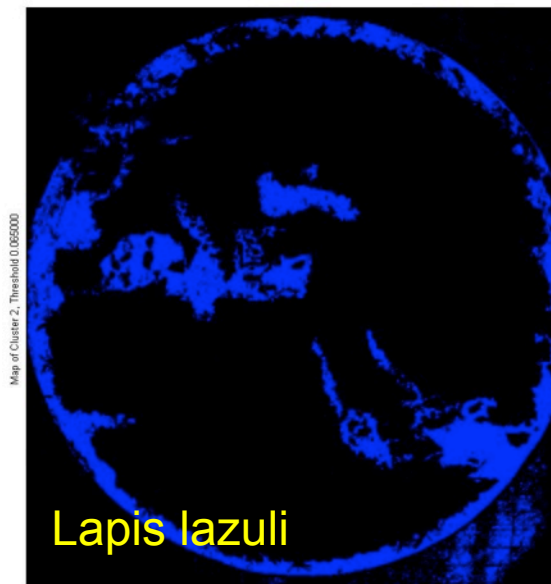


5 Images,
recorded at 5
different
wavelengths



Bodleian Douce-319 *fol. 8v*

Principal component analysis of multi-spectral images allows us to map pigments on the page – clusters of data are presented as false-colour images

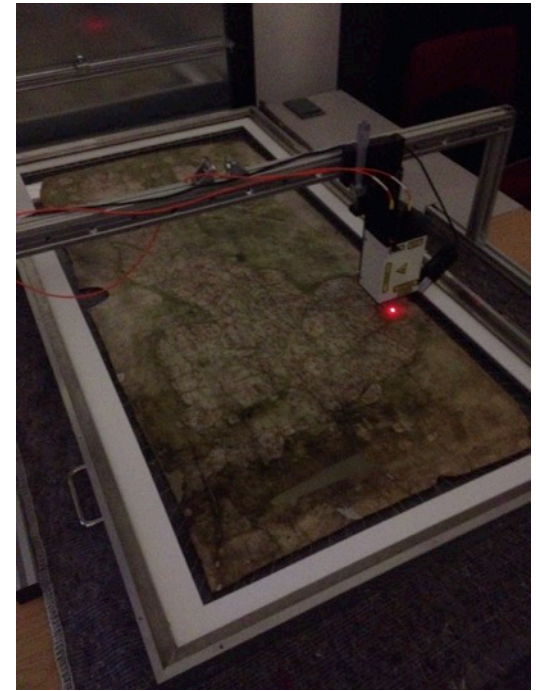
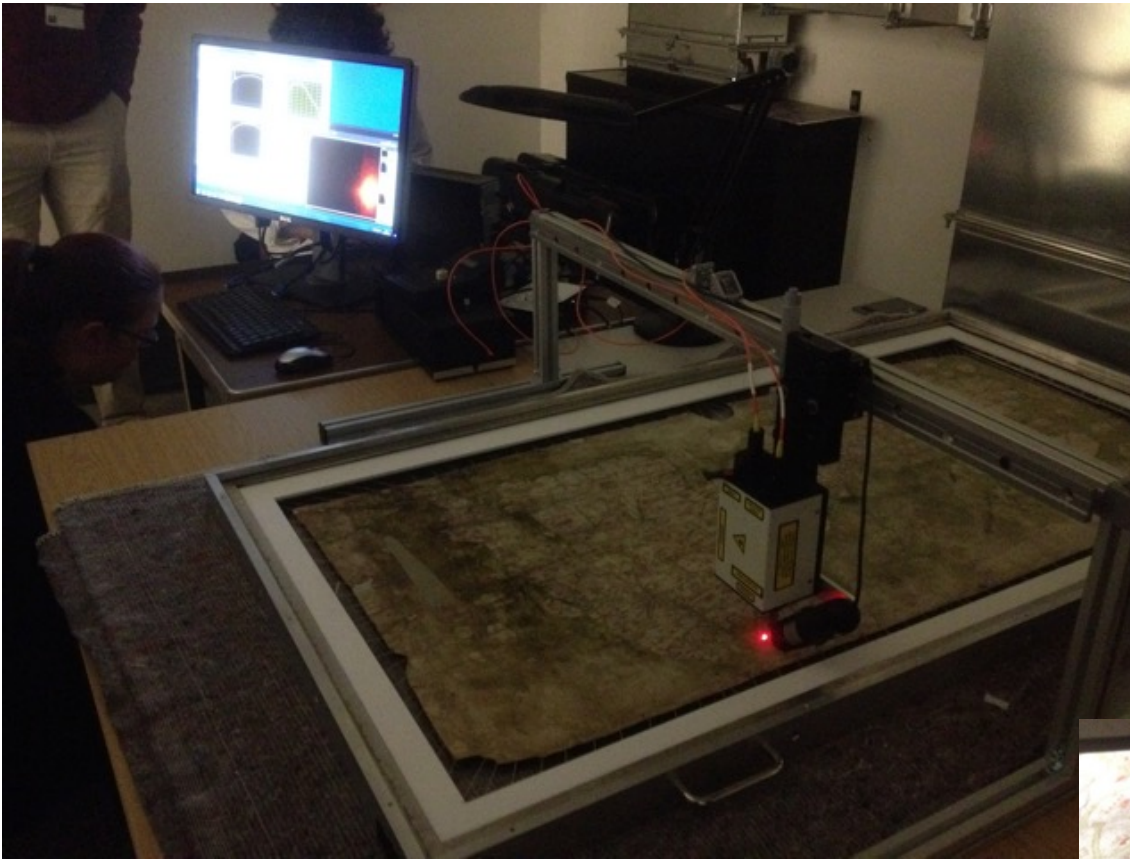


The Challenge of Maps



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

Cash and help...

- Rob and Felicity Shepherd
- Horiba (UK)
- Ocean Optics (UK)
- Andor (UK)
- AHRC

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