JANE DAVIES CONSERVATION Architectural Paint Research

PETERBOROUGH CATHEDRAL, NAVE CEILING

INVESTIGATION OF PAINTING MATERIALS AND TECHNIQUES, CONSERVATION PHASE 4, BAYS 9-17



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Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2
Summary
The nave ceiling at Peterborough is a rare survival of a thirteenth century timber ceiling <i>in situ</i> in England. It retains original thirteenth century paint although heavily restored in the 1740s and again in 1836. The ceiling is currently being conserved and recorded by the Perry Lithgow Partnership. As part of the conservation programme a thorough technical examination of the painting materials and techniques has been commissioned. Major research programme investigating the materials and techniques of the painted ceiling was undertaken by the Conservation of Wall Paintings Department, Courtauld Institute of Art. They have documented their findings in three reports dated September 1997, September 1998 and December 1999. Due to other commitments the Courtauld was unable to carry out further research. Therefore, in autumn 2000, Jane Davies was commissioned by Julian Limentani (of Marshall Sisson), the Cathedral Architect to examine paint samples, which had been gathered during the third and fourth phases of conservation. The findings of the third phase were documented in a report submitted by Jane Davies in October 2001. This report details the results of analysis of samples gathered during the fourth phase of conservation.
The aims of this research phase have been to identify and characterise paint thought to date to the thirteenth century, present below original nail heads which are now missing. Also to examine in further detail the original stepped chevron design, visible in relief below eighteenth and nineteenth century overpaint, which, in areas where original nail heads are absent, appears to remain exposed. Sampling to investigate the status of small <i>impasto</i> dots on the 'body' of original trefoils in bays 14 – 15 has also been undertaken. Through analysis of samples it has been possible to identify original paint below absent nail heads. Usually in paint combinations which have also been found in previous research programmes, suggesting a uniformity of painting technique across the breadth of the ceiling. Of great interest has been the confirmation of orpinent in a rich blue-green paint, which appears to be original and has not previously been identified. In addition realgar pigment has been identified, both as a pure pigment and, possibly, as a naturally occurring contaminant of orpinent. Examination of several samples from the stepped chevron has provided further information on the original design. Several samples show two distinct lead white based layers when examined under field reflected light at high magnification. In addition SEM EDX backscattered images of the samples reveal two layers with noticeably different topography and granulometry. Interestingly, within the lower lead white layer of samples from the stepped chevron, which were protected from overpainting by a nail, does suggest a white line on a dark background. Samples from the impasto dots do not bear more layers than those previously identified on the trefoil areas. Further sampling magnes from the stepped chevron, which were protected from overpainting by a nail, does suggest a white line or a dark background. Samples from the <i>impasto</i> dots do not

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	Peterborough Cathedral: Scient	ific examination of the nave ceiling Phase 4: 2001/2
SUM	MARY	
Cor	NTENTS	PAGE
-	BACKGROUND AND BRIEF	c
19	PAINT ANALYSIS	8
	2.1 METHODOLOGY 2.2 ILLUSTRATED DISCUSSION OF FINDINGS	
e	DISCUSSION OF FINDINGS	54

BACKGROUND AND BRIEF

1.1 INTRODUCTION

The nave ceiling at Peterborough is a rare survival of a thirteenth century timber ceiling in situ in England. It retains original thirteenth century Marshall Sisson), the Cathedral Architect to examine twenty-two paint samples which had been gathered during the third phase of conservation. Further sampling was undertaken during the fourth phase of conservation in which bays 9-17 were conserved and recorded. This report details Courtauld was unable to carry out further research. Therefore, during autumn 2000, Jane Davies was commissioned by Julian Limentani (of paint although heavily restored in the 1740s and again in 1836. The ceiling is currently being conserved and recorded by the Perry Lithgow undertaken. The major research was undertaken by the Conservation of Wall Paintings Department, Courtauld Institute of Art. They have These samples had been taken by Helen Howard (of the Courtauld Institute) and the first twelve samples mounted and analysis begun. The remaining ten samples required mounting analytical results of analysis of these samples were presented in a report, dated October 2001.² documented their findings in three reports dated September 1997, September 1998 and December 1999. ¹ Due to other commitments the Partnership. As part of the conservation programme a thorough technical examination of the painting materials and techniques has been the results of analysis of samples gathered during the fourth phase of conservation.

century overpaint and, in areas where original nail heads are now missing that appear to show a thirteenth century decoration in white on a black The aims of this research phase have been to identify and characterise paint thought to date to the thirteenth century, from below original nail heads which are now missing. Also to examine in further detail the original stepped chevron visible in relief below eighteenth and nineteenth background. Sampling to investigate the status of small impasto dots on the 'body' of original trefoils in bays 14-15. Similar dots were previously noted in bays 2 and 3.

Courtauld Institute of Art, September 1997. Howard, H. 'Peterborough Cathedral, Nave ceiling: Scientific examination of the original decoration of bays 36-39', unpublished report, Conservation of Wall Painting Department, Courtauld Institute of Art, September 1998. Kakoulli, J. 'Peterborough Cathedral, Nave Ceiling Paintings: Scientific ¹Howard, H. 'Peterborough Cathedral, Nave ceiling: Scientific examination of the original decoration', unpublished report, Conservation of Wall Painting Department, Examination Phase 2', unpublished report, Conservation of Wall Painting Department, Courtauld Institute of Art, December 1999.

² Davies, J., 'Peterborough Cathedral, Nave Ceiling Phase 3 investigation of painting materials and techniques and full analysis', report commissioned for the Dean and Chapter of Peterborough Cathedral, October 2001.

	Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2
1 2 BRIFF HIST	DRY OF THE CEILING ³
	out the for the for the former of 1000 and 1000
the nistory of the Therefore it is not	certing has been researched and reported in Howard's reports of 1997 and 1998 as well as in wakouth's work of 1999. It the intention of the author of this paper to reproduce the historical information here except in the briefest form:
c. 1140	Building of the nave commenced after 1140 under Martin de Bec, and was continued by William de Waterville
c. 1220	Painting of the nave ceiling.
1740s 1834/5	Kepair, washing and repainting of the ceiling Roof (Charles Layton received £30.00 for the repainting). ⁴
1880s 1890	Central tower rebuilt by Pearson. This intervention caused some disruption to the east end of the nave ceiling. I inewash removed from the walls of the nave This work is recorded in inscriptions on the frieze helow (26.8–27
	I].
1926	New roof over nave. The roof and also the ceiling were treated with 'Silvertown,' an insecticide containing sulphur chloride and carbon bisulphide. Structural repairs were necessitated by infestation of death watch beetle. ⁵ The
1994	upper surface of the boards was covered with hessian and glue at this time. Pollution tests by Dr. B. Knight of English Heritage indicate much soluble acid present in the wood. Tests for
	chlorides and
1995	surpriates also gave weakly positive results. Hirst Conservation undertakes cleaning and conservation testing and pigment analysis.
1996 1007	G. Lewis and J. Limentani inspect the ceiling from a hoist. G. Lewis samples the ceiling painting at this time.
1661	Conservation treatment and documentation of present conductor by the Ferry Lingow Farmership commences in the zones around St. Peter, St. Paul and the Psaltery Player. Commencement of major investigation of the materials
	and techniques of paint present on the ceiling by the Courtauld Institute of Art.
³ The author is indeb ⁴ Cave, C.J.P. & Bor ⁵ A report on the con 1925, 262 - 746.	ted to Helen Howard for this information and would draw the readers attention to her reports for a more detailed discussion. enius, T. 'The painted ceiling in the nave of Peterborough Cathedral, <i>Archaeologia</i> , 87, 1937:297-309. dition of the roof at this time is provided by the architect, see Moore, L.T., 'Peterborough Cathedral roof and its repair', <i>The Architects' Journal</i> , 58,

Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2
1.3 SUMMARY OF PREVIOUS RESEARCH FINDINGS
The Courtauld reports contain a great deal of valuable information. In addition to setting out the project brief, a selected history of the ceiling, research methodology and documentary evidence, they present a considerable body of evidence about the materials and techniques of both the original and later interventions. The findings of the previous reports are briefly summarised in the text below. The cumulative results of investigations of the original paint technique from all research phases including the present one are shown below as Table 1.
Original paint dating from the thirteenth century does survive in a number of areas, and some remains exposed, although more frequently it is covered by layers of eighteenth and nineteenth century overpaint. The original palette comprised natural azurite, red lead, lead white, basic verdigris, yellow and red iron oxide, carbon black and vermilion in a drying oil medium. Original flesh tones were painted with lead white, basic vermilion, a little yellow iron oxide and carbon black. Underpaint to flesh tones used azurite combined with lead white and a little yellow iron oxide. Calcium sulphate combined with a proteinaceous material (probably animal glue) was identified at the timber/paint interface although it is impossible to say whether this is an original preparation layer or a contaminant from a later intervention. In places a thin lead white ground was observed. Evidence of preparatory drawing was limited to the identification of dark brown (carbon black combined with a few brown and yellow iron oxide particles) and carbon black underdrawing. Alteration of dark brown (carbon black combined with a few brown and yellow iron oxide particles) and carbon black underdrawing. Alteration of the identification of dark brown (carbon black combined with a few brown and yellow iron oxide particles) and carbon black underdrawing. Alteration of natural azurite to copper oxalate and copper green to copper chloride was iron oxide particles) and carbon black underdrawing concentrations throughout paint layers of all dates was also recorded.
During later interventions overpaint was applied directly onto the original. With the exception of replacement boards and where extensive repainting was undertaken, for example, geometric border patterns. Where flesh tones where repainted lead white combined with red lead or carbon black appears to have been used. The palette of pigments used during both restoration phases is basically similar to the original. However, the 1740s work utilises Prussian blue and the nineteenth century work appears to introduce barium sulphate.

Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2

Cumulative summary of analysis results of investigation of the original painting scheme (research phases 1 to 3 inclusive)⁶ **TABLE 1**

Italics indicate that it is not clear if the material is original, or an alteration product or a contaminant

Medium	• Drying	oil	\bullet Animal	glue	I																						
Alterations/contaminants	 Azurite to copper 	Oxalate	 Copper green to copper 	chloride	 Calcium carbonate to 	calcium sulphate																					
ations	Red iron oxide in lead white	matrix	Red lead + calcium carbonate	Red lead + lead white + carbon	black	Red lead + carbon black	Vermilion in lead white matrix	Vermilion + yellow iron oxide	+carbon black in lead white	matrix	Vermilion + carbon black in	lead white matrix	Yellow iron oxide + siliceous	inclusions in lead white matrix	Azurite + yellow iron oxide	Azurite + yellow iron oxide in	lead white matrix	Copper oxalate + lead white +	calcium sulphate	Black + orange/red iron oxide in	lead white matrix	Carbon black in matrix of	calcium sulphate	Carbon black + brown & yellow	iron oxide + massicot	Carbon black + red & yellow	iron oxides + lead white
Combin	•		•	•		•	•	•			•		•		•	•		•		•		•		•		•	
Pigments	 Lead white 	 Red iron 	oxide	 Red lead 	 Vermilion 	 Yellow 	iron oxide	• Massicot	 Basic 	verdigris	 Natural 	azurite	 Carbon 	black													
/preparation	Lead white	Lead white + black + red	Lead white + <i>calcium</i>	sulphate	Lead white + <i>calcium</i>	sulphate + carbon black	lead white with clay-rich	material	calcium sulphate +	protein	(animal glue?)																
Ground	•	•	•		•		•		•		•																
Preparatory techniques	 Carbon black 	drawing	(under & over lead	white ground)	• Dark brown	preparatory	drawing line																				
Author/Date	Howard	1997		_	_	_	_	_	_	_	_	_	_	_	_	_		_				_	_			_	_

⁶ This table is based on Kakoulli, 1999, Table 11, p.25 and has been modified to show cumulative results, i.e. only new findings have been listed. Findings reproduced in each phase are not repeated. The table has also been revised to include results of phase 4 research.

Medium																							
Alterations/contaminants						 Azurite to 	copper chloride	• Arsenic ?									 Realgar to arsenic 	trioxide					
lations	Lead white + charcoal black	Lead white + vermilion	Red iron oxide + charcoal black	Red lead + lead white		Red iron oxide + calcium	sulphate + quartz inclusions	Red iron oxide + calcium	sulphate + quartz inclusions +	charcoal	Lead white + iron oxide	pigments	Lead white + vermilion + iron	oxide	Natural azurite + yellow ochre +	chalk	Natural azurite + yellow ochre +	chalk + lead white +orpiment +	barium sulphate	Natural azurite + yellow ochre +	lead white + chalk + orpiment +	realgar	Realgar + vermilion
Combin	•	•	•	•		•		•			•		•		•		•			•			•
Pigments	 Charcoal 	black		 Red ferric 	oxide	 Arsenic 	containing	pigment?									 Orpiment 	 Realgar 					
Ground/preparation						Lead white + natural	chalk																
Preparatory techniques	Relief carving of	trefoil	decoration																				
Author/Date	Howard	1998		Kakoulli	1999	Davies 2001											Davies 2002						

Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2

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2 PAINT ANALYSIS

2.1 Methodology

resin and polished in cross-section using a Metaserve 2000 grinding/polishing machine and a range of graded abrasives. Prepared cross-sections Paint samples were examined under low power magnification (2.5x-10x) and representative fragments mounted in acrylic modified polyester proteins (glue) and oils.⁷ Samples were also mounted as dispersions (in Meltmount, which has a refractive index of 1.662) and polarised light were examined under dark-field reflected light at magnifications 50x-500x using a Leica DMLM research grade microscope. Microchemical tests were carried out to identify some metallic ions and functional groups. Histochemical tests were undertaken to indicate the presence of microscopy (PLM) carried out. Representative samples were photographed for reproduction within this report.

Scanning electron microscopy with energy dispersive X-ray (SEM.EDX) analysis has been undertaken by Dr Andrew Beard at the Department of Geology, University College London.

⁷ The microchemical tests included: hydrochloric acid and potassium chromate, which produce a yellow stain for lead and hydrochloric acid, which results in the evolution of carbon dioxide to identify carbonates. Preliminary staining for oils used Sudan Black B which stains oils a blue black colour. Preliminary staining for proteins used Coomassie blue (R250) which stains proteins (glue) a mid-blue colour.

2.2 Sample 1 (3070)

Sample 1 (3070) was taken from location 12 II a, lozenge, blue paint from under an original nail head, which is now missing. Analysis required to confirm whether the blue paint is original.

Sample location photograph (below):



Description

The sample contains large particles of Prussian blue so cannot be original paint, but rather must represent later paint which was drawn

under the nail head whilst wet. The particle characteristics (varying size up to very large and angular) suggest the paint probably dates from the eighteenth century restoration.⁸ Interestingly SEM.EDX identified the presence of potassium associated with the blue, this might possibly originate from the saltpeter or alum used in manufacture of the pigment.⁹ Lead white and red iron oxide are also present.



Sample 1 (3070) photographed in cross-section under reflected light at 200 x magnification. (Printed magnification not calculated).

⁸ Welsh, F., 'Particle characteristics of Prussian Blue in an historical oil paint', JAIC 27 (1988): 55- 63.

⁹ Berrie, B., 'Prussian Blue', Artists' Pigments A Handbook of Their History and Characteristics, Vol. 3, Oxford University Press, Oxford, 1997, p.194.



200µm

SEM.EDX backscattered image of the sample showing points at which EDX spectra were made. Spectra 3 (*right*) confirms the presence of iron (fe) in the blue pigment, also of interest is the presence of aluminium, possibly arising from the inert base upon which the pigment has been struck. Lead, probably from the surrounding lead white pigment is also detected.. Spectra 1 and 4 from smaller blue particles show similar results. Spectra 2 detects iron in the red particle suggesting iron oxide. Spectra 2 a identifies a calcium rich particle, possibly calcium sulphate. Spectra 2 a confirms the presence of lead in the white particle.



Sample 2 (3071)

Sample 2 (3071) was taken from location 12 II a, lozenge, flesh tone from neck of King (4), below original nail head, which is now missing. Analysis required to confirm whether paint is original.

Sample location photograph (below):



Description

The flesh tone paint is a single application of lead white, vermilion, carbon black with a little iron oxide yellow. It appears to be original. This pigment combination has been identified in previous research and attributed to the thirteenth century (Howard 1997).



Sample 2 (3071) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 3 (3072)

Sample 3 (3072) was taken from location 13 III b, lozenge, red paint on the crown of King (4) from below original nail head which is now missing. Analysis required to confirm whether paint is original.

Sample location photograph (below):



Description

The paint is a single layer of red lead with a little carbon black and possible some calcium carbonate. The paint appearance is consistent with it being original.



Sample 3 (3072) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).



SEM.EDX backscattered image of the sample showing points at which EDX spectra were made. Spectra 2 (*right*) is representative of all four points examined and confirms the presence of lead. No mercury or sulphur was detected ruling out the presence of vermilion. Carbon was present confirming the presence of carbon black in the pigment mixture. Calcium also occurred on the spectra suggesting the presence of calcium carbonate. Interestingly chloride was identified, Howard 1997 attributed the presence of chlorides to treatment with *Silvertown*.



¹⁰ Howard 1997, op cit, p. 9.

Sample 4 (3073)

Sample 4 (3073) was taken from location 13 I a, lozenge, red-brown paint on base of organistrum, from below original nail head, which is now missing. Analysis required to confirm whether paint is original.

Sample location photograph (below):



Description

The upper layer of the sample comprises a thick layer of iron oxide, probably corrosion from the now absent nail head. The thin red layer below contains vermilion. SEM.EDX also detects arsenic in this area, suggestive of the presence of orange-red realgar. The brownish lower layer gives EDX spectra suggestive of vermilion and realgar. Realgar is known to alter to orpiment and white arsenic trioxide.¹¹



Sample 4 (3073) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

¹¹ West Fitzhugh, E., 'Orpiment and realgar', *Artists' Pigments A Handbook of Their History and Characteristics*, Vol. 3, Oxford University Press, Oxford, 1997, p.51.

Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2



SEM.EDX backscattered image of the sample area 1 showing points at which EDX spectra were made. Spectra 1 shows the particle to contain mercury (Hg) and sulphur (S), probably as mercuric sulphide, vermilion. Traces of iron (Fe) from the surrounding area were also noted. Spectra 2, from the upper layer is comprised mainly of iron, possibly a corrosion product from the nail head. Spectra 3 (*right*) shows arsenic (As) as well as indicating vermilion and iron oxide. The presence of arsenic is probably indicative of the orange-red pigment realgar (AsS). Spectra 4 identifies a similar range of elements.





90hm

SEM.EDX backscattered image of the sample area 2 showing points at which EDX spectra were made. Spectra 1, 3 and 4 all identify the presence of mercuric sulphide (HgS) together with arsenic (As) probably as the red-orange sulphide pigment realgar (AsS), traces of iron were also detected. Spectra 4 (*right*) illustrates the range of elements identified. Spectra 2 from the upper layer shows a fairly pure combination of iron and oxygen, suggesting iron oxide — possibly a corrosion product from the overlying nail head.



	Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2
Sample 5 (3074)	Description
Sample 5 (3074) was taken from location 13 I c, lozenge, green paint on drapery of organistrum, paint from below original nail head, which is now missing.	The sample shows a single layer containing a mixture of natural azurite with lead white, iron oxide yellow, chalk, orpiment (and possibly realgar). This paint is similar to the bright blue-green seen in previous research. ¹²
Sample location photograph (below):	In dispersion particles of yellow ochre, calcium carbonate and a blue copper pigment tan books like azurite, and the red-brown particles of cuprite confirm this identification. In dispersion some particles do resemble azurite, but the majority has undergone change to other copper salts. Particles of orpiment appear to be present. Some of the deeper red particles have a microscopic appearance consistent with realgar. Iron oxide and chalk are also present.

¹² Davies, 2001, *op cit*, sample 21 (3068), Howard, 1997, *op cit*, samples 2108 and 2115.



Sample 5 (3074) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).



Paint dispersion from the blue-green of sample 5 photographed in transmitted light at 200x magnification. (Printed magnification not calculated.)



100µm

SEM.EDX backscattered image of the sample area 1 showing points at which EDX spectra were made. Spectra 2 (*right*) shows significant peaks for copper (Cu), arsenic (As), sulphur (S), lead (Pb) and oxygen (O). Carbon (C) and chlorine (Cl) are also present. Spectra 1 detected iron (Fe) and silica (Si) in addition to the elements identified in 2. Spectra 3 detected calcium (Ca) — chalk particle. Spectra 5, 7, 9 and 10 all identified the same range of pigments. Spectra 4, 6 and 8. all showed silica and aluminium (Al) together with traces of potassium (K), magnesium (Mg) and iron. These appear to be particles of natural clay-rich earths.





SEM.EDX backscattered image of the sample area 2 showing points at which EDX spectra were made. Spectra 3 (*right*) shows the predominance of copper (Cu), arsenic (As), sulphur (S) and lead (Pb) occurring in the area examined. Iron (Fe) was detected as the major component of spectra 8. All other spectra show the same range of elements as seen in area 1 and spectra discussed above.



Sample 6 (3075)

Sample 6 (3075) was taken from location 14 III aa, lozenge, brown paint from background of logic, from below an original nail head, which is now missing.

Sample location photograph (below):



Description

The sample shows a single layer of red paint applied thinly to the timber substrate. The paint is a mixture of red lead with a little carbon black. Some red iron oxide also appears to be present, although this could result from contamination from the missing nail. The appearance of the paint is consistent with a thirteenth century date.



Sample 6 (3075) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).





SEM.EDX backscattered image of the sample area 1 showing points at which EDX spectra were made. EDX identified iron (Fe), lead (Pb), aluminum (Al), silicon (Si), calcium (Ca). For example, see spectra 4 (*right*). On a second area of the sample the same elements were identified, with the addition of tin in one discrete particle on the surface of the sample.



Sample 7 (3076)

Sample 7 (3076) was taken from location 17 II b, green paint from background of Grammar, paint from below original nail head, which is now missing.

Sample location photograph (*below*):



Description

The blue-green paint contains a similar pigment mixture to that found on sample 5 above, with the absence of any arsenic pigment. There appears to be a trace of metal from the absent nail head on the

sample surface. Carbon black is also present. Barium sulphate was present: see discussion on following page.



Above: Sample 7 (3076) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).



Left: Sample 7 (3076) photographed in crosssection under reflected light at 500x magnification. (Printed magnification not calculated).



pigments used in the paint mix. Also of note are particles 8 and 9 which both give strong readings for copper and chlorine, suggestive of the conversion of a copper associated with 19th C paint. However it appears to be present in the bright blue green paint as a contaminant. All other evidence suggests this paint is 13th. The EDX spectra were made. Interestingly EDX produced strong peaks for barium (Ba) and sulphur (S) at points 1 and 3, suggesting these are particles of barium sulphate. The presence of barium sulphate within this paint was also identified during phase 3, sample 21 (3068). Hitherto it had been suggested BaSO4 was BaSO4 may be a naturally occurring substance associated with the natural

Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2

Other spectra confirm the presence of copper and iron together with aluminium, silica, carbon, oxygen, potassium. The paint mixture therefore appears to be similar to that identified as sample 5 above, with the major omission of any

Spectra 1 (below) indicates the presence of barium, sulphur and oxygen.



¹³ Howard 1997, op cit, p. 9.

Sample 8 (3077)

Sample 8 (3077) was taken from location 17 II b, lozenge, red paint from background of Rhetoric, paint from below original nail head, which is now missing.

Sample location photograph (below):



Description

The sample shows a single layer of red lead. Some of the red lead appears to have converted to lead white.¹⁴ Appearance consistent with the sample being from original paint.



Sample 8 (3077) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

¹⁴ Pers. Comm. Sharon Cather to author. I am indebted to Ms Cather for describing the conversion of minium to cerussite (basic lead carbonate), then to brown lead (plattnerite), which the Courtauld Institute of Art, Conservation of Wall Paintings Department have come across in various contexts, for example, Canterbury Cathedral, St Gabriel's Chapel c. 1130; Westminster Abbey, Chapter House, c. 1380. This apparent alteration can also be seen on samples 9, 10 and 11 within this report.

Sample 9 (3078)

Sample 9 (3078) was taken from location 17 IV b, lozenge, red paint from outer groove, from below original nail head, which is now missing. Control sample for comparison with samples 10 and 11.

Sample location photograph (below):



Description

Appearance consistent with the sample being from original paint. Single layer of red lead. Some of the red lead appears to have altered to lead white.



Sample 9 (3078) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 10 (3079)

Sample 10 (3079 was taken from location 11 I s, grey chevron, red paint from middle groove, from below original nail head which is now missing. Very few instances of red paint have been found in middle grooves, so analysis of paint and comparison with other samples is required to establish the date of the red paint here.

Sample location photograph (below):



Description

The surface grey paint layer comprises lead white with calcium carbonate, the colouring pigments appear to be iron oxide, carbon black and an organic brown. The second white layer is also lead white with calcium carbonate, pigmented with a little iron oxide and carbon black. The orange-brown layer appears to consist of iron oxide, some red lead and carbon black in particles ranging from medium to very large. The carbon particles have a smooth even surface. The primary paint layer is red lead, with some white lead inclusions. The red lead paint appears to be consistent with a thirteenth century date.



Sample 10 (3079) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

from previous research¹⁵ to contain calcium sulphate at varying



300µm

readings for iron, calcium, sulphur and lead, suggesting a mixture of SEM.EDX backscattered image of sample 10, area 1 showing points (CaCO₃). Spectra 3 and 9, from the large dark particles of the orange lead white, some calcium also occurs, possibly as calcium carbonate iron oxide, red lead and calcium sulphate. The paint film is known readings consistent with basic lead carbonate (2PbCO₃.Pb(OH)₂) brown layer give readings for carbon. Spectra 4 (right) gives at which EDX spectra were made. Spectra 1, 2 and 8 all give

concentrations. Spectra 5, 6 and 7 all give readings for lead.



¹⁵ Howard, 1997, op cit, p. 9.



300µm

SEM.EDX backscattered image of sample 10, area 2 showing points at which EDX spectra were made. Spectra 1 detects calcium, carbon and oxygen, suggesting a particle of calcium carbonate. Spectra 6 gives readings for lead and calcium, as observed in this layer in previous area. Spectra 2, 7 and 5 all show strong readings for iron, suggestive of iron oxide. Traces of aluminium, silicon, magnesium and potassium are also present perhaps suggesting that the iron oxide is of natural origin. Again, calcium, lead and sulphur are



Sample 11 (3080)

Sample 11 (3080) was taken from location 11 I f, grey chevron, red paint from middle groove, from below original nail head which is now missing. Very few instances of red paint has been found in middle grooves, so analysis of paint and comparison with other samples is required to establish the date of the red paint here.

Sample location photograph (below):



Description

Appearance consistent with it being original paint, single layer of red lead applied directly to the timber surface.



Sample 11 (3080) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 12 (3081)

Sample 12 (3081) was taken from location 14 III k, extended chevron, paint from small *impasto* dot on 'body' of original trefoil. Similar embellishments found previously on some trefoil heads in Bays 2 and 3. Analysis required to identify *impasto* and examine stratigraphy of paint layers and their dates.

Sample location photograph (below):



Description

The sample shows lead white with a little calcium carbonate, over a thin carbon black layer, possibly representative of underdrawing. Identical layers have been observed in similar locations without a raised dot. 16



Sample 12 (3081) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

¹⁶ Davies, 2001, sample 17 (3064) from 18 II r extended chevron, where a raised trefoil design is just visible showing as black through the 1830s white background paint.

Sample 13 (3082)

Sample 13 (3082) was taken from location 15 I q, extended chevron, paint from small *impasto* dot on 'body' of original trefoil. Similar embellishments found previously on some trefoil heads in Bays 2 and 3. Analysis required to identify *impasto* and examine stratigraphy of paint layers and their dates.

Sample location photograph (below):



Description

The sample reveals two layers of lead white with a little calcium carbonate, over a thin carbon black layer, mixed with a thick translucent layer. The translucent layer contains no pigmentation, it stains weakly for protein and is probably an animal glue, which may arise from later intervention. The presence of two white layers is clearly revealed in the SEM.EDX backscattered shown on the following page. Similar layers have been observed in similar locations without a raised dot. Further sampling may elucidate this query.



Sample 13 (3082) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).



200µm

SEM.EDX backscattered image of sample13, area 1 showing points at which EDX spectra were made. Spectra 1 and 2 give readings for lead with traces of calcium. Spectra 3 and 4 give readings only for carbon and oxygen suggesting the translucent brown layer is organic



100µm

SEM.EDX backscattered image of sample 13, area 2 showing points at which EDX spectra were made. The carbon occurs from the black layer (underdrawing?). The brown area gives readings only for carbon and oxygen suggesting it is organic.

Sample 14 (3083)

Sample 14 (3083) was taken from location 14 III t, extended chevron, paint from small *impasto* dot on 'body' of original trefoil. Similar embellishments found previously on some trefoil heads in Bays 2 and 3. Analysis required to identify *impasto* and examine stratigraphy of paint layers and their dates.

Sample location photograph (below):



Description

The sample shows lead white with a little calcium carbonate, over a thin carbon black layer. Similar layers have been observed in similar locations without a raised dot. Further sampling may elucidate this query.



Sample 14 (3083) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 15 (3084)

Sample 15 (3084) was taken from location 9 I f, stepped chevron, original linear stepped chevron decoration visible in relief under 18th /19th century overpaint. Sample through white. Analysis required to identify original paint if present on sample.

Sample location photograph (below):



Description

The sample appears to show two layers of lead white. The upper layer being fairly thinly applied. The lower, thicker white contains a very few coloured particles, probably vermilion and carbon black. A translucent organic substance appears to be present at the paint timber interface.



Sample 15 (3084) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 16 (3085)

Sample 16 (3085) was taken from location 9 I f, stepped chevron, original linear stepped chevron decoration visible in relief under 18th /19th century overpaint. Sample through black. Analysis required to identify original paint if present on sample.

Sample location photograph (below):



Description

The sample shows brown on white on coarse orange-brown paint directly on the timber substrate. Microscopy suggests the paint dates from the eighteenth and nineteenth centuries, with any earlier paint absent from this specific location. The characteristic chunky orange-brown paint is present overlying apparently thirteenth century paint on sample 10 and it has therefore been tentatively assigned to the 1740s phase.



Sample 16 (3085) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 17 (3086)

Sample 17 (3086) was taken from location 9 I f, stepped chevron, original linear stepped chevron decoration visible in relief under 18th /19th century overpaint. Sample through black. Analysis required to identify original paint if present on sample.

Sample location photograph (below):



Description

The sample appears to show only off-white paint. Under reflected light it is just possible to discern two off-white paint layers, the upper one being thinly applied. Noticeable at the base of the sample is a beige layer, probably with an animal glue medium.¹⁷



Sample 17 (3086) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

 17 The layer stains weakly positive for protein.

Sample 18 (3087)

Sample 18 (3087) was taken from location 9 I f, stepped chevron, original linear stepped chevron decoration visible in relief under 18th /19th century overpaint. Sample through black. Analysis required to identify original paint if present on sample.

Sample location photograph (below):



Description

The upper layers of the sample appear to date from the 1830s. The brown is comprised of umber, natural iron oxide, calcium and barium sulphate. The upper white layer is lead white and calcium carbonate. The lower again lead white and calcium carbonate. The characteristic coarse orange-brown is identical to that observed on previous samples. The lowest white layer is basic lead carbonate and may date from the thirteenth century. The beige layer visible at the base of the sample appears to be calcium sulphate in an animal glue binder.



Sample 18 (3087) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).



e0µm

SEM.EDX backscattered image of the sample18, area 1 showing points at which EDX spectra were made. Spectra 1 indicates the presence of magnesium (Mn), iron, sulphur and barium, with traces of calcium, oxygen, carbon, lead, aluminium and silica. Following microscopy this is interpreted as indicative of the pigments natural iron oxide, umber, barium sulphate and calcium sulphate. Spectra 6 identifies a large particle of silica and spectra 7 (*right*) a large particle of barium sulphate. Spectra 2 and 3 confirm the presence of lead and calcium. Spectra 5, 4 and 8 are all from the characteristic orange-brown layer discussed on previous samples. Spectra 9

confirms the lowest white layer is a fairly pure basic lead carbonate. The beige layer at the base of the sample gives readings suggestive of calcium sulphate.



Sample 19 (3088)

Sample 19 (3088) was taken from location 9 I f, stepped chevron, original linear stepped chevron decoration visible in relief under 18th /19th century overpaint. Sample through white. Analysis required to identify original paint if present on sample.

Sample location photograph (below):



Description

The sample appears to show two layers of lead white. The upper layer being fairly thinly applied. The lower, thicker white contains a few coloured particles, probably vermilion and carbon black. The beige layer visible at the base of the sample appears to be calcium sulphate in a glue binder.

Boundary of white layers suggested by break in sample



Sample 19 (3088) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

a EDX backscattered image. Both layers consist primarily of basic lead carbonate with small amounts of extender and coloured	pigments. Interestingly the lower layer contains a small copper blue particle, possibly natural azurite, which would seem to associate that paint layer with the thirteenth century paintwork.		Blue pigment	Sample 20 (3089) photographed in cross-section under reflected light at 200x magnification (Diriged magnification at colorlated)
19 th century overpaint. Sample through white. Analysis required to dentify original paint if present on sample.	ample location photograph (below):			

The presence of two distinct white layers can be seen on this sample

Description

under dark and bright field reflected light and even more clearly on

Sample 20 (3089)

Sample 20 (3089) was taken from location 12 III e, stepped chevron, original linear stepped chevron decoration visible in relief under 18th

41



П 100µm

SEM.EDX backscattered image of sample 20, area 1 showing points at which EDX spectra were made. The two separate layers can be clearly distinguished. Spectra from all areas give simple readings for lead carbonate.



100µm

SEM.EDX backscattered image of sample 20, area 2 showing points at which EDX spectra were made. Spectra from the blue particle detects the presence of copper, lead, carbon and oxygen. This copper blue could be azurite, thereby associating the layer with the original paint containing azurite, which was being applied elsewhere.

mple 21 (3090) was taken from location 12 III e, 12 III e, stepped	This sample has a very similar appearance to sample 18 discussed
evron, original linear stepped chevron decoration visible in relief	above. The brown is comprised of umber, natural iron oxide,
der 18 /19 century overpaint. Sample through black. Analysis quired to identify original paint if present on sample.	calcium and barium sulphate. The characteristic coarse orange- brown is identical to that observed on previous samples. The lowes
	white layer is basic lead carbonate and may date from the thirteenth
mple location photograph (below):	century. The beige layer visible at the base of the sample appears to be calcium culmbate in an animal clue binder

Sample 21 (3090)

Description

Sar

Sample 21 (3090) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 22 (3091)

Sample 22 (3091) was taken from location 12 III e, stepped chevron, original linear stepped chevron decoration visible in relief under 18th /19th century overpaint. Sample through white. Analysis required to identify original paint if present on sample.

Sample location photograph (below):



Description

The sample shows a lead white paint applied over the characteristic orange-brown discussed above. The lower white lead layer may be dated to the thirteenth century.



Sample 22 (3091) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 23 (3092)

Sample 23 (3092) was taken from location 17 IV g, stepped chevron, white paint from raised linear stepped chevron pattern, below original nail head, which is now missing. Analysis required to confirm whether this is the original paint and if so, it's material composition.

Sample location photograph (below):



Description

The sample shows a very thinly applied white lead layer directly on the timber substrate. It has not been overpainted. Its microscopic appearance is consistent with it being of thirteenth century date.



Sample 23 (3092) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 24 (3093)

Sample 24 (3093) was taken from location 17 IV g, stepped chevron, black paint from background area adjacent to raised linear stepped chevron pattern, below original nail head, which is now missing. Analysis required to confirm whether this is the original paint and if so, its material composition.

Sample location photograph (below):



Description

The sample appears to show unpainted timber. Surface deposits appear to be accretions of dust and debris, rather than a deliberately applied paint finish.



Sample 24 (3093) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 25 (3094)

Sample 25 (3094) was taken from location 15 I f, stepped chevron, white paint from raised linear stepped chevron pattern, below original nail head, which is now missing. Analysis required to confirm whether this is the original paint and if so, its material composition.

Sample location photograph (below):



Description

The sample shows a thinly applied white lead layer directly on the timber substrate. It has not been overpainted. Its appearance may be consistent with a thirteenth century date.



Sample 25 (3094) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 26 (3095)

Sample 26 (3095) was taken from location 15 I f, 17 IV g, stepped chevron, black paint from background adjacent to raised linear stepped chevron pattern, below original nail head, which is now missing. Analysis required to confirm whether this is the original paint and if so, its material composition.

Sample location photograph (below):



Description

The sample appears to show unpainted timber. Surface deposits appear to be accretions of dust and debris, rather than a deliberately applied paint finish. It has not been overpainted. However, iron corrosion products, probably from the now absent nail head are present on its surface.



Sample 26 (3095) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 27 (3096)

Sample 27 (3096) was taken from location 14 I w, lozenge board, off-white paint from neck of organistrum, from below original nail head, which is now missing.

Sample location photograph (below):



Description

The paint appears to be a single application of lead white, vermilion, carbon black with a little iron oxide yellow. Its appearance is consistent with it being of thirteenth century date. A similar paint mixture has been identified in previous research and attributed to the original decoration (Howard 1997).



Sample 27 (3096) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 28 (3097)

Sample 28 (3097) was taken from location 14 I w, lozenge board, black paint from neck of organistrum, from below original nail head, which is now missing.

Sample location photograph (below):



Description

The sample reveals a dark paint containing carbon black and a little iron oxide. The paint layer is intermingled at its lower boundary with a white lead paint, which appears to contain a particle of azurite. The appearance of the paint is consistent with a thirteenth century date.



Sample 28 (3097) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 29 (3098)

Sample 29 (3098) was taken from location 14 II bb, pink paint from body of organistrum, from below an original nail head, which is now missing.

Sample location photograph (below):



Description

The paint appears to be a single application of lead white, vermilion, carbon black with a little iron oxide yellow. Its appearance is consistent with it being of thirteenth century date. A similar paint mixture has been identified in previous research and attributed to the original decoration (Howard 1997).



Sample 29 (3098) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Sample 30 (3099)	Description
Sample 30 (3099) was taken from location 8 III c, key. Paint below 1830s hanging bolt (temporarily removed during treatment). Black paint on raised area between outer groove and outer edge of board. Current theory is that these raised areas were originally unpainted.	Sample shows a thinly applied carbon black layer over white lead paint directly on the board. No evidence useful for specifically dating the paint layers has been noted on the sample.
Sample location photograph (below):	
	Sample 30 (309) photographed in cross-section under reflected light at 200x magnification. (Printed magnification not calculated).

Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2

Sample 31 (3100)

Sample 31 (3100) was taken from location 12 II d, black paint from raised area between outer and middle groove from below an original nail head, which is now missing. Current theory is that these areas were originally unpainted.

Sample location photograph (below):



Description

The sample appears to show unpainted timber. Surface deposits appear to be accretions of dust and debris, rather than a deliberately applied paint finish.



Sample 31 photographed in cross-section under reflected light at 200x magnification (on slide). (Printed magnification not calculated).

by two white layers. It may be tentatively suggested that the thirteenth century scheme had dark trefoils on an unpainted background, with a few white dots placed on them. These would then have been overpainted during one of the later restoration campaigns. However this remains conjectural. Further sampling may provide confirmatory evidence.	Inrougn analysis of samples it has been possible to identify original paint below absent nail neads. Usually in paint combinations which have also been found in previous research programmes, suggesting a uniformity of painting technique across the breadth of the ceiling. Of great interest has been the confirmation of orpiment in a rich blue-green paint, which appears to be original and has not previously been identified. In addition realgar pigment has been identified, both as a pure pigment and, possibly, as a naturally occurring contaminant of orpiment.	on a dark background. Sampling to investigate the status of small <i>impasto</i> dots on the 'body' of original trefoils in bays 14 –15 was also undertaken. ¹⁸	The aims of this research phase have been to identify and characterise paint thought to date to the thirteenth century, from below original nail heads now absent from bays 9–17. Also to examine in further detail the original stepped chevron visible in relief below eighteenth and	3 DISCUSSION OF FINDINGS	Peterborough Cathedral: Scientific examination of the nave ceiling Phase 4: 2001/2
	Examination of several samples from the stepped chevron have provided further information on the original design than was previously available. Several samples show two distinct lead white based layers in reflected light at high magnification. In addition SEM.EDX backscattered images of the samples reveal layers with noticeably different topography and granulometry. Interestingly, within the lower lead white layer of sample 20 a single copper blue particle is present. As it has been shown that natural azurite was used during the original painting, it is tempting to suggest that this particle is probably natural azurite and thereby associate the early white with the thirteenth century painting. Further, the evidence of samples from the stepped chevron, which were protected from overpainting by a nail, does suggest a white line on a dark or unpainted background.	Through analysis of samples it has been possible to identify original paint below absent nail heads. Usually in paint combinations which have also been found in previous research programmes, suggesting a uniformity of painting technique across the breadth of the ceiling. Of great interest has been the confirmation of orpiment in a rich blue-green paint, which appears to be original and has not previously been identified. In addition realgar pigment has been identified, both as a pure pigment and, possibly, as a naturally occurring contaminant of orpiment. Examination of several samples from the stepped chevron have provided further information on the original design than was previously been identified. In addition realgar pigment has been identified, both as a pure pigment and, possibly, as a naturally occurring contaminant of orpiment. Examination of several samples from the stepped chevron have provided further information on the original design than was previously available. 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Samles from the <i>immasto</i> dots do not hear more lavers than those nreviously identified on the trefoil areas. An initial carbon black is followed		Through analysis of samples it has been possible to identify original paint below absent nail heads. Usually in paint combinations which have also been found in previous research programmes, suggesting a uniformity of painting technique across the breadth of the ceiling. Of great interest has been the confirmation of orpiment in a rich blue-green paint, which appears to be original and has not previously been identified. In addition realgar pigment has been identified, both as a pure pigment and, possibly, as a naturally occurring contaminant of orpiment.	nneteenth century overpaint and, in areas where original nail heads are now missing, that appear to show a thirteenth century decoration in white on a dark background. Sampling to investigate the status of small <i>impasto</i> dots on the 'body' of original trefoils in bays 14–15 was also undertaken. ¹⁸ Through analysis of samples it has been possible to identify original paint below absent nail heads. Usually in paint combinations which have also been found in previous research programmes, suggesting a uniformity of painting technique across the breadth of the ceiling. Of great interest has been the confirmation of orpiment in a rich blue-green paint, which appears to be original and has not previously been identified. In addition realgar pigment has been identified, both as a pure pigment and, possibly, as a naturally occurring contaminant of orpiment.	The aims of this research phase have been to identify and characterise paint thought to date to the thirteenth century, from below original nail heads now absent from bays 9–17. Also to examine in further detail the original stepped chevron visible in relief below eighteenth and nineteenth century overpaint and, in areas where original nail heads are now missing, that appear to show a thirteenth century decoration in white on a dark background. Sampling to investigate the status of small <i>impasto</i> dots on the 'body' of original trefoils in bays 14–15 was also undertaken. ¹⁸ Through analysis of samples it has been possible to identify original paint below absent nail heads. Usually in paint combinations which have also been found in previous research programmes, suggesting a uniformity of painting technique across the breadth of the ceiling. Of great interest has been the confirmation of orpiment in a rich blue-green paint, which appears to be original and has not previously been identified. In addition realgar pigment has been identified, both as a pure pigment and, possibly, as a naturally occurring contaminant of orpiment.	3 DISCUSSION OF FINDINGS The aims of this research phase have been to identify and characterise paint thought to date to the thirteenth century, from below original nail heads now absent from bays 9 –17. Also to examine in further detail the original stepped chevron visible in relief below eighteenth and nineteenth century overpaint and, in areas where original nail heads are now missing, that appear to show a thirteenth century decoration in white on a dark background. Sampling to investigate the status of small <i>impasto</i> dots on the 'body' of original trefoils in bays 14 –15 was also undertaken. ¹⁸ Through analysis of samples it has been possible to identify original paint below absent nail heads. Usually in paint combinations which have also been found in previous research programmes, suggesting a uniformity of painting technique across the breadth of the ceiling. Of great interest has been the confirmation of orpiment in a rich blue-green paint, which appears to be original and has not previously been identified. In addition realgar pigment has been identified, both as a pure pigment and, possibly, as a naturally occurring contaminant of orpiment.

 $^{^{18}}$ Similar dots were previously noted in bays 2 and 3.