

Article

The Unexpected Discovery of Syngenite on Margarito d'Arezzo's *The Virgin and Child Enthroned, with Scenes of the Nativity and the Lives of the Saints* (Probably 1263–4) and Its Possible Use as a Yellow Lake Substrate

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Abstract: The oldest painting in the National Gallery collection, *The Virgin and Child Enthroned* by Margarito d'Arezzo (NG564), dated to about 1263–4, depicts the Virgin and Child in a mandorla, surrounded by scenes of the Nativity and lives of the saints, set within red and decorative black borders, against a gilded background. The materials and technique were investigated using a combination of non-invasive techniques, such as Fibre Optic Reflectance Spectroscopy (FORS) and macro X-ray fluorescence scanning (MA-XRF), and the analysis of a small number of paint samples using energy dispersive X-ray analysis in the scanning electron microscope (SEM-EDS), High-Performance Liquid Chromatography (HPLC), Attenuated Total Reflectance—Fourier transform infrared spectroscopy (ATR-FTIR) and micro X-ray Diffraction (micro-XRD). The results provided evidence for the use of a number of organic colourants, with both indigo and red lake pigments identified. The finding of an unusual compound, syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), is here postulated as a potential substrate for an organic yellow lake pigment. In addition, reference pigments were prepared to explore this hypothesis. Although documentary evidence confirms that yellow lakes were being produced from an early date, there is very little direct evidence for their use in 13th-century panel paintings.

Keywords: syngenite; yellow lake; safflower; organic colourants

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1. Introduction

The Virgin and Child Enthroned by Margarito d'Arezzo (NG564), dated to about 1263–4, is the oldest painting in the National Gallery collection. It is of considerable interest since the technique and materials of the Gallery's paintings of this period have not so far been studied in any depth. The panel shows the Virgin and Child in a mandorla, surrounded by scenes of the Nativity and lives of the saints, set within red and decorative black borders, against a gilded background (Figure 1).

The recent conservation campaign of this altarpiece focused on the reassessment of a past intervention on the painting, mainly the re-gilding of the original frame and overpainting of the adjoining red and black border. This work was probably undertaken by the Florentine restorer Ugo Baldi in preparation for the panel's sale in the mid-19th century.

Investigations undertaken during the conservation treatment used a combination of non-invasive techniques, such as Fibre Optic Reflectance Spectroscopy (FORS) and macro X-ray fluorescence scanning (MA-XRF), together with the analysis of a small number of paint samples using energy dispersive X-ray analysis in the scanning electron microscope (SEM-EDS), High-Performance Liquid Chromatography (HPLC), Attenuated Total Reflectance—Fourier transform infrared spectroscopy (ATR-FTIR) and micro X-ray Diffraction (micro-XRD). The results provided evidence for the use of a number of inorganic pigments, such

as orpiment, azurite, vermillion and red and yellow earths, as well as the organic colourants indigo and lac lake in the original painting. As expected, analysis of several samples indicated an egg tempera medium (ATR-FTIR and transmission FTIR).



Figure 1. *The Virgin and Child Enthroned* by Margarito d'Arezzo (92.1 × 183.1 cm). NG564, after conservation. © The National Gallery, London.

The presence of indigo was identified non-invasively (using FORS) at various locations on the panel. It is present in the inscriptions above the narrative scenes, for example, and, perhaps most notably, was used for the blue sea in the scene depicting *The Miracle of Saint Nicholas*. This paint layer now appears very dark and opaque and conceals the details of sea creatures, probably painted in carbon black, and known only from the infrared reflectogram (IRR) (Figure 2). The use of indigo in paintings of this period is not unusual and has been confirmed in other 13th-century works, including the *Madonna and Child* from Arezzo, for example, where it was used as an underpaint for azurite [1].

Organic colourants such as red and yellow lake pigments rarely survive on paintings of this date and have been successfully analysed even less frequently. Their identification generally requires the analysis of small samples to detect both the organic dye components and the inorganic substrate onto which the dye molecules were precipitated or adsorbed. Furthermore, the pattern of major and minor dye components identified can, in favourable circumstances, provide details of the precise biological source from which they were extracted. One such paint sample was removed from the Virgin's skirt, next to an area of existing damage in the central motif, where the modelling of the fabric relies on the application of a red lake pigment over the top of a vermillion underlayer. Analysis by High-Performance Liquid Chromatography (HPLC) confirmed the dye source of the pigment to be lac, made from the dyestuff extracted from the lac insect *Kerria lacca* Kerr, while analysis by SEM-EDS indicated that it had been precipitated onto a hydrated alumina substrate. Although similar analyses have not yet been conducted on any comparative material from the National Gallery collection, lac lakes have been identified by HPLC in a number of English and Norwegian panel paintings, wall-paintings and sculptural polychromy from the mid-13th to the early 14th centuries [2].

The identification of yellow organic ("lake") pigments on paintings from this period is particularly rare, partly because few have been studied in-depth, but also because of

the light-sensitive nature of many of the yellow dye sources. Thus, the detection of the inorganic substrate is often the only remaining clue that a yellow organic pigment might once have been present. There are few early recipes, but those that do exist generally suggest the use of a white substrate, perhaps a local white earth or a calcium salt, to adsorb (rather than precipitate) the dye molecules and produce the yellow pigment (see discussion in Section 4.1). It is in the context of a substrate for a yellow organic pigment that the identification of syngenite in a yellow glaze layer on *The Virgin and Child Enthroned*, described below, is significant. While no evidence for the presence of organic dyes was obtained, the identification of syngenite, together with additional contextual information, strongly suggests a yellow organic pigment was used as a glaze on the decorative border of the painting.



Figure 2. Detail of *The Miracle of Saint Nicholas*. Infrared reflectogram (IRR) revealing the sea creatures. © The National Gallery, London.

The removal of 19th-century overpaint from the decorative border revealed an original foliate decoration, painted in a fairly opaque, strong yellow over an (original) red background (Figure 3).

Close examination of the paint surface revealed what appeared to be a translucent yellow paint or glaze layer surviving on the surface of the yellow foliate design (Figure 4), perhaps applied to enhance the yellow colour or to imitate the type of gold foliate border seen in contemporary paintings, such as Guido da Siena's *Virgin and Child with S. Francis, John the Baptist, John the Evangelist and Mary Magdalene* (Siena Pinacoteca).

This paper details the analytical investigations undertaken to establish the presence of syngenite in the glaze layer on the surface of the yellow foliate design. In addition, reference organic pigments were prepared to explore the hypothesis that syngenite is present as a substrate for a yellow organic lake pigment.

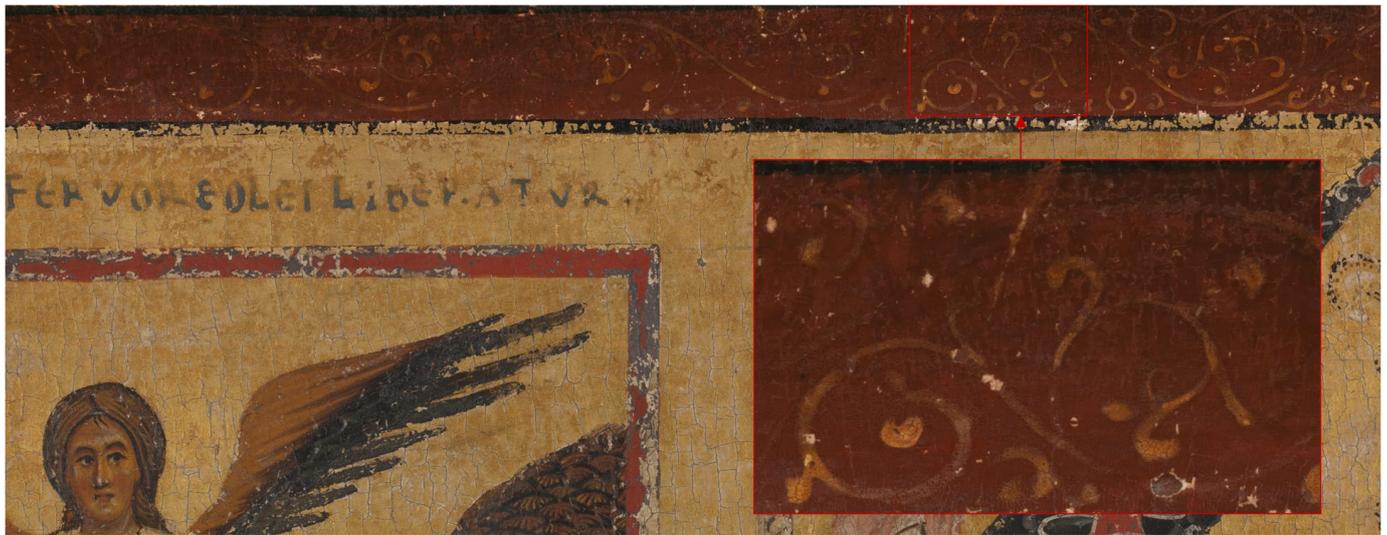


Figure 3. Detail of Figure 1 showing: part of the angel in the scene of *St. John the Evangelist in a Cauldron of Boiling Oil*; the inscription above this scene contains indigo; and the newly revealed border with a yellow foliate design painted on the red background. The inset shows a detail of this border. © The National Gallery, London.

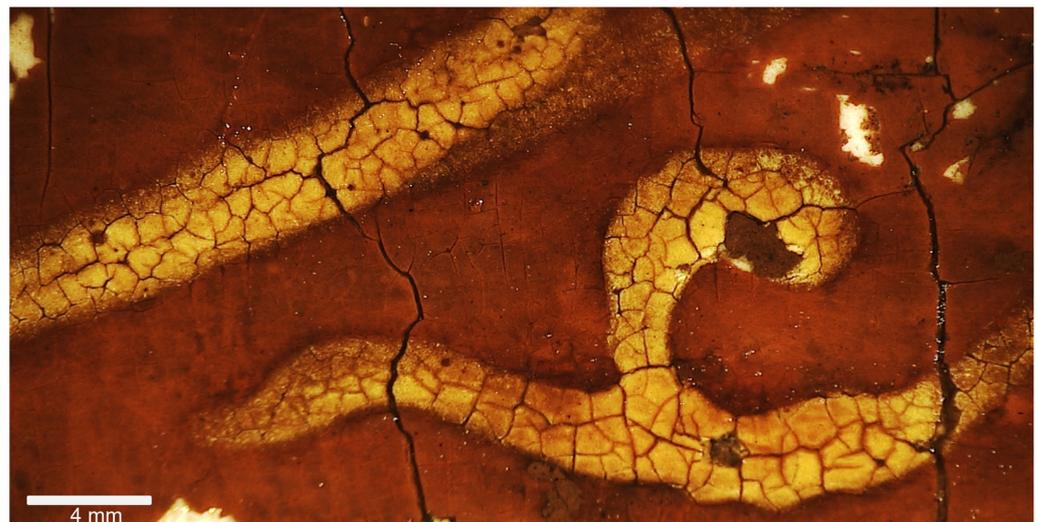


Figure 4. Hirox microscope image of a detail of the yellow border showing craquelure of the yellow paint layer/s. © The National Gallery, London.

2. Materials and Methods

2.1. Analytical Techniques

2.1.1. HPLC

The lake samples were extracted using 4% BF_3 in MeOH (*ca.* 3–6 μL). The solutions were left overnight, before being centrifuged for 1 min at 3000 rpm and the supernatant collected and analysed using a standard protocol developed at the National Gallery for the analysis of lake pigments extracted from historical paint samples. An Agilent Technologies High-Performance Liquid Chromatography system, comprising a 1200 series capillary pump and vacuum degasser and an HP 1100 series column oven and Photo Diode Array (PDA) detector, was used. The samples were injected manually via a Cheminert Valco low-dispersion 6-port injector with a 2 μL sample loop. Agilent OpenLab CDS (Chemstation edition) was used to control the equipment and process the data. The flow cell path length was 10 mm (0.5 μL volume) and the bandwidth (resolution) of the detector was 8 nm. The method used a Phenomenex LUNA C18(2) reverse phase column, 5 mm particle

size, 150×0.5 mm (length \times i.d.). The total run time was 80 min (+15 min post-run at initial conditions) at a flow rate of $10 \mu\text{L min}^{-1}$ and the column was maintained at a temperature of 40°C . A binary solvent system was used; A = 0.1% aqueous trifluoroacetic acid, B = 94.9% acetonitrile, 5% methanol, 0.1% trifluoroacetic acid. The elution program was a linear gradient from 95A:5B to 70A:30B (0 to 25 min), followed by a linear gradient to 5A:95B (65 min). Isocratic conditions were maintained (75 min) before a linear return to the starting conditions, 95A:5B (80 min).

2.1.2. (ATR) FTIR

Spectra were acquired using a Bruker Tensor 27 FTIR Spectrometer connected to a Hyperion 3000 Series microscope, fitted with a mid-band MCT detector (range = $12,000\text{--}600 \text{ cm}^{-1}$) and a 64×64 (4096 pixels) FPA detector (range = $4500\text{--}900 \text{ cm}^{-1}$). Both detectors were cooled with liquid nitrogen. The microscope was fitted with a CCD camera, x-y stage (adjustment accuracy of $0.1 \mu\text{m}$), knife-edge apertures and two glass objectives ($4\times$ and $20\times$ magnification), a $15\times$ Cassegrain objective and a dedicated ATR objective ($20\times$ magnification). The ATR had a germanium crystal with a tip size of $250 \mu\text{m}$. Both the spectrometer and microscope were purged with water- and CO_2 -free air. For transmission measurements, samples were compressed between the windows of a Spectra-Tech micro-compression diamond cell, then spectra acquired with the uppermost window removed. Bruker Opus software, version 8.7 was used to control the equipment and process the data. Spectra were collected with 4 cm^{-1} spectral resolution and were the sum of 128 scans.

2.1.3. XRD

Five small fragments from a sample taken from the glaze layer on the yellow foliage design on the red border of the painting were mounted on carbon fibres using small drops of epoxy. The mounted samples were fixed on a goniometer head in the XRD instrument. XRD measurements were carried out using a Rigaku Dmax Rapid II Micro-XRD. The samples were analysed using copper radiation at 40 kV and 36 mA. The X-ray beam was conditioned to a size of $300 \mu\text{m}$. The samples were moved during the measurements along two axes (omega and phi-rotation) to improve particle statistics. Measurement times varied between 1 and 5 h.

The collected 2D data were converted to conventional 1D XRD patterns using the DP software (Rigaku). Phase identification was carried out using HighScorePlus (Panalytical) in combination with the PDF-2 database from ICDD. The XRD patterns were background subtracted before phase identification.

2.1.4. SEM-EDS

Samples were mounted as paint cross-sections and analysed in a Zeiss EVO MA10 variable pressure scanning electron microscope (VPSEM) with Oxford Instruments X-max large area Energy Dispersive X-ray Spectroscopy (EDS) and Silicon Drift Detector (SDD) at 25 keV, 200 pA, 44 Pa (Air) working distance 8.48 mm.

2.1.5. MA-XRF

MA-XRF scanning was undertaken using a Bruker M6 Jetstream macro X-ray fluorescence (MA-XRF) scanner which allows paintings to be scanned while secured on an easel in front of the scanner, with no contact being made with the paint surface. The measuring head consists of a 30 W Rhodium-target microfocuss X-ray tube with a maximum voltage of 50 kV and a maximum current of 0.6 mA. With the Bruker M6, only elements heavier than silicon can be detected. The painting was scanned in 6 sections with acquisition parameters: Tube, 600 μA , 50 kV; detector, 275 kcps; spot size, $580 \mu\text{m}$; step size, $580 \mu\text{m}$; dwell time 10 ms; number of cycles, 1.

2.2. Synthesis of Syngenite

Syngenite was first synthesised using gypsum and potassium sulfate following an adapted version of a published method [3]. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; 12.1 g) was added to an aqueous solution of potassium sulfate (K_2SO_4 ; 14.2 g in 100 mL) at room temperature with constant stirring. After 3 h, the suspension, which had become noticeably “fluffy”, was filtered under vacuum, and the resulting solid dried in an oven at 80 °C overnight. Syngenite was then synthesised in an identical manner using gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; 12.1 g) and an aqueous solution of potassium carbonate, K_2CO_3 (9.7 g in 100 mL) following an adapted version of a published method [4]. In both cases, analysis of the dried powder by FTIR confirmed the absence of gypsum (no bands present at 3560 and 3430 cm^{-1}) and indicated the presence of syngenite ($\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$; signature absorption bands at 758 and 658 cm^{-1}) [5], with chalk (CaCO_3 ; signature absorption bands at 1430 and 877 cm^{-1}) also present in the second sample (Figure 5).

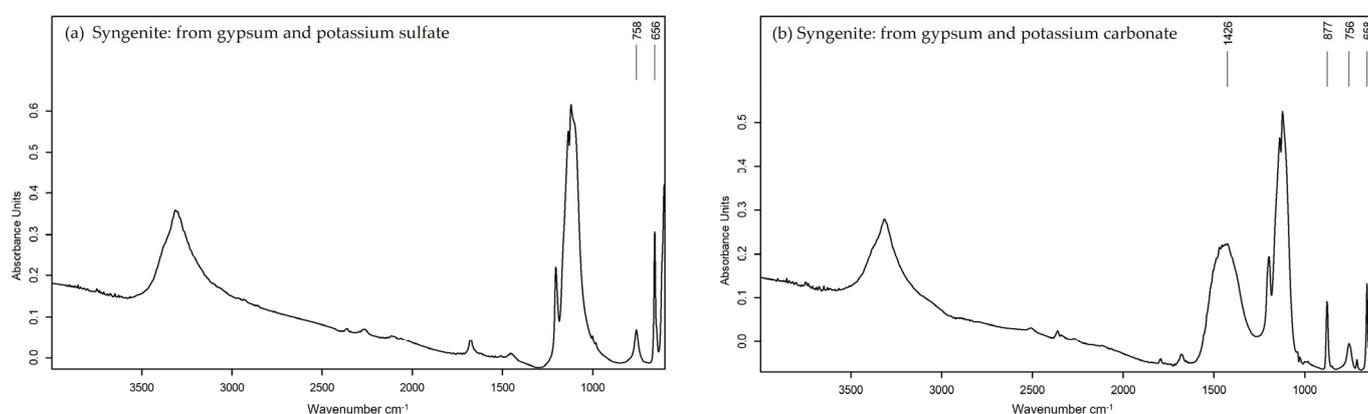


Figure 5. FTIR absorbance spectra indicating the presence of syngenite, synthesised from (a) gypsum and potassium sulfate and (b) gypsum and potassium carbonate (also containing chalk).

2.3. Preparation of Reference Organic Pigments

2.3.1. Weld on Gypsum Support

The dried weld (2.5 g) was placed in distilled water (250 mL) and left to soak for *ca.* 48 h. The solution was then heated to between 60 °C and 80 °C for 30 min before being left to cool for another 30 min, then filtered. One aliquot of the filtered solution (100 mL) was used for the syngenite experiment (see Section 2.3.2), while a second aliquot (100 mL) was placed in a beaker and gypsum (1.2 g) added. This was left for *ca.* 24 h (with occasional stirring) before the solid, now slightly yellow in colour, was removed and placed on a watch-glass to dry in a desiccator. To increase the amount of dye adsorbed onto the surface and produce a more intensely coloured pigment, a portion of the pale-yellow solid (0.7 g) was then placed in a second weld dye solution, prepared in a similar fashion to the first, and left for *ca.* 24 h (with occasional stirring) before being removed and placed on a watch-glass to dry in a desiccator. The same procedure was then repeated with a portion of the solid from the second immersion (0.4 g), thus producing three separate pigments which had been immersed in one, two and three fresh dye solutions, respectively.

As expected, immersion in successive dye solutions produced pigments with slightly deeper shades of yellow, however, all three pigments were still relatively pale in colour, so a further experiment was conducted using a more concentrated weld solution. In this case, the dried weld (15 g) was placed in distilled water (200 mL) and left to soak for *ca.* 24 h. The solution was then heated to boiling for 60 min before being left to cool for another 30 min, then filtered. The filtrate was placed in a beaker and heated, allowing the solution to evaporate until only *ca.* 10 mL remained. The resultant solution, slightly syrupy in consistency, was left to cool for *ca.* 30 min before an aliquot (5 mL) was removed and added to a beaker containing gypsum (1.2 g). This was left for *ca.* 24 h (with occasional stirring)

before the solid was removed and placed on a watch-glass to dry in a desiccator. This produced a yellow pigment, deeper and darker in shade than those produced previously.

2.3.2. Weld on Syngenite Support

An aliquot (100 mL) of the weld solution prepared above (Section 2.3.1) was placed in a beaker and syngenite (prepared using gypsum and potassium sulfate in Section 2.2; 4.0 g) was added. This was left for *ca.* 24 h (with occasional stirring) before the solid, now slightly yellow in colour, was removed and placed on a watch-glass to dry in a desiccator. Analysis by FTIR confirmed the substrate, now slightly yellow in colour, had remained as syngenite and had not decomposed back to gypsum.

In an identical manner to that described in Section 2.3.1, a second pigment was prepared with the aim of increasing the amount of dye adsorbed onto the surface. However, when a portion of the solid from the first immersion (1.9 g) was added to an aliquot of the second weld solution and left for *ca.* 24 h (with occasional stirring) then removed and placed on a watch-glass to dry in a desiccator, it became apparent that it had decomposed. Analysis by FTIR confirmed the substrate was now gypsum.

In order to produce a more intensely coloured pigment with only one immersion, a further experiment was conducted using a more concentrated weld solution. An aliquot of the concentrated weld solution described in Section 2.3.1 (5 mL) was left to cool for *ca.* 30 min before adding syngenite (prepared using gypsum and potassium sulfate in Section 2.2; 2.3 g). This was left for *ca.* 24 h (with occasional stirring) before the solid was removed and placed on a watch-glass to dry in a desiccator. While analysis by FTIR confirmed the presence of syngenite, it was no longer the only component within the substrate. It is therefore apparent that although, in principle, syngenite can be used as a substrate for a yellow organic pigment, it remains as a pure substrate only under certain conditions.

2.3.3. Safflower

Safflower petals contain two dyes; the water-soluble yellow dye is generally washed out before the red dye (soluble in alkali) is extracted (see discussion in Section 4.1). However, the use of an alkali in the preparation of the dye solution makes safflower a particularly interesting dye source to consider in the present study as it provides a compelling reason for the addition of an alkali to the dye solution. It perhaps offers an explanation as to how a substrate such as syngenite might be produced from gypsum and an alkali such as potassium carbonate (following a synthetic route such as that outlined in Section 2.2) or potassium hydroxide. This first exploratory experiment was unsuccessful and did not produce syngenite, but the method is reported here nevertheless.

Safflower petals (10 g) were washed in distilled water and left to soak for 1 week to remove a large proportion of the yellow dye. They were then washed again five times with distilled water (the first and second washes used 500 mL and the petals were left to soak for *ca.* 1 h, then the third and fourth washes used *ca.* 250 mL before a final wash using *ca.* 200 mL). Approximately half the petals were then placed in a desiccator and the other half added to a potassium carbonate solution (100 mL; 9.7 g), warmed slightly, and left for one hour. The gypsum was then added (12.1 g) and the mixture stirred for *ca.* 30 min before being left overnight. The following day, the solution was stirred for several hours before citric acid (10%; 10 mL) was added and the solid, now yellowish-orange in colour, removed and placed on a watch-glass to dry in a desiccator. Before addition of the acid, a small sample of the solid was removed and allowed to dry in a desiccator. FTIR analysis indicated the presence of syngenite together with gypsum and chalk. However, analysis of the dried solid after the addition of citric acid indicated that syngenite was no longer present.

The second portion of washed and dried safflower petals (*ca.* 5 g) was mixed with solid potassium carbonate (0.64 g) in a process based on historical methods for testing or extracting the red dye (see Section 4.1) and then transferred to a Buchner funnel with filter paper. Deionised water (50 mL) was gradually added and allowed to drip through (not under vacuum). The same liquid was collected and allowed to drip through the petals

again before a second portion of distilled water (50 mL) was gradually added and allowed to drip through. Any remaining liquid was collected by filtration under vacuum and the combined filtrate (*ca.* 80 mL) split into two equal portions. Citric acid (10%; 5 mL) was added to the first portion until a fine precipitate appeared, indicating that safflower red pigment was indeed present and had been soluble in the alkaline solution. The pigment was left to settle and then removed from the solution and allowed to dry in a desiccator. It is very possible that such a pigment could have been manufactured then ground with a suitable white substrate, such as gypsum or syngenite. However, another possibility is that the white material was added to the dye solution, thus syngenite (prepared from gypsum and potassium sulfate in Section 2.2; 1.0 g) was added to the second portion, followed by citric acid (10%; 5 mL). The mixture was stirred for *ca.* 30 min, then the solid, now red in colour, removed and placed on a watch-glass to dry in a desiccator. However, FTIR analysis of the dried solid confirmed that the syngenite had decomposed and was no longer present.

3. Results

The analytical investigations undertaken to establish the presence of syngenite in the glaze layer on the surface of the yellow foliate design are presented below.

3.1. Analysis of Layer Structure of Yellow Foliate Pattern of Border

A cross-section prepared from a paint sample taken from the yellow foliate pattern revealed the following stratigraphy (Figure 6a,b). Directly on top of the red earth paint of the background (1) is an opaque yellow paint layer (2) containing bright yellow particles with thin tabular and foliated fragments. These are clearly visible in the back-scattered electron (BSE) image (Figure 7) and SEM-EDS analysis of these yellow pigment particles confirmed the presence of arsenic (As) and sulfur (S), suggesting the presence of the arsenic sulfide pigment orpiment (Figure 8), and this was confirmed by micro-XRD. A few particles with similar characteristics and elemental profile were also found to be present in the overlying semi-translucent yellow layer (3). In UV illumination (Figure 6b), the substantial translucent yellow glaze layer seemed, in addition to the few inclusions of orpiment, to also contain other particles. There was also a thin fragmentary layer on the surface which fluoresced a milky white in UV; this was most probably varnish (4).

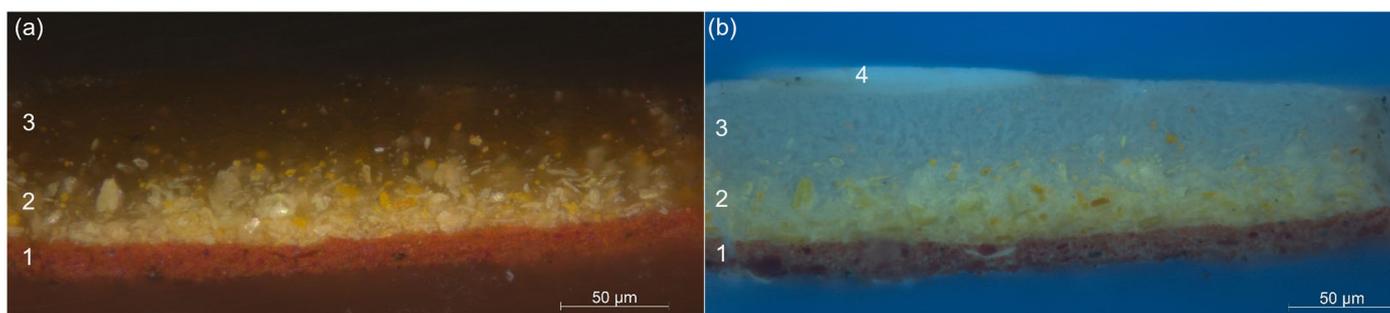


Figure 6. (a) Paint cross-section taken from the yellow border design in dark field-reflected light. Stratigraphy from the bottom upwards: 1. Red iron earth paint layer; 2. orpiment 3. yellow glaze layer with a few particles of orpiment present, particularly in the lower portion where layers 2 and 3 are intermixed. (b) Paint cross-section in 5a photographed in ultraviolet light (excitation filter 340–380 nm). 1. Red iron earth paint layer; 2. orpiment; 3. in UV illumination a particulate structure is visible in the yellow glaze layer; 4. trace of early/original varnish which remains on the surface of the sample. © The National Gallery, London.

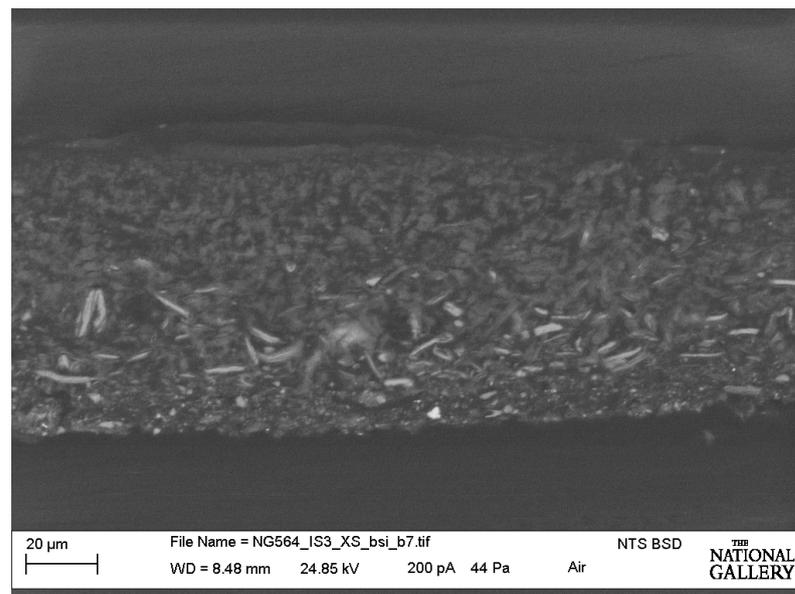


Figure 7. Back-scattered electron (BSE) image of the paint cross-section in Figure 6, clearly showing the particles present within the glaze layer.

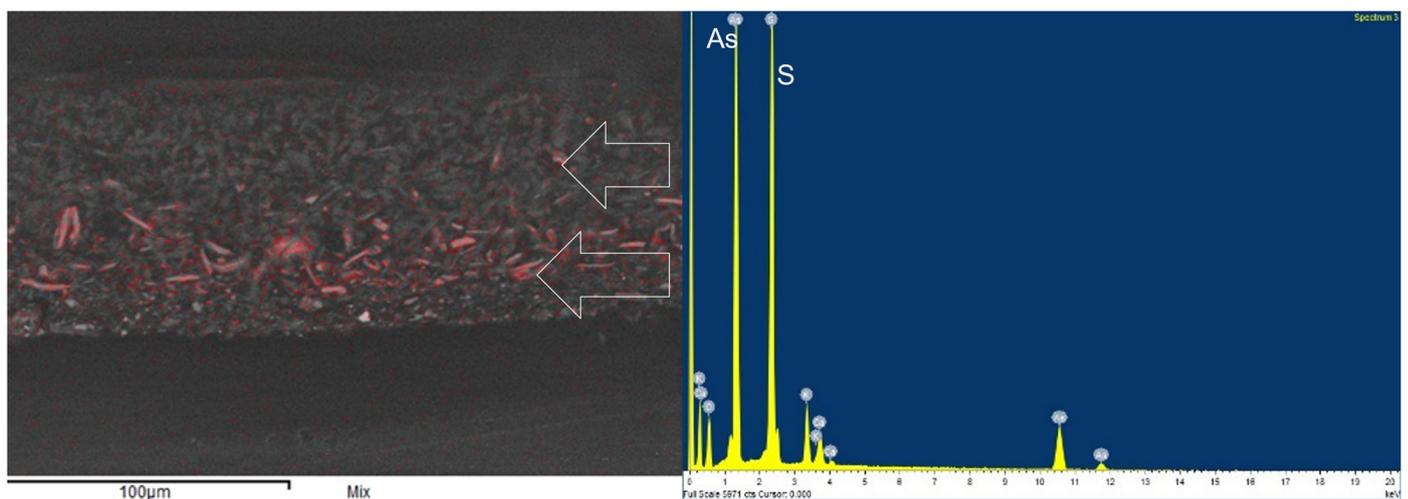


Figure 8. (Left) Back-scattered electron image of the paint cross-section with X-ray map for arsenic (As) in red, indicating the presence of particles of orpiment in the yellow paint layer and also a few within the overlying glaze. (Right) SEM-EDS spot spectrum confirming the presence of arsenic (As) and sulfur (S). This spectrum is representative of a large number of particles that were analysed in the sample.

To gain a clearer idea of the structure and composition of the particles visible under UV illumination in the translucent glaze layer and in the BSE image, SEM-EDS analysis was undertaken. This indicated the presence of sulfur, potassium and calcium, suggesting a complex potassium sulfate salt within the layer (Figure 9). ATR-FTIR analysis indicated that the inorganic component was homogeneous in composition and excluded the presence of either calcium sulfate or indeed chalk (data not shown). It also confirmed that the egg tempera binder was present in both the upper and lower layers, suggesting that the upper yellow layer was a paint or glaze layer rather than a degradation crust or discoloured varnish. Thus, it seems likely that the inorganic material within the upper layer is the substrate for a yellow organic “lake” pigment, which would have been used to produce a yellow glaze paint over the yellow foliate pattern painted in orpiment.

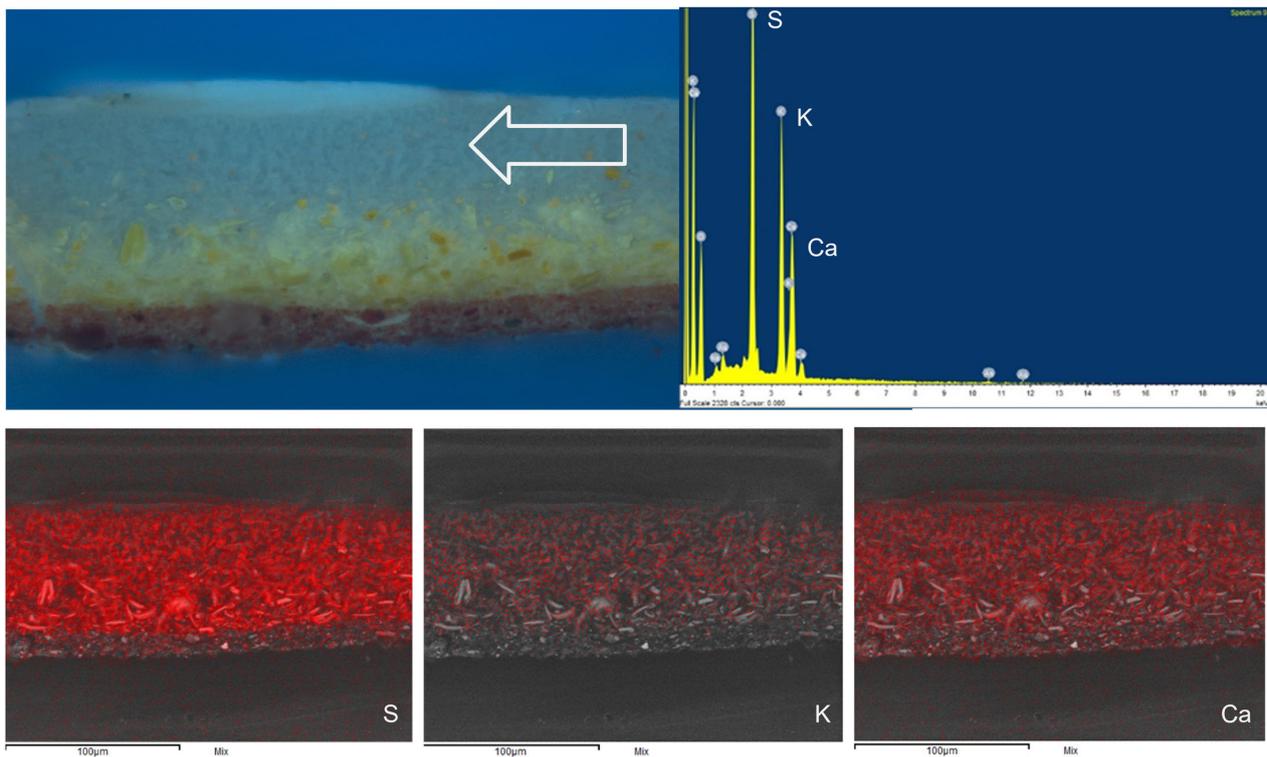


Figure 9. Image of the cross-section as shown in 6b with an SEM-EDS spot spectrum from a representative particle within the glaze layer showing the presence of sulfur (S), potassium (K) and calcium (Ca). **Below (from left to right)** are back-scattered electron images with X-ray maps (in red) for sulfur, potassium and calcium.

MA-XRF mapping provided further evidence for the painting technique used for the foliate perimeter border. The arsenic map (Figure 10) clearly shows the location of the yellow, orpiment-rich (As_2S_3) paint of the foliate pattern painted over the red iron oxide background. The foliate pattern is also visible in the potassium map (present in syngenite), which shows where the yellow lake glaze was applied over the orpiment paint along the entire length of the border design. The foliate design is visible as a negative in the iron (Fe-KA) map because the signal for iron is masked by the arsenic from the orpiment-containing yellow paint on top.

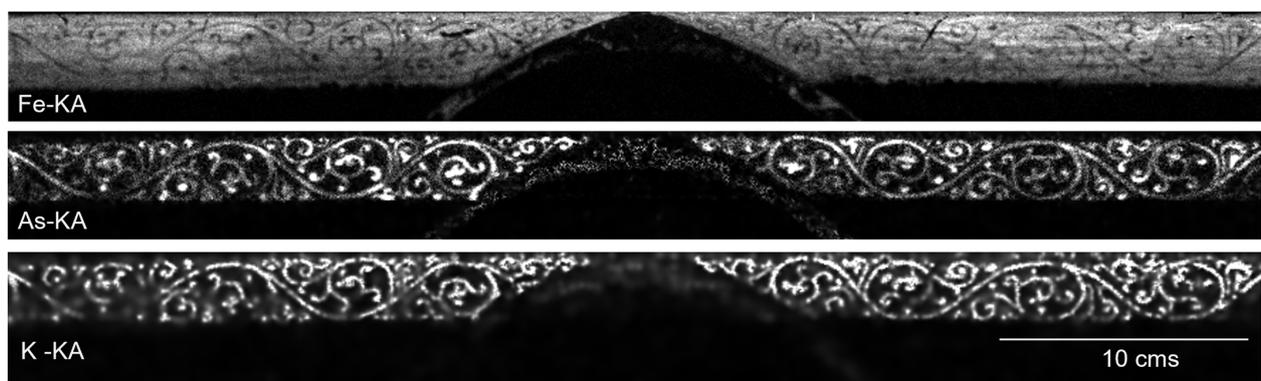


Figure 10. MA-XRF scanning: **(top)** iron distribution map (Fe-KA) showing the red iron earth paint of the background; **(centre)** arsenic distribution map (As-KA), showing the location of the arsenic sulfide pigment orpiment; **(below)** potassium distribution map (K-KA), showing the location of potassium present in syngenite from the yellow glaze layer along the whole length of the border design on the upper edge of the painting. © The National Gallery, London.

3.2. Identification of Syngenite (Micro-XRD Analysis)

In order to precisely identify the complex sulfate indicated by SEM-EDS and FTIR analysis, micro-XRD was undertaken. The major phase present in all the sub-samples from an unmounted fragment of the glaze layer was confirmed to be syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$. The XRD pattern for one of these sub-samples (IS3-5) is shown in Figure 11. The major and minor phases identified in all sub-samples are summarised in Table 1.

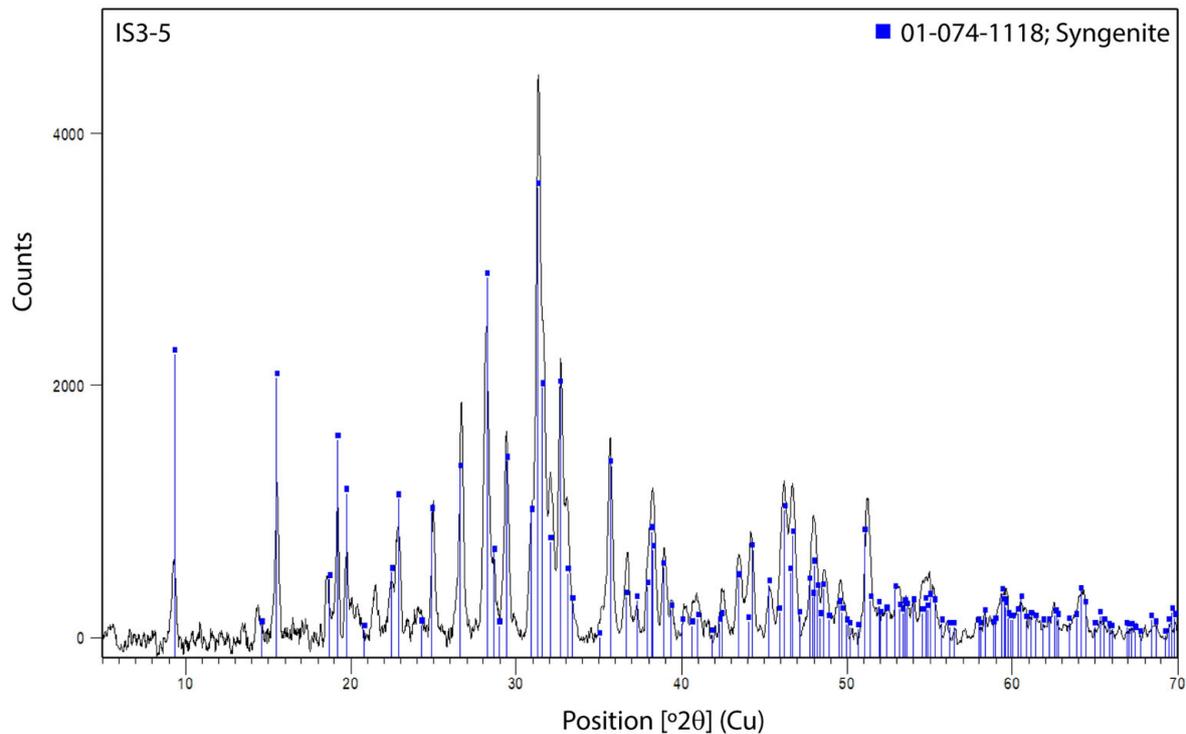


Figure 11. Micro-XRD pattern of an unmounted fragment (sub-sample IS3-5) from the glaze layer, confirming the presence of syngenite as the major phase.

Table 1. Phases identified from micro-XRD patterns of the unmounted sub-samples from the yellow glaze layer.

Sample ID	Major Phase	Minor Phase/s
IS3_1	syngenite	weddellite; calomel or polyhalite
IS3_2	syngenite	weddellite; calomel or polyhalite; anhydrite
IS3_3	syngenite	calomel or polyhalite; possibly trace of weddellite
IS3_4	very weak diffraction signal indicating the presence of amorphous material	
IS3_5	syngenite	Calomel or polyhalite

There is no doubt about the identification of the major phase syngenite in all fragments from the sample. The minor phases are harder to confirm, but the results suggest small quantities of weddellite (calcium oxalate) in three of the five fragments from IS3. The presence of small amounts of oxalate is not unusual in very aged paint layers, particularly at or near the surface. A trace of anhydrite was also suggested in one sample, while an unassigned peak with low intensity at 21.5° in four of the fragments could be explained with calomel (Hg_2Cl_2) or with polyhalite $K_2Ca_2Mg(SO_4)_2 \cdot 2H_2O$, which has a similar composition to syngenite.

4. Discussion

4.1. Organic Lake Pigments: Recipes and Possible Dye Sources

By the mid-13th century, the method of making red lake pigments by extracting the dye from the raw material using alkali and precipitating the pigment by the addition of potash alum had been known for several hundred years [6] (for lac and kermes, see nos. 174A–6, pp. 52–53, for example or for madder, nos. 188–9, p. 54). The deep-crimson lac lake in particular has been identified quite frequently in 13th- and 14th-century works [7] (pp. 89–95), and the way this translucent pigment has been used to paint the shadows in the folds of the Virgin's skirt is very characteristic. Yellow organic pigments seem to have been used as glazing pigments less frequently; in fact, they are rarely identified in paintings of this period, perhaps partly because they are not lightfast, and analytical evidence is thus lacking. They have, however, been identified in 14th-century Italian (Tuscan) paintings used in mixtures: for example, with blue pigments, such as azurite, to give greens, and with rather muted yellow ochres to give a brighter, more vibrant yellow [8]. In the present case, HPLC analysis was undertaken on a small paint sample taken from the foliate design in an attempt to identify any remaining dyestuff in the glaze layer, but no result was obtained. This is probably due to the very tiny sample size and perhaps also because yellow dye components are notoriously light-fugitive [9].

Yellow lake pigments are not well-documented: there are very few recipes for them dated before the late 14th century. Those that are known indicate that the pigments were made by precipitation or adsorption onto a suitable white substrate, which could include a local white earth or limestone, gesso, marble chips, lead white or even white flour, sometimes with the addition of alum to the dye solution. The earliest pigments based on organic dyes were made in this way and examples are recorded in Classical Roman sources: in *De architectura* (c. 30–20 BCE), Vitruvius describes how to make a yellow ochre-coloured pigment by heating dried violets in water and grinding the coloured solution with chalk [10]. Pigments were also made from flower petals directly, expressing the juice and mixing it with a suitable white substance. This, too, was a very old method, described in the first book of the so-called *De coloribus et artibus romanorum*, attributed to Eraclius (or Heraclius). This text consists of three books, the first two of which are in verse form. These probably date from around the 10th century and the author is believed to have been Italian. In a recipe from the first book, fresh flowers were ground on a smooth stone with raw gypsum, giving a pigment that could be stored dry. The third book, which is a prose text probably dating from the 13th century and by a French author, contains similar instructions to those described by Vitruvius centuries earlier [11] (vol. 1, no. II, pp. 184–185, no. LV (245) pp. 250–251). These methods were often used to make pigments from blue flowers, such as cornflowers (adding lime if a green was required) and are repeated in later sources. It is worth noting that these pigments probably were intended for use in aqueous media on parchment or paper.

It was only towards the end of the 14th century that recipes incorporating alum as an ingredient, together with a white material as substrate, began to appear, although in practice, pigments of this sort were probably used considerably before this. The 15th-century *Segreti per colori*, better known as the Bolognese manuscript from its publication by Mrs Merrifield in 1849, contains instructions for a bright yellow for use on paper made with saffron and lead white and a more familiar yellow, named *arzica*, made using a concentrated solution of the dye from weld (*Reseda luteola* L.) to which alum and either finely ground marble or lead white were added [11] (vol. 2, nos. 184, 194, pp. 480–483). Similar instructions occur in other 15th-century Italian sources. Alkali is rarely mentioned as an ingredient, although one example is a recipe for a yellow described as 'finer than orpiment or German giallolino', made using a strong extract of ripe buckthorn berries (*Rhamnus cathartica* L.) to which is added a solution of strong alkali mixed with alum. This gives a green solution, which is mixed with a fine white earth, repeating this several times to build up the colour [11] (vol. 2, no. 105, pp. 428–429). It is slightly surprising that this recipe should give a yellow as the ripe berries are the source of the pigment sap

green; unripe berries are generally used for yellow pigments. Yellow pigments made from buckthorn berries are notably warmer in colour than those given by weld, which can be cool and acidic-looking.

The absence of alum from the yellow lake pigment found over the orpiment used to paint the decoration on the red border suggests that the yellow pigment was made in the simplest way, mixing a concentrated solution of yellow dye extracted from a plant source with the white material forming the substrate, repeating this process to build up the colour as required. If the pigment was a warm yellow colour, buckthorn could be a source of the dye, although other sources such as sawwort or weld are also possible.

Although there is no evidence at all for the use of alkali in making such a pigment at a date as early as the 13th century (required if it is assumed the syngenite substrate was unexpectedly synthesised during the lake-making process), there is no reason against this being done either; the use of alkali to extract flavonoid dyes such as these does result in more intense colours, and this might have been observed by dyers [12]. However, the possible identification of safflower red in the trace of red glaze on the border of the Virgin's veil in a damaged 13th-century painting of the Virgin and Child in the Istituto Santa Caterina in Arezzo suggested that safflower red was worth studying: this is unusual in that alkali must be used for extraction of the dye [1].

As mentioned above (Section 2.3.3), safflower contains two dyes, a red and a yellow, neither of which is lightfast; the water-soluble yellow dye must be washed out before the red can be extracted. The use of safflower in Europe as early as the 13th or 14th centuries is not well-documented, least of all in painting; the tentative identification of the pigment used as a glaze over gold in the 13th-century painting in Arezzo by Daveri and co-workers is a rare example [1] (pp. 401–402), [13]. By contrast, it was quite regularly used in 14th-century Middle Eastern manuscript production for illumination over gold, exactly as seen in the Arezzo painting, and was also used to dye paper [14,15]. It seems likely that, like several other dyes, the extraction and use of the safflower red dye in Italy had its origins in Arabic practice spreading across Mediterranean regions and then further north; certainly early descriptions of the dye and its extraction are found in 10th- and 11th-century Arabic sources [16] (see p. 195, attributed to Abū Mūsā Jābir ibn Ḥayyān, died around 806–816 CE), [17] (pp. 30–31, 44–45; al-Mucizz ibn Bādīs, written in about 1025 CE). By the first decade of the 14th century, its use in dyeing was well-understood and is, for example, recorded in Lucca [18]. A few years later in 1316, also in Lucca, dyeing equipment sold to Landino Parpaglioni by the merchant Ranieri Malisardi included two presses of some description, a wide, shallow vessel and a sieve, all for working with safflower [18] (p. 170). That safflower was a regular item of trade is also indicated by the description of how to test its quality by the Florentine merchant Francesco Balducci Pegolotti in *La pratica della mercatura*, a handbook compiled between about 1320 and 1340. Pegolotti describes how the sample of safflower to be assessed is tested in a way very similar to the manner described in Section 2.3.3 above, washing out the yellow dye and then obtaining the red by mixing the washed petals with dry wine lees, pouring water through the mixture, and finally acidifying with strong vinegar. If a good vermilion red colour is produced, with very little effervescence, the sample is of good quality; if the solution becomes white, with a lot of effervescence, the safflower is of bad quality [19].

Pegolotti's description matches the few extant dyeing recipes from this period very closely [20,21]: if he had put a piece of textile into the final solution the red colour would have been precipitated onto it. To make a pigment, the red material could be allowed to settle, collected, and ground with a suitable white substrate. Alternatively, the white material (gesso, for example) could be present in the vessel so that precipitation took place onto it. However, not enough is known about workshop practices at this time to provide a firm indication of how such a pigment would have been made and, without positive identification of any dye components from HPLC analysis, the dye source remains unknown for the presumed organic pigment on the yellow foliate design on the border of *The Virgin and Child Enthroned* by Margarito d'Arezzo.

4.2. Syngenite and Its Possible Use as a Substrate for a Yellow Organic Lake Pigment

Syngenite has previously been identified on paintings, but it has generally been found only in very small amounts and usually as a degradation product [22–24]. For example, syngenite was identified in an orpiment-containing paint layer, applied in imitation of gold, on a 13th-century painting by Cimabue [22]. The authors suggest that syngenite is present as a secondary mineral following the degradation of the orpiment-containing paint layer. Similarly, syngenite was identified together with schultenite, mimetite and palmierite in areas originally painted with orpiment in a 17th-century Dutch painting [23]. It is also suggested that these secondary minerals formed as a result of the degradation of orpiment.

However, in the sample taken from the Margarito painting under discussion, no evidence of orpiment degradation was found by SEM-EDS analysis and no arsenolite was identified during XRD analysis. Arsenolite is usually the starting point for deterioration of orpiment via light-induced photooxidation and its absence in the samples under investigation is significant. Indeed, the syngenite observed on the painting by Margarito is homogeneously present within an apparently continuous glaze layer over the yellow foliate design of the border (Figures 6–10). This is puzzling and requires explanation. It is our hypothesis that its presence is most likely explained as the substrate of a yellow organic “lake-type” pigment which, when applied over a layer of orpiment (see Figure 6) must have produced a rich and intense yellow or orange-yellow colour (depending on the dye source used), perhaps intended to imitate the appearance of gold.

Assuming the syngenite does indicate the presence of a yellow organic pigment, the question then arises as to whether the syngenite itself was used as a white substrate on which to adsorb a yellow dye (see discussion in Section 4.1) or whether it is an alteration product of some kind. While it is impossible to come to any definitive conclusions in this regard, some possible scenarios are outlined below.

The syngenite may have been found, either in mineral form or precipitated from solution (perhaps accidentally) and used in the lake-making process as a convenient white substrate. Although rare in absolute terms, syngenite can be found in marine and volcanic deposits [25,26], and this would be the simplest and most straightforward explanation. In Italy, for example, deposits are known in the Campania, Piemonte, Lazio and Apulia regions. However, the particles in the cross-section are relatively small and fairly uniform in size and do not have the appearance of having been ground from a mineral source. In addition, although exploratory experiments using syngenite to adsorb a yellow dyestuff (in this case, extracted from weld) were partially successful (Section 2.3.2) they also indicated that syngenite is prone to decomposition and only remains as a pure substrate during the pigment-making process under certain conditions.

Syngenite can be prepared relatively easily by stirring stoichiometric amounts of gypsum with potassium sulfate [3], and much of the modern scientific literature on this topic is focused on trying to avoid its formation during the production of the relatively useful potassium sulfate from industrial waste streams containing phosphogypsum [27]. Although potassium sulfate is unlikely to have had any technological uses in the 13th century, if it was known at all, the extremely low solubility product of syngenite means that it will readily precipitate from a solution containing the correct proportion of calcium, potassium and sulfate ions. It is therefore possible to imagine an alternative scenario, avoiding the need to collect the syngenite, whereby it was unexpectedly synthesised during the manufacture of the organic pigment itself, perhaps from a ‘standard’ white substrate such as gypsum.

Preliminary experiments exploring the possibility of syngenite production during the lake-making process indicated that it could be formed by the addition of gypsum to a solution containing potassium carbonate—a substance that would have been available in the 13th century, either converted from cream of tartar, or in the form of wood ash alkali (Section 2.2). The use of potassium carbonate (or any other alkali) when preparing a yellow organic pigment is unusual, but would have been necessary when using a dye source such as safflower (see discussion in Section 4.1). A more pressing problem in this case,

however, is that calcium carbonate (chalk) is also formed during the reaction and no chalk was observed in the syngenite-containing layer in the cross-section from the Margarito painting. The recipe for the preparation of safflower pigments requires the addition of acid (in the form of citric acid from lemon juice or acetic acid from vinegar) and while this has the potential to remove the chalk, preliminary experiments were unable to produce a syngenite-containing substrate (Section 2.3.3). Another possibility, not yet explored, is the use of a strong alkali, potassium hydroxide, made by putting wood ash ley over quick lime.

It should be acknowledged that when making pigments of this type, the process of adding the substrate to a strongly coloured solution was often repeated to build up the colour and this repetition (and the exact conditions in the dye solutions) are particularly difficult to recreate. Thus, while it is entirely possible that syngenite, either collected or unexpectedly synthesised, was used as the white substrate on which to adsorb a yellow dye, there is currently no specific evidence for this. The alternative possibility, whereby the syngenite is a degradation product, formed within the paint due to degradation of a 'standard' yellow lake substrate such as gypsum, is also worth considering but is similarly speculative and is perhaps the least likely scenario. Firstly, there is no obvious source of potassium ions within the paint layers, nor any indication of how they would have migrated throughout the paint to create such a uniform layer of syngenite. It is possible that a harsh cleaning of the painted surface using alkali may have provided such an environment; however, the relatively low density of syngenite compared to gypsum would presumably result in a significant dimensional change to the paint layer during any such transformation. The paint layer containing the syngenite is still intact, following closely to the yellow orpiment lines of the design and does not appear to have been disrupted in this way.

5. Conclusions

A multi-analytical approach has provided evidence for the use of several types of organic colourant on *The Virgin and Child Enthroned* by Margarito d'Arezzo, with both indigo and a red lake pigment unequivocally identified. Micro-XRD analysis confirmed syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) was present in a translucent paint layer on top of a yellow scroll design on the border, and it is argued that this is likely to be the substrate for an organic yellow lake pigment. Exploratory experiments to investigate whether the syngenite itself may have been used as a white substrate on which to adsorb a yellow dye or whether it might represent an alteration product of some kind were inconclusive, but documentary evidence confirms that yellow organic pigments were being produced from an early date and several possible dye sources suggested. Since there is very little direct evidence for the use of yellow organic pigments in 13th-century panel paintings, the identification of syngenite as a possible substrate or alteration product is both an unusual and an important observation.

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