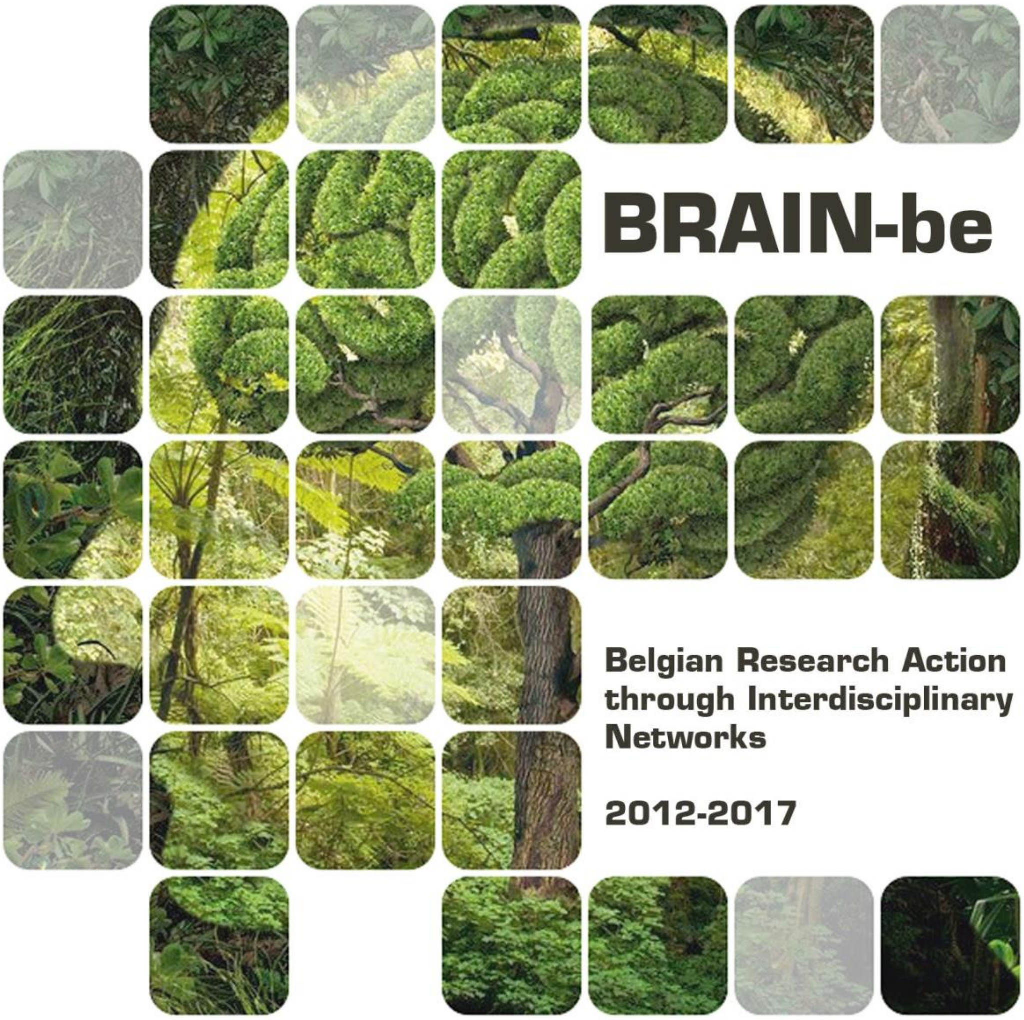

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Networks

2012-2017

The MetOx Project

A macro-to-microscale investigation of the metal-oxalates phenomenon in Southern Netherlandish oil paintings from the 15th to the 17th centuries

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Metal-oxalates in the 15th to 17th Century Southern Netherlandish oil paintings

Contract - BR/165/A6/Metox

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ABSTRACT

Context

For more than two decades, heritage science has attempted to describe the complex physicochemical mechanisms governing oil binder and pigment transformations as oil paintings age through time. Metal oxalates constitute one of the families of ionic species that have recently been identified as a new type of alteration products in numerous oil paintings. These coordination complexes are considered highly problematic as they can precipitate on the paint surface, forming a thick, opaque, highly insoluble crust, which radically modifies the visual properties of an artwork and alter its readability. However, unlike metal soaps, the mechanistic aspects of metal oxalate formation within oil paintings had been much less investigated at a fundamental level until they were systematically addressed by the MetOx project.

Objectives

The MetOx project was based on three major research axes: (i) the multi-instrumental, microanalytical characterization of cross-sections belonging to major Southern Netherlandish oil paintings produced from the 15th to the 17th centuries; (ii) the non-invasive and non-destructive macroanalysis of a selection of historical Southern Netherlandish oil paintings belonging to the study group; and (iii) the macro-to-micro characterization of the alteration phenomena in different model systems collections of varying compositions and ageing conditions. These research endeavours pursued a threefold objective:

i. To develop an analytical protocol comprising a macro-to-microscale approach making it possible to localize and qualitatively evaluate the presence of metal oxalates formed in oil paint surfaces and strata.
ii. To propose and experimentally verify a mechanism for metal oxalate formation from the results of the analyses of the selected Southern Netherlandish 15^{th} to 17^{th} century paintings and from modelling and fabrication of equivalent mock-up samples, that were subjected to accelerated ageing and macro-to-micro analysis.
iii. To propose preventive conservation-restoration guidelines aimed at reducing the rate of formation of metal oxalates in Southern Netherlandish oil paintings on the basis of the information obtained by application of the developed analysis protocol.

Conclusions

By interlinking results obtained at the macro and microscales, both in historical paintings and model systems, we have identified that certain pigments (e.g. red lakes, verdigris, smalt and ultramarine), fillers (e.g. calcium carbonate used in a paint's ground layer) or driers (e.g. white vitriol) unequivocally favour the formation of specific metal oxalates within oil paint layers. Furthermore, we have been able to prove that, in the presence of the above-stated materials, the oxalate anion is produced through a humidity-mediated, photochemical degradation of the oil binder, thus offering novel insights into the transformation processes that lead to the formation of metal oxalates within oil paint layers as they age.

Keywords

Southern Netherlandish Painting - Metal-oxalates – Oil paint alteration

1. INTRODUCTION

Historical oil paintings are highly complex chemical systems composed of mixtures of inorganic and organic materials such as pigments, extenders, ground fillers, driers and drying oil-based binders [1]. During ageing, these materials undergo numerous chemical transformations influenced by the material composition of the artwork itself but also by environmental factors such as light, temperature, air-borne pollutants and relative humidity [2-4]. Some of these transformations threaten the long-term stability and preservation of the paint materials and, consequently, of the aesthetic, historic, social and technological values that are embodied in the materiality of these artworks. It is thus essential to preserve the visual and material aspects of these artworks as little changed as possible for future generations.

Accordingly, for more than two decades, heritage science has attempted to describe the complex physicochemical mechanisms governing oil binder and pigment transformations as paintings age through time. As research advances, our model of an oil paint layer has shifted from that of a dispersion of pigment particles in a relatively stable, predominantly covalently-bound, cross-linked oil network towards a reactive, metastable mixture of oxidized and ionic compounds in which complex pigment-binder interactions systematically occur [4-9].

Such an ionic nature has been proven to be of fundamental importance to explain the mechanical properties of an oil pictorial layer [10, 11], its sensitivity to solvents [4, 12-14] or some of its alteration processes [4-6,15]. Of the various ionic species formed during the ageing of the paint layer, metal oxalates and soaps are the most frequently described [16-18]. The formation of these carboxylate species within the paint film needs to be considered as they modify the physical, chemical and aesthetic properties of paintings. For instance, the presence of metal soaps has been associated with an increase in a painting's brittleness or transparency or with delamination [8]. They have also been found to produce highly disfiguring efflorescent hazes or crusts [19] or pustule-like protrusions [10]. Likewise, precipitated metal oxalates sometimes form thick, opaque and completely insoluble crusts at the surface of paintings [20]. Consequently, the international heritage community is actively engaged in understanding the underlying physicochemical mechanisms that produce these species as well as the environmentally-induced or conservation-related factors that promote their formation.

The MetOx project was created to tackle some of these fundamental unknowns. This research venture, coordinated by the Royal Institute for Cultural Heritage (KIK-IRPA), brought together two Belgian universities (University of Antwerpen (UA) and the Catholic University of Louvain-la-Neuve (UCLouvain)), the Royal Museum of Fine Arts of Belgium (RMFAB), as well as two international partners, the National Gallery London (NGL) and the European Synchrotron Research Facilities (ESRF). Overall, 13 different researchers and 7 B.Sc., M.Sc. and PhD students from the above-mentioned institutions were involved for almost 5 years in the characterization of fundamental aspects (*e.g.* chemical composition, spatial distribution, pigment-specific reactivity patterns, etc.) of the metal oxalate phenomena in major Southern Netherlandish oil paintings created from the 15th to the 17th centuries. Likewise, in order to identify which pigment-binder interactions and environmental conditions can cause the formation of the different metal oxalates found in such oil paint layers, model systems were purposedly designed and evaluated. The results of these endeavours strongly contribute to the advancement of our current understanding of the complex chemical transformation processes occurring in oil paint layers as they age.

2. STATE OF THE ART AND OBJECTIVES

Metal oxalates are coordination complexes composed of the oxalate anion and a metal cation. In the case of oil easel paintings, the most commonly found oxalate complexes include calcium [18, 21], copper [18, 22], zinc [23, 24] and rarely, lead [18] as metal cations. However, the mechanistic aspects of the metal oxalate formation in oil paintings have been little investigated at a fundamental level and thus their precise origin has not yet been fully elucidated [18, 21, 23, 24-26].

Results published in the scientific literature suggest that the genesis of the oxalate anion involves different mechanisms, depending on the artworks' constituent materials and the environmental conditions to which they were exposed. For instance, in the case of outdoor wall paintings and monuments constituted of calcareous stone materials, the formation of calcium and copper oxalates has been explained and demonstrated mainly by microbiological activity [27-30], though formation due to applied conservation treatments and atmospheric pollution has also been proposed [31, 32]. For easel (and other weather-protected) paintings the presence of metal oxalates has been attributed to chemical interactions between the pigment and the varnish layer [23, 26], to reactions between the pigment and oxalic acid present in aerosols [24], or to photodegradation of the binder [21, 33], especially given if the latter has a high lipidic content such as in drying oils and egg tempera [34]. Indeed, it has been demonstrated that ageing conditions including exposure to ultraviolet (UV) radiation and high relative humidity (%RH), can induce the oxidation of fatty acids and favour the formation of low molecular weight dicarboxylic acids [34, 35]. In such a process, the catalytic role played by certain copper, lead, zinc and chromium-based pigments has been also noted [21, 23, 35]. Nonetheless, direct proof of the formation of the oxalate anion from an oil binder under these environmental conditions (*e.g.* UV radiation and high RH) and the presence of such transition metals is yet missing.

Pigments are also considered to be one of the possible sources of the metal cations forming the oxalate coordination compounds [20, 36], thus determining the type of metal oxalate found in certain historical oil paint layers. For instance, copper oxalates have been commonly found in oil paint films containing either copper acetate or basic copper chloride pigments, such as in a series of XVth century Gothic Catalan paintings [18] or Hans Memling's *Christ with Singing and Music-making Angels* altarpiece [20]. Nonetheless, they seem to be absent in paint films containing other copper-based pigments such as azurite [36]. Lead oxalate has very rarely been found and only in red layers containing minium (Pb_3O_4) or in lead-tin yellow-containing paint layers [18, 25] while cadmium oxalates have been found associated to cadmium yellow (CdS) in paintings such as *Flowers in a blue vase* by Vincent van Gogh [37] and in *Le bonheur de vivre* by Henri Matisse [33]. Zinc oxalate has been found in several XIXth and XXth-century oil paintings by Munch or Picasso [24] and by van Gogh [36]. In the above-mentioned paintings, it was proven that zinc oxalate originated from the zinc white pigment, possibly due to this pigment's recognized photoactivity [23]. As for calcium oxalates, the most frequently found metal oxalate in easel paintings [18, 20, 22, 36], the origin of the calcium cation is usually attributed to either calcium-containing materials (*e.g.* ground fillers or lake substrates) in the paint and ground layers or from particulate matter such as dirt deposited onto the paint surface [20, 22].

Notwithstanding the different scientific reports indicating the presence of oxalates in historical paintings, this category of metal carboxylates has not yet been systematically studied by the heritage science community. Thus, it is not yet clear which mechanism(s) are involved in the formation of the oxalate anion in oil paint films. Moreover, it is not known which compositional (*e.g.* binder type, pigments, etc.) or environmental conditions (*e.g.* light or relative humidity) promote their formation. Furthermore, available reports indicate that these coordination compounds are mostly found at the surface at the pictorial layer but very little is known about their occurrence, chemical composition and spatial distribution within the paint layers themselves.

Considering the above important gaps in our understanding of the metal oxalate phenomena in historical oil paintings, the MetOx project aimed to:

i. Develop an analytical protocol from the macro to the microscale to allow the evaluation of the abundance, chemical identity and spatial distribution of metal oxalates formed in oil paint surfaces and strata.
ii. Propose and experimentally verify a mechanism for metal oxalate formation based on the use of model systems subjected to accelerated ageing.
iii. Propose preventive conservation-restoration guidelines aimed at reducing the rate of formation of metal oxalates in Southern Netherlandish oil paintings on the basis of the information obtained by application of the developed analysis protocol.

3. METHODOLOGY

The MetOx research venture was based on three major research axes:

i. The non-invasive and non-destructive macroanalysis of historical oil paintings selected according to the microanalytical results.
ii. The multi-instrumental, microanalytical characterization of cross-sections belonging to historical oil paintings.
iii. The macro-to-micro characterization of the alteration phenomena in three different collections of model systems of varying materialities and ageing conditions.

In order to lead such research endeavours, a series of selection criteria was applied. Thus, the project was focused only on historical oil paintings, and associated cross-sections, produced between the 15th and the 17th centuries in the Southern Netherlands and mostly belonging either to the Royal Museums of Fine Arts of Belgium (RMFAB) or the National Gallery, London (NGL). Furthermore, only areas that were red, green or blue in colour at the surface of such paintings and their corresponding samples were studied. Indeed, previous experience from the researchers involved in this project indicated that metal oxalates were more commonly found in such coloured zones, suggesting the paint materials employed to produce those hues influenced the formation of the oxalate species.

The methodology employed for each research axis is briefly described below.

3.1 Non-invasive and non-destructive macroanalysis of Southern Netherlandish oil paintings

Three different macroscopic imaging techniques were used during the MetOx project: macro X-ray fluorescence (MA-XRF), macro reflection Fourier-transformed infrared spectroscopy (MA-rFTIR) and macro X-Ray powder diffraction (MA-XRPD) in reflection mode. Further specifications for the analytical instrumentation employed can be found in **Table 1**.

Table 1 – List of instruments employed for the macroanalysis of historical paintings

Acronym	Name	Instrument specifications
MA-XRF	Macro X-ray fluorescence	XOS Xbeam microtube with a Rh anode coupled to a Vortex EX-90 SDD detector on a motor stage (scan travel range: 57x60 cm^2)
MA-rFTIR	Macro reflection Fourier-transformed infrared spectroscopy	Bruker Alpha FTIR spectrometer with a frontal reflection module mounted on motorized stages (scan travel range: 10x25x10 cm^3)
MA-XRPD	Macro X-Ray powder diffraction	Custom-built scanner featuring an Incoatec Cu^{HB} X-ray source, a Dectris PILATUS 200K 2D diffraction detector and motor stages (scan travel range: 30x30x10 cm^3)

These analytical techniques, developed by the Antwerp X-ray Imaging and Spectroscopy laboratory (AXIS) from the University of Antwerpen (UA), were employed to scan regions from 11 paintings selected from the Royal Museum of Fine Arts of Brussels (RMFAB) collection (see **Table 2**).

The paintings and corresponding regions to be scanned were selected on the basis of two main conditions: a) that they fitted the project's methodological framework concerning the artwork's chronological (*e.g.* produced between the 15th and the 17th centuries) and chromatic (*e.g.* perceived surface colour must be red, green or blue) criteria; and b) that positive evidence for the presence of metal oxalates had been obtained from historical paint cross-sections belonging to these paintings and analysed according to the methods described in section 3.2 below.

Each one of the employed macroscopic imaging techniques produced different types of chemical information about the paintings in a non-invasive and non-destructive manner. MA-XRF allowed the distribution of chemical elements in the paint layers to be visualised and while this information is crucial to produce refined hypotheses on the composition of such paint layers, in this research project this technique was mostly employed to facilitate the interpretation of both MA-rFTIR and MA-XRPD data. These latter two techniques allowed either molecular moieties (MA-rFTIR) or crystalline phases (MA-XRPD) attributable to metal oxalates species to be spatially located at a painting's surface.

The use of MA-rFTIR and MA-XRPD required the compilation of technique-specific metal oxalate reference databases. Consequently, a selection of metal oxalates were analysed using both macroimaging techniques, as either pure powders or as dispersions in linseed oil. Characteristic features were determined that allowed the different analytes of interest to be identified and differentiated based on their rFTIR spectra and rXRPD diffraction patterns.

Table 2 – List of Southern Netherlandish historical oil paintings analysed using macroanalytical techniques during the MetOx project from the collections of the Royal Museums of Fine Arts of Belgium (RMFAB) and Saint Bavo's Cathedral Ghent (SBG).

Century	Painter	Title	Collection
XV	Albrecht Bouts	Assumption of the Virgin Mary	RMFAB
	Jan and Hubert Van Eyck	Adoration of the Mystic Lamb	RMFAB, SBG
	Petrus Christus	Pietà	RMFAB
	Master of the view of St. Gudula	Visitation	
		Fragment of St. Ursula	
XVI	Adriaen Isenbrant	Yaris van de Velde, Mayor of Bruges, and his wife Barbara presented with their children	
	Michiel Coxie	Copy of The Ghent Altarpiece polyptych	
	Colijn De Coter	Saint Michael	
	Master of the Holy Blood	The Holy Trinity	
	Master of the Lyversberg Passion	Christ on the cross between two thieves	
	Master of the Mansi Magdalene	Adam and Eve	
	Wenceslaz Coebergher	The Entombment	

3.2 Microanalysis of historical paint samples

99 embedded paint cross-section samples belonging to the archives of the Royal Institute of Cultural Heritage (KIK-IRPA) or the National Gallery London (NGL) laboratories were selected for this study.

Such a large sample selection was performed to ensure that: (i) the obtained microanalytical results had a statistical significance; and (ii) each category of the project's chronologic and chromatic criteria stated above were equally represented (*e.g.* 33 samples per century and/or per surface colour). As shown in **Table 3**, this sample set includes 45 different, major historical oil paintings produced by 31 of the most renowned old masters and some anonymous painters of the 15th to the 17th centuries in the Southern Netherlands.

Table 3 – List of historical oil paintings produced in the Southern Netherlands from the 15th to the 17th centuries mainly found in the collections of the Royal Museums of Fine Arts of Belgium (RMFAB) and the National Gallery London (NGL). The remaining paintings belong to the Royal Museum of Fine Arts Antwerp (KMSKA), the Louvre (LO), the Maagdenhuis Museum (MA), the City Museum Wuyts-Van Campen en Baron Caroly (LIE), Saint Bavo's Cathedral Ghent (SBG), Cathedral of Our Lady Tournai (TOU), Cathedral of Our Lady Antwerp (ANT), the Church of Saint Martin in Baarle-Drongen (DRO) and the Church of Saint John the Baptist at the Béguinage in Brussels (BRU).

Century	Painter	Title	Collection
XV	Anonymous	Last judgement	RMFAB
	Anonymous	Banner of Gunsmiths	RMFAB
	Albrecht Bouts	Assumption of the Virgin Mary	RMFAB
	Dirk Bouts	Justice of Emperor Otto III	RMFAB
		The Virgin and Child	NGL
	Petrus Christus	Pietà	NGL

	Master of the view of St. Gudula	Visitation and St. Simon Stock	RMFAB
		Fragment of St. Ursula	RMFAB
	Hans Memling	Virgin and Child	NGL
	Jan and Hubert Van Eyck	Adoration of the Mystic Lamb	RMFAB, SBG
	Jan Van Eyck	Portrait of Giovanni Arnolfini and wife	NGL
XVI	Adriaen Isenbrant	Yaris van de Velde, Mayor of Bruges, and his wife Barbara presented with their children	RMFAB
	Joachim Beuckelaer	The four elements: air	NGL
		The four elements: water	NGL
	Hieronymus Bosch	Christ mocked (The crowning with thorns)	NGL
	Pieter Brueghel the Elder	The fall of the rebel angels	RMFAB
	Albert Cornelis and associates	The Virgin and Child in Landscape	NGL
		The Virgin and Child with Sainte Anne (*attributed to*)	NGL
	Michiel Coxie	Copy of Van Eyck's polyptych	RMFAB
	Gérard David	God the Father blessing with 2 angels	LOU
	Colijn De Coter	Saint Michael	RMFAB
	Master of the Holy Blood	The Holy Trinity	RMFAB
	Master of the Legend of the Magdalene	Triptych Of The Quesnoy-Van der Tommen Family	RMFAB
	Master of the Lyversberg Passion	Christ on the cross between two thieves	RMFAB
	Master of the Mansi Magdalene	Adam and Eve	RMFAB
	Marten van Heemskerck	The Virgin and saint John the Evangelist	NGL
	Marinus van Reymerswale (workshop of)	Two tax gatherers	NGL
	Pieter Brueghel the Young	The Preaching of St. John the Baptist	LIE
	Wenceslaz Coebergher	The Entombment	RMFAB
	Frans Hals	Three children with a goat cart	RMFAB
XVII	Jacob Jordaens	Lamentation over the dead Christ	MA
		Portrait of Corenlis van Diest and his Wife	NGL
	Pieter Paul Rubens	Portrait of Paracelsus	RMFAB
		Saint Bavo is received by Saint Amand and Floribert, right panel	NGL
		The descent from the cross	ANT
		The elevation of the cross	ANT
		The resurrection of the Christ	ANT
		The Road to Calvary	RMFAB
	Antoon Van Dyck	Deposition or Lamentation over the dead Christ	KMSKA
		Equestrian portrait of Charles I	NGL
		Saint Martin dividing his cloak with a beggar	DRO
	Theodore Van Loon	An Angel Liberates St. Peter	BRU
		The adoration of the shepherds	RMFAB
		The Holy Trinity with the Virgin and Saint John the Baptist	BRU

Two smaller sample sets, each composed of 8 cross-sections, were created. These samples were drawn from the KIK-IRPA's archive in order to determine if two lead-based pigments, known to be highly reactive in terms of lead soaps formation, also had a tendency to produce metal oxalates and, more specifically, lead oxalates. The first sample set consisted of lead-tin yellow (type I)-containing cross-sections obtained from different panels of the Ghent altarpiece. The second sample set consisted of lead white-containing cross-sections sourced from different historical oil paintings as described in **Table 4**.

Table 4 – List of Southern Netherlandish historical oil paintings from which cross-sections containing mainly lead white were extracted and analysed in this study. The acronyms designating the owning collections are the same as indicated in Table 3.

Century	Painter	Title	Collection
XV	Jan and Hubert Van Eyck	Adoration of the Mystic Lamb	SBG
XVI	Adriaen Isenbrant	Yaris van de Velde, Mayor of Bruges, and his wife Barbara presented with their children	RMFAB
	Wenceslaz Coebergher	The Entombment	RMFAB
XVII	Pieter Paul Rubens	The resurrection of the Christ	ANT
	Antoon Van Dyck	Deposition or Lamentation over the dead Christ	KMSKA

All samples were (re)documented by optical microscopy (MO-VIS/UV) at KIK-IRPA or the NGL. Also, laboratory reports regarding these samples were retrieved from the archives of both institutions and relevant results available from previous analytical campaigns were gathered. Four complementary analytical techniques were selected for the in-depth chemical characterization of the metal oxalate phenomena at the microlevel (see **Table 5**). These techniques were: Attenuated Total Reflection Fourier Transform Infrared microspectroscopy (ATR-mFTIR); Scanning Electron Microscopy - Energy Dispersive using X-Ray analysis (SEM-EDX); microRaman spectroscopy (mRaman); and Time of flight secondary ion mass spectroscopy (ToF-SIMS).

Table 5 –Analytical techniques employed for the microanalysis of historical paint samples

Acronym	Name	Instrument specifications	Institution
MO-VIS/UV	Optical microscopy under polarized (VIS) and ultraviolet (UV) light	Zeiss Axio Imager M1 equipped with a CCD Deltapix camera	KIK-IRPA
		Leica DM4000 M microscope equipped with a Zeiss AxioCam HRc camera	NGL
ATR-mFTIR	Attenuated Total Reflection Fourier Transform Infrared microspectroscopy	Bruker Vertex 70 FTIR coupled to a Bruker Hyperion 3000 FTIR microscope equipped with a 250mm diameter germanium ATR tip	KIK-IRPA
		Bruker Tensor 27 FTIR coupled to a Bruker Hyperion 3000 FTIR microscope equipped with a 250 µm diameter germanium ATR tip	NGL
t-mFTIR	Transmission Fourier Transform Infrared microspectroscopy	Bruker Vertex 70 FTIR coupled to a Bruker Hyperion 3000 FTIR microscope	KIK-IRPA
mRaman	microRaman spectroscopy	Renishaw InVia coupled to a Leica DMLM microscope	KIK-IRPA
SEM-EDX	Scanning Electron Microscopy - Energy Dispersive using X-Ray analysis	Zeiss EVO LS 15 SEM coupled to an Oxford Instruments X-Max^{N} EDX detector	KIK-IRPA
TOF-SIMS	Time of flight secondary ion mass spectroscopy	IONTOF GmbH	UCLouvain

Spectral reference databases of different metal oxalates were constructed for each spectroscopic technique. Samples composed of metal oxalates as both pure powders or dispersions in linseed oil, were analysed using the project partners' analytical expertise: ATR-mFTIR and mRaman spectroscopies at KIK-IRPA's laboratories; and ToF-SIMS at the SUCH platform (UCLouvain). For each analytical technique, the spectral features (or regions of interest, ROI) that allowed identification and differentiation of the different metal oxalates were determined.

Methodological developments allowing the accurate characterization of metal oxalates in oil paint layers were also performed for the ATR-mFTIR and ToF-SIMS techniques.

In the case of ATR-mFTIR, different data-treatment procedures were tested and implemented using OPUS, Orange and PyMCA software in order to fine-tune a methodology allowing the systematic extraction, treatment and archiving of the obtained results. This rigorous approach allowed comparison of results across the large ATR-mFTIR dataset created during the project, composed by 199 different FTIR-imaging measurements.

Regarding ToF-SIMS, a novel data-acquisition methodology was developed. First, a pre-sputtering of the measured surfaces was conducted using an Ar gas cluster ion beam (Ar-GCIB; ion distribution centered around Ar_{3000}^{+}) in order to remove a thin surface layer that was affected by contamination (historical cross sections) and/or non-crosslinked oil (model paint systems) and maximize the pigment/oxalate signals. Then, a highly-focused (0.3 µm) Bi_3^{++} liquid metal ion source (energy 60 keV) was used to produce high resolution secondary ion images, with interlaced bombardments by non-destructive Ar-GCIB to refresh the surface and reach optimal signal/noise ratios.

Finally, as a result of the possibilities offered by the new Historical Materials BAG access to the ID13 beamline of the European Synchrotron Radiation Facility (ESRF), a selection of historical paint cross-sections was investigated using synchrotron-based micro X-ray powder diffraction (SR-µ-XRPD) to investigate their crystalline composition at the microscale.

3.3 Modelling of oxalate formation phenomena

Three different sets of model samples were analysed during the MetOx project:

a) Mock-up stratigraphic oil paint systems
b) Individual paint swatches
c) Zinc-based oil paint swatches

These different sample sets will be shortly described below.

3.3.1 Mock-up stratigraphic oil paint systems

A series of mock-up stratigraphic oil paint systems, composed of twenty-four different combinations of binder, resin and pigment were created at KIK-IRPA in order to determine if pigment-binder (oil or natural resin) interactions could lead to the formation of metal oxalates.

Two types of oil binder (purified and mucilage-containing cold-pressed linseed oil, Kremer 73054 & 73020, designated O1 and O2 respectively), one terpenoid resin (colophony resin) and eight different pigments were mixed and applied following the scheme described in Figure 2 below. Materials were prepared and applied following historical recipes and techniques. Three stratigraphic variations were tested: a first one, codenamed (b), in which the selected oil binder was mixed with the pigments; a second, indicated (v), in which a pine resin varnish was applied on top of a (b) layer; and a third, named (br), in which a mixture of oil and pine resin was used to bind the pigment (see Figure 1). The overall arrangement of the binders/pigments/resin combinations are shown in Figure 2.

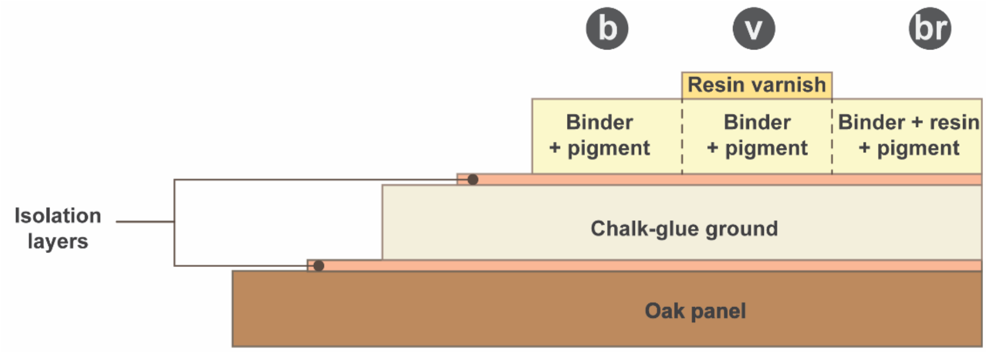


Figure 1 – Stratigraphy of the mock-up panels

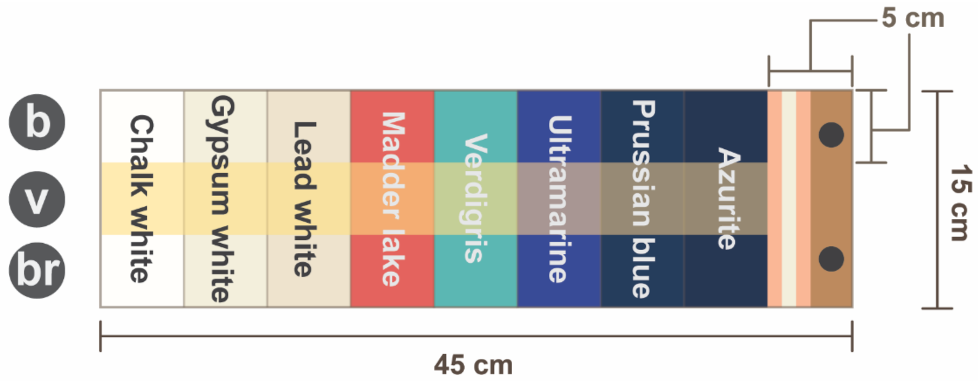


Figure 2 – Dimensions and arrangement of the different pigment-binder-resin combinations in the mock-up panels

Both mock-up panels, named O1 and O2 according to the type of employed linseed oil binder, were placed in an artificial ageing chamber (Weiss Technic , Global UV tester model UV 200 RB/20DU type BAM) at UA. Ageing was performed under the following conditions: UV-A (31,5 ± 2,6 W/m^2) and VIS (1250 ± 210 lux) radiations, 40 °C and a relative humidity (RH) of 80 % (dew point: 35.9 °C). The total artificial ageing time was of 10 weeks. Afterwards, the panels were stored and naturally aged for three years, in the dark, at 20 ºC and 50% RH.

Macroscopic Reflectance Fourier transformed infrared spectroscopy (MA-rFTIR) and Macroscopic X-ray powder diffraction (MA-XRPD), both in line scanning mode, were performed at the AXIS research facilities (UA) before ageing and then, throughout the period of artificial ageing, once a week for 2 weeks, followed by every fortnight, a further 4 times. During the ensuing natural ageing, the panels were again scanned twice, at a one-year time interval.

Following the macroanalytical investigation of these panels, samples were also extracted and transformed into embedded cross-sections at time t_3 (4 weeks) and t_6 (10 weeks) during the period of artificial ageing. Likewise, cross-sections were prepared twice, during the natural ageing of the panels, after the execution of the MA-rFTIR and MA-XRPD analyses. In all cases, these samples were analysed using ATR-mFTIR spectroscopy (Bruker µ-FTIR Hyperion 3000 with a 150-micron Germanium tip) at KIK-IRPA's laboratories, using the same methodology employed for the historical paint samples analyses.

3.3.2 Individual paint swatches

29 samples created by the NGL during various different research projects and stored in their archives were also analysed in the context of the MetOx project. The objective was to complement the results obtained with the mock-up panel painting series described in section 3.3.1 above, by allowing the screening of similar pigments and ground fillers but employed in a wider combination of binders and exposed to a variety of ageing conditions.

In these samples, linseed oil (with or without different types of driers), polysaccharides (gum Arabic) or proteins (glue or egg tempera) were employed as binders. These binders were mixed with six pigments (smalt, verdigris, malachite, artificial and natural ultramarine or madder lake), calcium carbonate-based ground materials or alumina-based lake substrates without the dyestuff components. The resulting mixtures were applied on Teflon or glass substrates and aged under different illumination and humidity conditions, as summarized in **Table 6**.

All samples were analysed using both, transmission Fourier transformed infrared microspectroscopy (t-mFTIR) at KIK-IRPA, and Macroscopic X-ray powder diffraction (MA-XRPD), in point and line scanning modes at the AXIS research facilities (UA).

Table 6 – Description of the paint materials, binders and ageing conditions used in the samples produced by the National Gallery London and reanalysed during the MetOx project

Category	Material	Binder	Ageing conditions
Grounds	Commercially available chalk, marble dust, dolomite	Linseed oil	Unspecified
Aluminium-based lake substrates	Commercial and historical recipe-made alumina-containing lake substrates	Linseed oil with manganese driers	Naturally aged in the dark
Pigments	Commercial and historical recipe-made madder lakes	Linseed oil (with and without Mn-driers), egg tempera	Naturally aged in the dark
	Commercial smalt	Linseed oil with Mn-driers, egg tempera	Unspecified or 30ºC, 45% RH, 5.76 MLux
	Commercial natural and artificial ultramarine	Linseed oil, egg tempera, animal glue	ULT-Plate C conditions, unspecified
	Commercial azurite	Linseed oil, animal glue	High (90%RH) and low (10% RH) under light, 24-27ºC
	Commercial verdigris	Linseed oil with Mn-driers, gum Arabic	High (90%RH) or low (32% RH) under light or in the dark, 24-27ºC
	Commercial malachite	Linseed oil with Mn-driers, gum Arabic	High (90%RH) or low (32% RH) under light or in the dark, 24-27 ºC

3.3.3 Zinc-based oil paint swatches

In order to test the influence of UVA light irradiation and relative humidity in the formation of zinc oxalates, zinc white (ZnO) and zinc yellow ($KZn_2(CrO_4)_2(H_2O)(OH)$) paints were produced by mixing these pigments with raw linseed oil with 5 %(w/w) *Siccative de Haarlem* (Talens 24285085) . A binder-to-pigment (B/P) ratio of 30 was used for both paints. 100 µm-thick paint films were applied on glass microscope slides using a Zehntner ZUA 2000 Universal Applicator. Samples were dried in the dark in a fume hood for one month before ageing.

Ageing under UVA light was performed in a light-curing oven (Egger EL 1 plus N2) using compact UVA fluorescent lamps (Osram Blue UVA 9W/76) with 350-400 nm radiation wavelengths. Six lamps were used, four at the top and two at the sides. The measured UVA intensity was 160.000 µW/lumen (160 W/m^2) while the measured temperature (T = 28 °C) was caused by the fluorescent lamps. The paint samples were then subjected to a repeating cycle of UVA exposure in an Egger box followed by elevated relative humidity exposure in a desiccator containing water. The RH is expected to be around 100 % in the desiccator and low in the Egger box due to the fluorescent lamps. The time intervals are shown in **Table 7**.

Likewise, in order to test if natural resins (*e.g.* dammar, shellac and colophony) have an influence in the formation of zinc oxalates in zinc white paint films, a series of oleo-resinous mixtures were prepared. In these experiments, the B/P ratio for ZnO in the various binding media was also 30. The ZnO paint was mixed with an equivalent mass of 10 %(w/w) solution of: a) dammar in mineral turpentine, b) shellac in ethanol, and c) colophony in ethanol. The paint films were prepared and dried as described above.

Artificial sunlight ageing of such dried samples were performed in an Atlas Weather-O-Meter Ci3000 fitted with a 4500 W water-cooled xenon arc lamp having combined borosilicate soda-lime glass and coated with infrared absorbing outer filter (CIRA) suppressing radiation below 300 nm. The light intensity was 120,000 lux with a radiation strength at 80 W/m2 (300-400 nm) and 800 W/m2 (400-800 nm). The light ageing was performed for 300 h at RH = 80%. The measured temperature interval, T = 35-39 °C, was caused by the xenon arc lamp and was not a chosen parameter.

Finally, zinc white's capacity to reduce $CO_{2(g)}$ into the oxalate anion was tested by exposing the ZnO raw linseed oil paint films, prepared and dried as described above, to ^{13}C labelled $CO_{2(g)}$. Indeed, semiconductor-mediated reduction of CO_2 into different carbon-containing species such as oxalates are currently being investigated as part of environmental chemistry research. Thus, it was worth investigating the influence of atmospheric CO_2 as a possible source of the oxalate anion in the zinc oxalate (ZnOx) formed in zinc white-containing oil paint layers.

Light ageing experiments in a $^{13}CO_{2(g)}$ enriched atmosphere were performed at concentrations of 4 and 40% (v/v) of $^{13}CO_{2(g)}$ in the Weather-O-Meter and in UVA light (40% (v/v)). The light ageing was performed for 500 h for all trials. The samples were placed in a gas-tight container made from tubular ESCAL™ Neo gas-barrier film, a heat-sealable polyester film coated with transparent ceramic (Mitsubishi Gas Chemicals). The container was fitted with a 2 mm quartz glass window (10×15 cm), which was attached over a hole cut in the gas-barrier film using a double (side by side) bonding with epoxy and silicone glue. The samples of ZnO paint applied on glass microscope slides were placed inside the bag and held in place by double-sided adhesive tape. The volume of the bag was 400 mL and the concentration of $^{13}CO_{2(g)}$ were obtained by injecting $^{13}CO_{2(g)}$ with a glass gas syringe via an inserted needle after which the bag was heat sealed. High RH measured to vary between 70 and 80 % was obtained by placing water drops in the plastic bag.

All samples were analysed using both ATR-Fourier transformed infrared microspectroscopy (ATR-mFTIR) at KIK-IRPA or the Royal Danish Academy of Fine Arts, and Macroscopic X-ray powder diffraction (MA-XRPD), in point and line scanning modes at the AXES research facilities (UA).

Table 7 – Reaction time (hours) under UVA light and in desiccator at 100% RH. Accumulated reaction time after each UVA or desiccator cycle is given in the corresponding Σ columns. Total

Reaction	Time (h)	Σ UVA	Σ Desiccator
UVA	50	50	
UVA	174	224	
Desiccator	408		408
UVA	166	390	
Desiccator	72		480
UVA	70	460	
Desiccator	432		912
UVA	100	560	
Desiccator	72		984
UVA	92	652	
Desiccator	96		1080
UVA	74	726	
Σ TOTAL		**726**	**1080**

3.4 Determination of ATR-μFTIR spectroscopy’s limit of detection (LOD) of metal oxalates

As mentioned in the previous sections, Attenuated Total Reflection Fourier Transform Infrared microspectroscopy (ATR-mFTIR) was employed to analyse a very large number of cross-sections extracted from both historical oil paintings and mock-up or model systems. Considering the large extent of such an ATR-mFTIR-based dataset and the importance of the results derived therefrom, it was important to determine the FTIR technique’s limit of detection (LOD) for metal oxalates in its ATR configuration. The LOD is the lowest analyte concentration that can be consistently detected in a sample with a given probability (typically at 95% certainty).

In order to determine the technique’s LOD, the three main types of metal oxalates consistently found in the historical paint cross-sections (*e.g.* calcium, copper and zinc oxalates) were dispersed at 6 different mass concentrations (*e.g.* 0.1, 1.0, 2.5, 5.0, 7.5 and 10% m/m) in a sodium chloride matrix. An internal sodium sulfate (Na_2SO_4) standard was also added at 10% m/m in all mixtures.

Each mixture was carefully ground using a quartz mortar and pestle for 30 minutes, followed by a 5-minute vortex agitation homogenization. 3 different pellets were pressed out of each mixture using an Specac 15.011 hydraulic press to apply a 5 tons-pressure for 2 minutes.

In each pellet, 5 analysis zones were defined and 2 analyses, spaced 250 microns away, were performed in each zone using KIK-IRPA's Hyperion 3000 FTIR microscope coupled to a Vertex 70 FTIR module (Brüker). In total, 30 measurements per mass concentration were performed in ATR mode employing a 250 micron diameter germanium tip to detect FTIR signals between 4500 and 600 cm^{-1} with a liquid nitrogen-cooled mercury-cadmium telluride (MCT) detector. Each spectrum was collected with a resolution of 4 cm^{-1}, by means of 128 scans (see **Figure 3**).

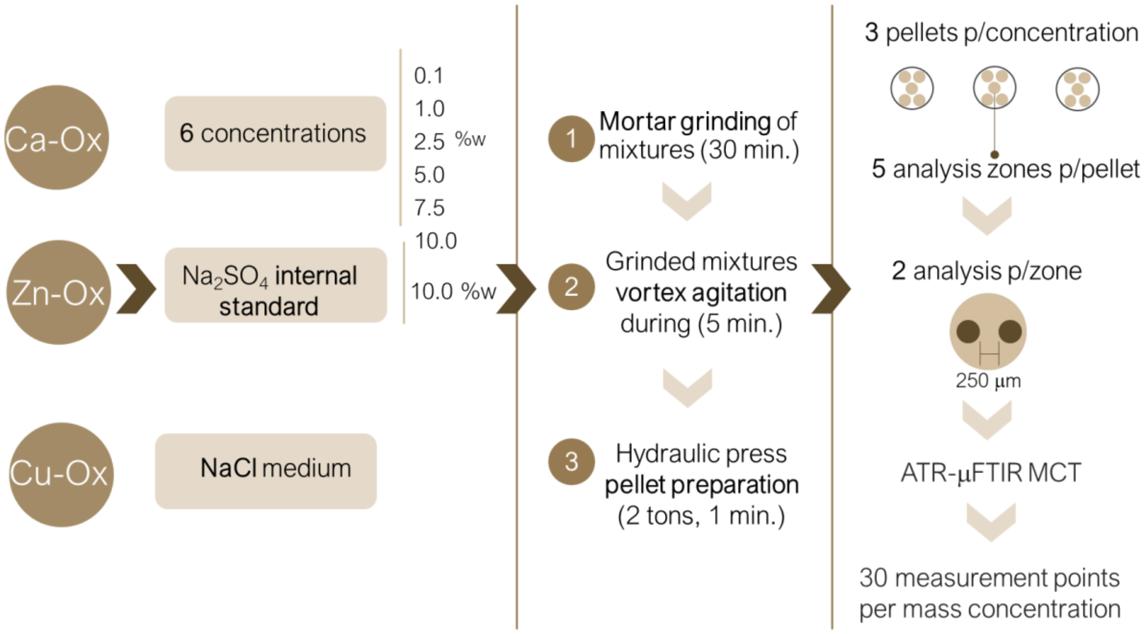


Figure 3 – Flowchart indicating the steps of sample preparation and measurement employed for the determination of the ATR-μFTIR technique LOD.

Collected spectra were then treated using the Orange Data Mining software (University of Ljubljana, Slovenia), using a specifically programmed script. The standardized data treatment routine batch-treated the data collected for each investigated metal oxalate at each mass concentration separately. For each spectrum, only those spectral signals collected between 1740 and 1000 cm^{-1} were kept, the baseline was corrected using an Orange-integrated "Rubber band" method and a peak area normalization was performed using the internal standard signal (SO_4^{2-} stretching vibration, between 1190 and 1076 cm^{-1}).

Afterwards, characteristic IR peaks for calcium, copper and zinc oxalates (see **Table 8**) as well as for the Na_2SO_4 internal standard were integrated from the baseline in order to determine their relative intensity. Relative intensity ratios (S_1/IS, S_2/IS, S_{2a}/IS, S_{2b}/IS) were then calculated by dividing each metal oxalate's peak relative intensities (S_1, S_2, S_{2a}, S_{2b}) by that found for the internal standard (IS). Finally, a one class support vector machine (SVM) with non-linear kernels method (Nu= 50%, Kernel coefficient = 0.01) was applied to detect outliers for all collected spectral ratios, given a particular metal oxalate mass concentration. The as-detected outlier spectral ratios were not considered for further data treatment.

Table 8 – Wavelength integration ranges for IR peaks used to calculate relative peak intensity ratios

Integrated IR peak		IR peak integration ranges (cm^{-1})			
		Metal oxalates			Internal standard
Code	**Description**	Calcium oxalate	Copper oxalate	Zinc oxalate	Sodium sulfate
S1	Asymmetric O-C=O stretching	1700-1570	1700-1570	1700-1570	
S2a	Symmetric O-C=O stretching, individual doublet signals		1380-1340	1341-1293	
S2b			1340-1301	1380-1347	
S2	Symmetric O-C=O stretching, singlet or full doublet	1346-1293	1380-1301	1380-1293	
IS	Asymmetric S=O stretching				1190-1076
Calculated relative intensity ratios		S_1/IS, S_2/IS	S_1/IS, S_2/IS, S_{2a}/IS, S_{2b}/IS		

Retained values from the outlier analysis were then averaged for each combination of metal oxalate type, mass concentration and relative intensity ratio. A typical example of a dataset matrix is shown for copper oxalate in **Table 9** .

Table 9 – Dataset matrix obtained for copper oxalate's four calculated relative intensity ratios at the different mass concentrations. N indicates the number of retained values after the outlier analysis

Mass %	N	S_1/IS	S_{2a}/IS	S_{2b}/IS	S_2/IS
0.1%	9	0.0601	0.0040	0.0039	0.0108
1.0%	10	0.1272	0.0151	0.0082	0.0432
2.5%	12	0.4255	0.0392	0.0275	0.0817
5.0%	18	0.4771	0.0508	0.0347	0.1083
7.5%	15	0.8373	0.1213	0.0857	0.2596
10.0%	15	1.2621	0.1585	0.1123	0.3389

For each metal oxalate, a linear regression correlating the mass concentration ranges and a given calculated relative intensity ratio was performed using Microsoft Excel's integrated Data Analysis Regression tool. Linear regressions were executed with a 95% confidence level for each one of the calculated relative intensity ratios shown in **Table 8**. The limit of detection (LOD) was calculated from the obtained linear regression results, using the following formula:

$$LOD=3.3\frac{SE\sqrt{\sum N}}{m}$$

Where *SE* is the standard error of the regression dataset, *N* is the number of retained values after the outlier analysis, per mass concentration, and *m* is the slope of the linear regression trendline.

4. SCIENTIFIC RESULTS AND RECOMMENDATIONS

4.1 Development of a macro-to-micro analytical methodology for the study of the metal oxalate phenomenon in historical oil paintings

One of the main objectives of the MetOx project was to develop a macro-to-micro analytical methodology to allow the characterisation of the metal oxalate phenomenon in historical oil paintings at different length scales. Highly successful results were obtained by combining state-of-the-art non-destructive and non-invasive macroanalytical techniques, applied on selected areas of historical oil paintings, with a large array of microanalytical techniques applied on a large number of cross-sections obtained from such paintings.

As described below, *The Visitation* panel painting, attributed to the Master of the view of Saint Gudula, was used as a case-study to illustrate how the different analytical approaches were combined to obtain relevant information on the metal oxalate phenomenon from the macro to the microscale. A more detailed overview of the general trends obtained during the MetOx project, regarding the relative abundance, spatial distribution and chemical speciation of the metal oxalates both at the surface of oil paintings as well as inside the oil paint layers is given in section 4.2.

4.1.1 A case study- *The Visitation* panel by the Master of the View of St. Gudula

In 2015, the King Baudouin Foundation's Léon Courtin-Marcelle Bouché Fund acquired for the RMFAB two fragments from the shutters of a dismembered altarpiece, dedicated to the Virgin Mary, of which the museums already possessed a part. The scenes pictured on the two altarpiece shutters (see **Figure 4**), the central part of which is still missing, represent *The Presentation of the Virgin in the Temple* and *The Visitation*. On the outer faces, a fragment of *Saint Ursula* and *Saint Simon Stock receiving the scapular from the hands of the Virgin of Mount Carmel* are represented.

These panels were unknown before their publication in the Köller Auctions sale catalogue in 2015 (Köller Auctions Ltd, Zurich, Switzerland, 18/09/2015). They were attributed on stylistic grounds to the Master of the View of St. Gudula, an anonymous painter active in Brussels in the late fifteenth century, named after a careful representation of the city's St. Gudula Cathedral visible on the *Pastoral Instruction* (the Louvre collection, Paris, France). The expressive style of this artist, who ran a very active workshop in Brussels, is easily recognizable among other things by his taste for bright colors and the abundant use of gold.

The representation of Saint Simon Stock on the reverse of the right shutter panel is a rare iconography in the Southern Netherlands at the end of the fifteenth century and is the oldest representation of this saint listed to date in this region. Its presence indicates that the altarpiece was intended for a church of the Carmelites, and more probably that of the Carmelites of Brussels. This prestigious church enjoyed the protection of the Dukes of Burgundy.

As soon as they were acquired, the panels benefited from a restoration financed by the King Baudouin Foundation's René and Karin Jonckheere Fund, which aimed to improve the condition of the panels' wooden support and to remove a yellowed, thick varnish and old retouchings that hindered the appreciation of the original pictorial work. The restoration was carried out at the RMFAB workshops by restorers Etienne Costa (wooden support), Marie Annelle Mouffe and Géraldine Van Overstraeten (pictorial layers).

As both the paintings' restoration and the MetOx project developed simultaneously, it was decided to apply the entire MetOx macro-to-micro analytical methodology to the *Visitation* shutter panel. This oil painting's scientific investigation not only offered a thorough characterization of its painting materials and comprehension of the artist(s)' pictorial technique, but also contributed to decision-making during the conservation-restoration process, especially when performing cleaning choices. Likewise, it also allowed the MetOx researchers to clearly define the contribution of each analytical technique to the multiscale comprehension of the metal oxalate phenomenon (*e.g.* chemical composition, spatial distribution and pigment-specific reactivity patterns), both at a painting's surface as well as inside its pictorial layers. The following subsections will illustrate the type of metal oxalate-oriented results that were obtained by applying the MetOx analytical approach to *The Visitation* panel. Results concerning the panel's materiality and execution technique have been published elsewhere (see **Section 6**).

Panel I Dimensions: 103 x 86 cm	**Panel II** Dimensions: 95,5 x 17,3 cm

The Visitation (IF)

Saint Simon Stock receiving the scapular from the hands of the Virgin of Mount Carmel (OF)

The Presentation of the Virgin in the Temple (IF)

Saint Ursula (OF)

Figure 4 – Inner (IF) and outer (OF) faces of the two oil painted panels attributed to the Master of the View of Saint Gudula, prior to their restoration. King Baudouin Foundation, in deposit at the RMFAB

4.1.1.1 Non-invasive macro analytical techniques

As mentioned in section 3.1, three different macroscopic imaging techniques were used during the MetOx project: macro X-ray fluorescence (MA-XRF), reflection Fourier-transformed infrared spectroscopy (MA-rFTIR) and macro X-Ray powder diffraction (MA-XRPD). *The Visitation* panel was scanned in its entirety with MA-XRF (bottom-left area excluded) in order to gain insight into the pigment composition through the elemental distributions (see **Figure 6**) as well as to highlight areas of interest for analysis with MA-rFTIR and MA-XRPD. The latter techniques were used in four different analysis zones as shown in **Figure 5**.

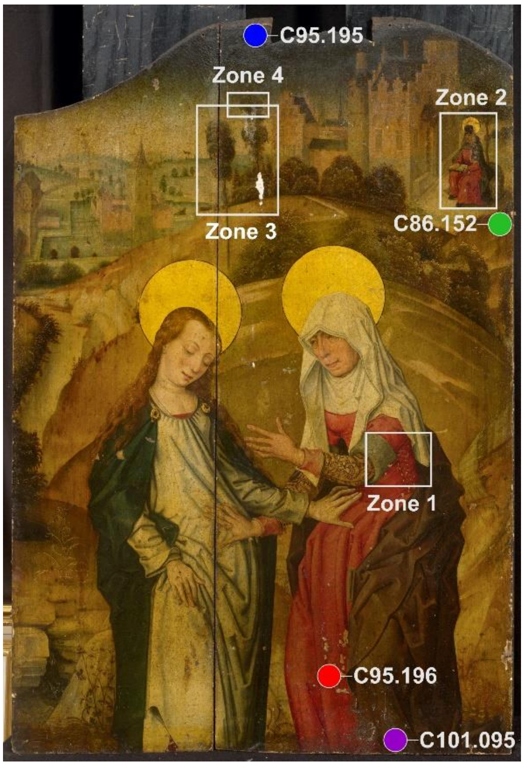


Figure 5 – White rectangles indicate the zones of The Visitation panel scanned with both, MA-rFTIR and MA-XRPD. The entire painting was scanned with MA-XRF except for its bottom-left area. Red, green, blue and purple paint layers were also micro-sampled in specific locations of the panel, indicated by the like-coloured dots. Associated KIK-IRPA cross section numbers are indicated as a reference

While pigment identification with MA-XRF is indirect, several preliminary conclusions can be drawn from the elemental composition. For instance, the halo surrounding the two women was created using metallic gold (Au-L line) while St. Anna's red robe was painted using a mercury-based pigment (Hg-L line), very likely vermilion or cinnabar. The calcium signal (Ca-K line) seems most intense in areas where the ground layer is exposed (*e.g.* lacunas) but might also originate from calcium-based compounds (*e.g.* chalk or gypsum) in the paint layers. The presence of tin (Sn-L line) in the yellow landscape suggests the use of a lead-tin yellow pigment. The iron distribution (Fe-K line) suggest the use of earth pigments, most notably in Virgin Mary's brown-colored hair. The lead (Pb-L line) distribution implies the usage of lead white and its co-localization with tin also supports the identification of lead tin yellow in certain areas. Copper (Cu-K line) is closely related to the blue areas on the panel, *e.g.* Virgin Mary's blue robe or the sky, but also to St. Anna's violet drapery or the background's green foliage. Copper is co-localized with arsenic and zinc (As-K and Zn-K lines respectively), possibly hinting at the presence of an impurity in these areas. Finally, a weak signal for potassium (K-K line) was detected, being the most intense in the depicted characters' red robes, suggesting the use of a red lake pigment in these areas [38].

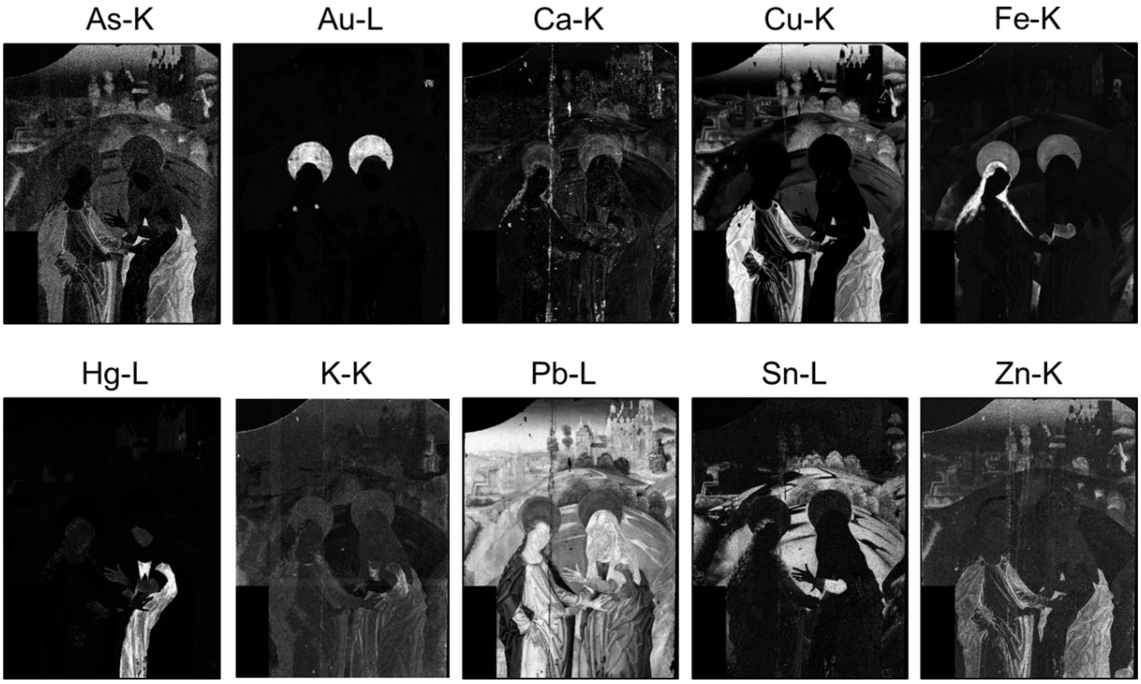


Figure 6 – MA-XRF elementary distribution images obtained for The Visitation panel. Brighter zones indicate higher relative concentrations of the selected species in the different mappings.

MA-rFTIR measurements were hindered by the presence of the thick, oxidized varnish layer that covered *The Visitation* panel. Indeed, spectra obtained were dominated by features related to this layer, obscuring the clear visualization of other chemical species underlying this topmost stratus. Interestingly, MA-rFTIR measurements performed on the *Saint Ursula* panel, presenting a similar varnish to that found on *The Visitation* panel, did allow detecting characteristic calcium oxalate signals (results not shown). These contrasting results suggest that in the case of the *Saint Ursula* panel, calcium oxalates are to be found either at the paint surface or within the uppermost section of the varnish layer.

Considering these initial results, MA-rFTIR scans had to be repeated once the varnish removal operation had been completed on *The Visitation* panel. As shown in **Figure 7**, the results obtained during the analysis of Zone 1 allowed the spatial location of calcium oxalates either at the surface of the unvarnished painting or at the topmost section of the pictorial layers themselves. Their distribution is not homogeneous and they seem to be mainly localized in the red and purple areas, where higher potassium concentrations observed in MA-XRF suggest the use of a red lake, mixed with or superposed over either vermillion in the red areas or azurite in the case of the purple hue (see Figure 7).

The MA-XRPD analysis of this zone also allowed detection of the presence of crystalline calcium oxalate of the weddellite type ($CaC_2O_4{\cdot}2H_2O$). As with the MA-rFTIR results, the spatial distribution of this oxalate species seems to be correlated to red and purple areas.

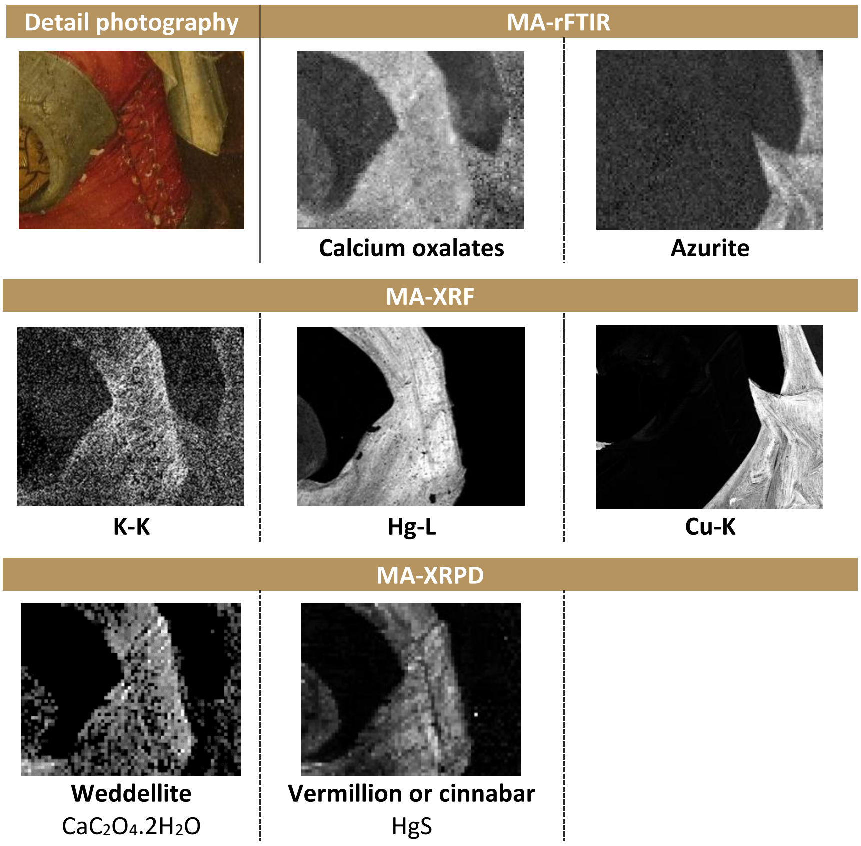


Figure 7 – Selected element or compound-specific distributions obtained with MA-rFTIR, MA-XRF and MA-XRPD for Zone 1 of *The Visitation* panel attributed to the Master of the view of St. Gudula. Brighter zones indicate higher relative concentrations of the selected species in the different techniques' mappings.

In Zone 2, similar results to those previously presented were found using MA-rFTIR, which allowed detection of calcium oxalates in the red and purple robes of the sitting elder saint found in the background of the painting (see **Figure 8**). As described above, the MA-XRF results suggest the use of a red lake in the red areas, mixed with azurite in the case of the purple cape. However, only faint signals of crystalline weddellite calcium oxalate were detected with MA-XRPD, matching those areas indicated by MA-rFTIR. These results suggest that in these areas crystalline and amorphous calcium oxalates coexist. Nonetheless, it is not clear if whether the weaker crystalline signals indicate that such a phase is present in smaller quantities than its amorphous counterpart or if it is located in a deeper paint layer and thus its characteristic signals are attenuated. Interestingly, weddellite was also found in the brownish green tree and bushes analysed in Zones 3 and 4, as shown in **Figure 8**. As shown with MA-XRPD, these elements of the composition are mostly azurite-based and are rich in calcite, present as an adulterant of this pigment as revealed during the microanalytical investigation of sample C95.195 (results not shown in this report).

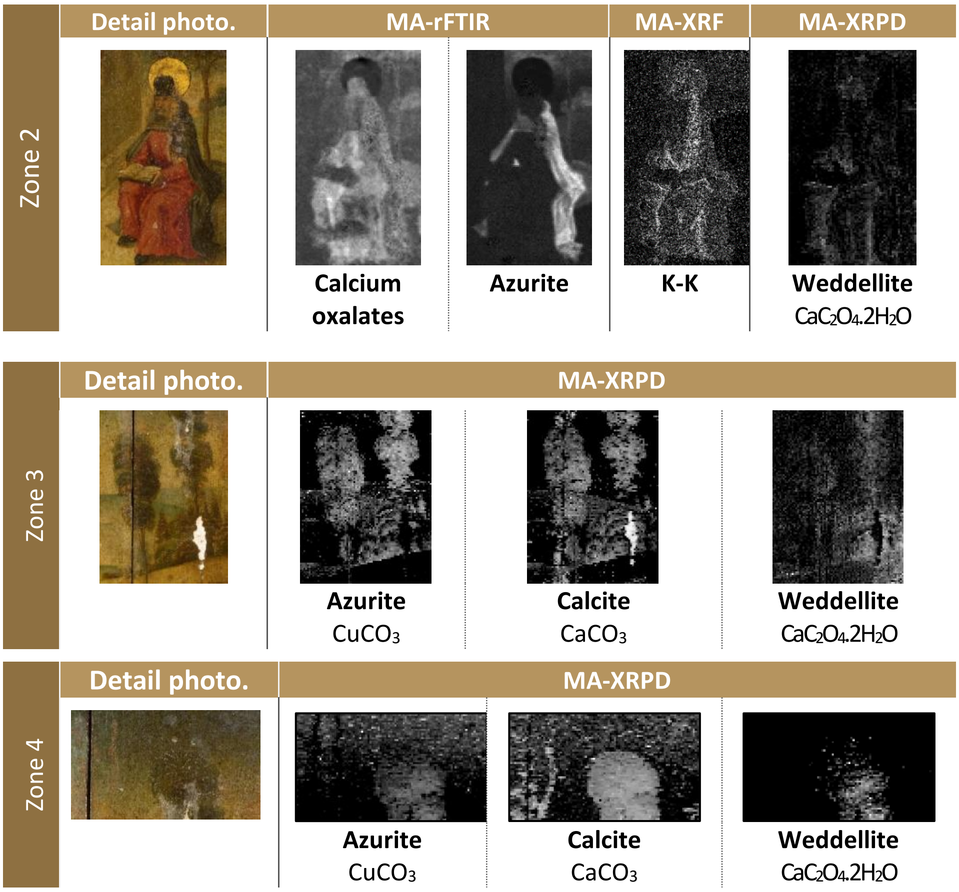


Figure 8 – Selected element or compound-specific distributions (dist.) obtained with MA-rFTIR, MA-XRF and MA-XRPD for Zones 2-4 of *The Visitation* panel. Brighter zones indicate higher relative concentrations of the selected species in the different techniques' mappings

These results demonstrate that both MA-rFTIR and MA-XRPD are able to detect metal oxalates in historical paintings in a non-invasive manner. Unlike MA rFTIR, MA-XRPD makes it possible to identify and discriminate closely chemically-related metal oxalates types (*e.g.* differentiating weddellite ($CaC_2O_4 \cdot 2H_2O$) from whewellite ($CaC_2O_4 \cdot H_2O$)), but only if they are crystalline. However, MA-rFTIR is sensitive to the presence of such alteration compounds, irrespective of their solid phase state (*e.g.* crystalline or amorphous). The application of both techniques thus allows a comprehensive picture of the surface spatial distribution of metal oxalates on historical paintings to be acquired. Likewise, it promotes pigment-to-metal oxalate correlation patterns to be identified, as outlined for *The Visitation* panel. In the case of this panel painting, only calcium oxalates were found. Nonetheless, these techniques allowed the detection of other metal oxalate species, such as copper oxalate, in other historical paintings (see Section 4.2.1).

4.1.1.2 Microanalytical techniques

Four different microsamples were taken from *The Visitation* panel (see **Figure 5**), following the project's colour-related analysis criteria. St. Anne's purple mantle was also sampled considering the previously obtained macroanalytical results. It was indeed shown that such purple hues were produced with the same main pigments (*e.g.* a mixture of azurite and a red lake) as those found in the blue and red sampled zones respectively, thus allowing exploration of the effect of the combination of pigments in the formation of metal oxalates.

The entire set of microanalytical techniques described in **Table 5** above were applied to these samples. ATR-mFTIR was the technique that allowed the fastest and most reliable results to be obtained concerning the composition and spatial distribution of the metal oxalate moieties found in such paint layers. **Figure 9** summarizes typical results obtained for the localisation of calcium oxalate (CaOx) in the four extracted microsamples. It can be seen that calcium oxalate is invariably found in the uppermost stratum of the paint structure, either in surface degradation layers (*e.g.* samples C95.196 and C86.152) or within the surface varnish (*e.g.* C95.195 and C101.095), in some cases agglomerated in nodules. However, it is also found within the paint layers themselves. In those containing madder red lakes as determined by high performance liquid chromatography (HPLC) (*e.g.* samples C95.196 and C101.095, results not shown in this report), characteristic calcium oxalate (CaOx) signals are more intense, possibly indicating a higher concentration of the oxalate moiety. It was also observed that the CaOx also tends to agglomerate in nodules. In paint layers containing azurite (C95.195) or verdigris (C86.152), CaOx seems less concentrated and present a hazy spatial distribution.

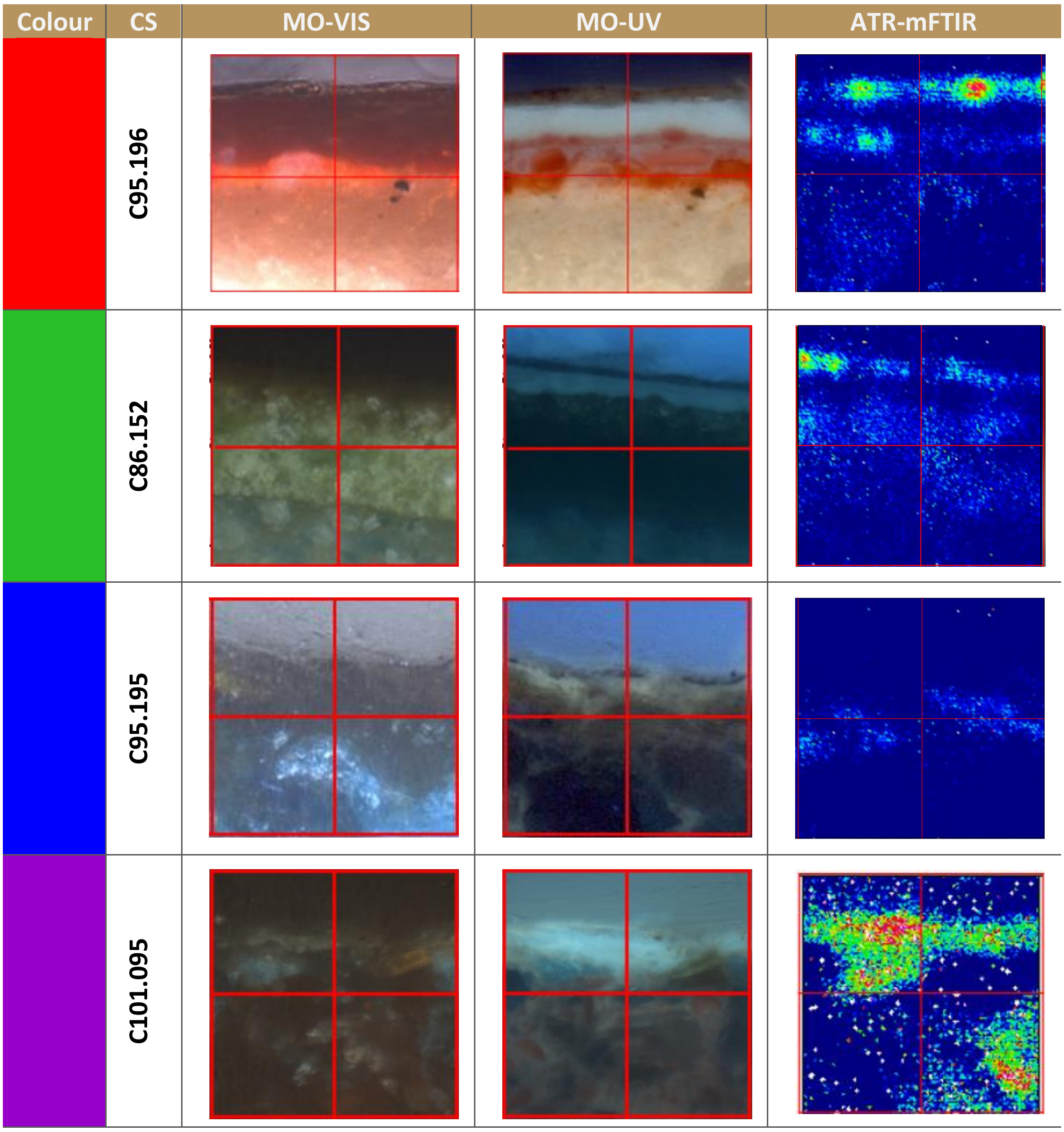


Figure 9 – ATR-mFTIR mappings showing calcium oxalate C-O symmetric stretching distribution (1336-1296 cm^{-1}) in the cross-sections (CS) from red, green, blue and purple paint passages. In each mapping, false-colour scale ranges from deep blue to pink white, indicating the absence or the highest relative intensity of the visualized vibration, respectively. The corresponding microphotographs of the analysed zones are shown under polarized (MO-VIS) and ultraviolet (MO-UV) illumination.

Copper oxalates (CuOx) were also found in sample C86.152 using mATR-FTIR (see **Figure 10**). Unlike what was observed for CaOx, copper oxalates are not found at the surface of the paint structure but exclusively within a paint layer in which verdigris is expected to have been used, mixed with lead-tin yellow. No CuOx were found in the underlying azurite-based paint layer nor in sample C95.195 which is also primarily composed of azurite. Interestingly, the detected CuOx are located in close spatial vicinity to other types of copper carboxylates, such as copper soaps.

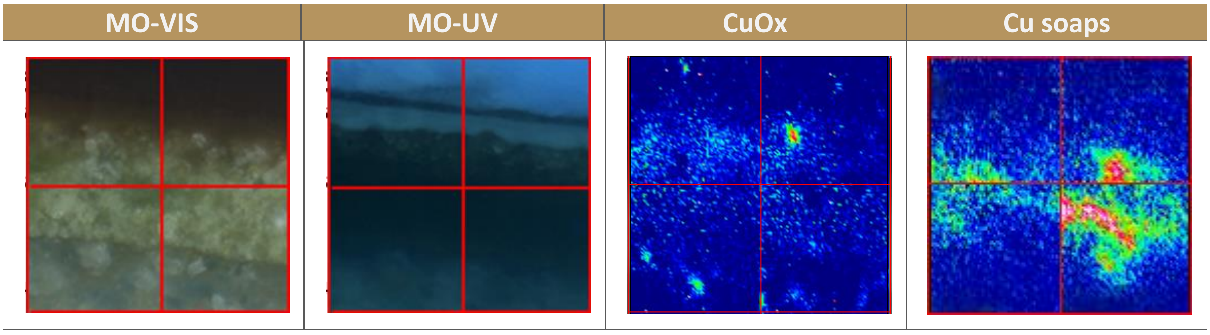


Figure 10 – ATR-mFTIR mappings showing the spatial distribution of copper oxalate (1375-1355 cm^{-1}) and copper soaps (1597-1577 cm^{-1}) in the verdigris-rich paint layer of cross-section C86.152. In each mapping, false-colour scale ranges from deep blue to pink white, indicating the absence or the highest relative intensity of the visualized vibration, respectively. The corresponding microphotographs of the analysed zone are shown under polarized (MO-VIS) and ultraviolet (MO-UV) illumination.

The presence of CuOx in the verdigris-rich layer were confirmed with ToF-SIMS, as shown in **Figure 11**. Interestingly, characteristic ions associated with CuOx were also detected in the bottom lead-tin yellow-rich paint layer (not analysed by mATR-FTIR). Note that the ToF-SIMS technique was not capable of detecting CaOx, possibly due to its low ionisation probability.

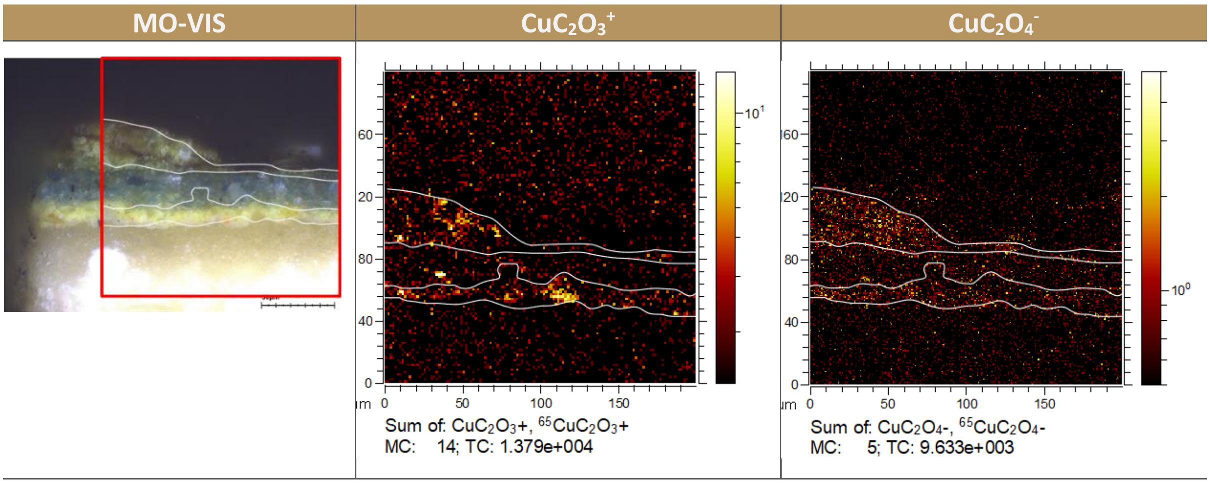


Figure 11 – ToF-SIMS mappings showing copper oxalate spatial distribution in a zone of cross-section C86.152 (marked in red in the MO-VIS microphotograph). Characteristic CuOx ions were detected in both, positive ($CuC_2O_3^+$) and negative ($CuC_2O_4^-$) mode.

4.1.2 Determination of ATR-mFTIR spectroscopy's limit of detection (LOD) of metal oxalates

Considering Attenuated Total Reflection Fourier Transform Infrared microspectroscopy (ATR-mFTIR) was extensively employed throughout the MetOx project, it was important to determine the FTIR technique's limit of detection (LOD) of metal oxalates in its ATR configuration.

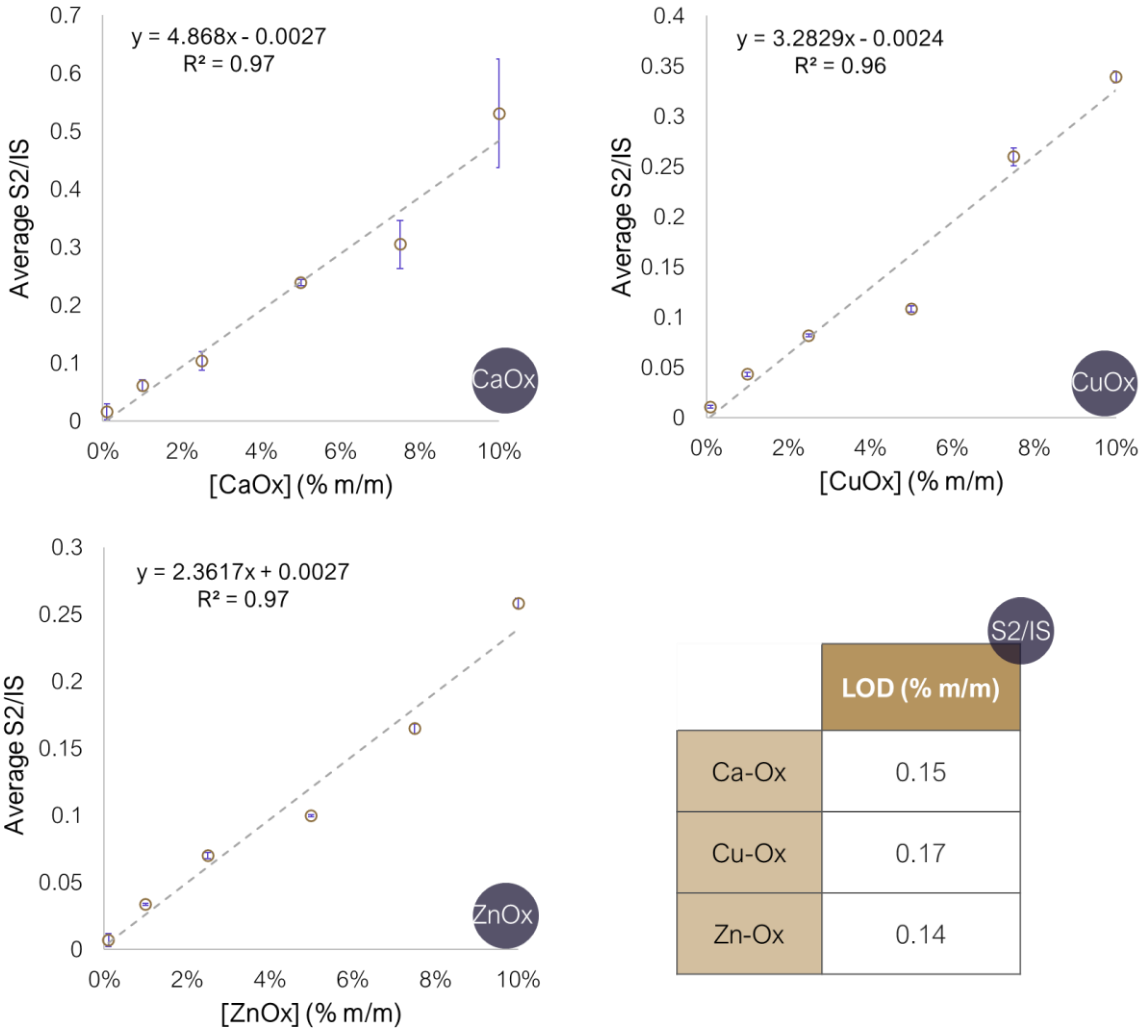
As described in Section 3.4 and summarized in **Table 8**, different infrared vibration bands characteristic for calcium, copper and zinc oxalates were chosen. These bands were integrated to determine their relative intensity and relative intensity ratios were calculated by dividing each chosen metal oxalate's band by that found for the employed internal standard. A linear regression was performed to correlate the mass concentration ranges and each set of calculated relative intensity ratios. **Table 10** summarizes the R-squared values (*e.g.* the percentage of the dependent variable variation that a linear model explains) obtained for the linear regression of each metal oxalate and each of the chosen relative intensity ratios.

Table 10 –R-squared (R^2) values obtained in the linear regressions performed for each set of chosen relative intensity ratios (RI) for calcium, copper and zinc oxalates

Chosen IR vibrations for relative intensity ratio calculations		**Linear regression R^2 values**		
RI Code	**Description**	Calcium oxalate	Copper oxalate	Zinc oxalate
S1/IS	Asymmetric O-C=O stretching	97%	96%	95%
S2a/IS	Symmetric O-C=O stretching, individual doublet signals		96%	97%
S2b/IS			97%	97%
S2/IS	Symmetric O-C=O stretching, singlet or full doublet	97 %	96%	97%

Considering the R-squared values obtained for the different linear regressions, the S2/IS datasets were chosen to calculate the LOD for all three metal oxalates types. **Figure 12** shows the employed linear regressions and the calculated LOD values for each one of the investigated metal oxalates. Interestingly, the obtained LOD values are similar, ranging from 0.14 to 0.17 % on a weight basis (% m/m). It is most probable that the slight differences in LOD values are more related to experimental variance than to the metal oxalate type. Thus, the ATR-mFTIR limit of detection for metal oxalates would average around 0.15 % m/m or 1,500 ppm.

The obtained value ranges are in the same order of magnitude to those found for other analytes [39] using a similar instrumental configuration. Interestingly, it has been found that the technique's sensitivity level can be increased tenfold by switching from a conventional mercury cadmium telluride (MCT) detector, such as the one used in this experiment, to a focal plane array (FPA) detector. Considering all of the ATR-mFTIR mappings performed during the study of historical cross-sections employ the FPA detector, it is highly possible that we are able to detect even more minute amounts of metal oxalates in such samples.



	LOD (% m/m)
Ca-Ox	0.15
Cu-Ox	0.17
Zn-Ox	0.14

Figure 12 – Linear regressions and calculated limit of detection (LOD) for the S2/IS relative intensity ratios of calcium (CaOx), copper (CuOx) and zinc (ZnOx) oxalates

4.2 The occurrence of metal oxalates in historical oil paintings from the Southern Netherlands produced between the 15th and the 17th centuries

The previous section offered a succinct overview on how the macro-to-micro MetOx analytical methodology allowed the effective characterization of the presence of metal oxalates in a historical oil painting or a series of microsamples taken therefrom.

As mentioned in section 3.1 and 3.2, the macroscopic imaging techniques were employed to scan selected areas of 11 historical oil paintings, while as many as 107 microsamples, representative of 45 different Southern Netherlandish masterpieces, were analyzed. Thus, the MetOx project produced an impressive volume of results which were thoroughly analyzed, allowing clear trends regarding the chemical oxalate composition and spatial distribution within the paint structure to be identified, as well as pinpointing a series of paint materials, the presence of which seems to be correlated to that of particular types of metal oxalates. The following subsections offer an overview of such trends.

4.2.1 Trends in chemical oxalate composition in relation to employed paint materials

As described in section 3.1, microanalytical techniques were employed to firstly assess the presence and chemical composition of metal oxalates in historical cross-sections. The results obtained were employed to select areas for the macro analytical investigation in historical paintings to which these cross-sections belonged.

This multiscale investigation allowed the chemical composition of metal oxalates in historical paint layers to be successfully identified, as showcased in section 4.1.1.1 for *The Visitation* panel. Furthermore, by combining results obtained from the large number of analyzed cross-sections with the centimeter-scale mappings produced during the macro-imaging of the historical paintings themselves, it was possible to elucidate representative trends in the composition of the oxalate species found in such paint layers.

Considering the results obtained, it is evident that the occurrence of metal oxalates is a widespread phenomenon in historical Southern Netherlandish paintings produced during the 15th to 17th centuries. Indeed, the vast majority of historical oil paintings (*e.g.* 10 out 11 paintings) and of cross-sections (*e.g.* 97 out of 107 samples), submitted to either a macro or microanalytical investigation respectively, tested positive for at least one type of metal oxalate.

The chemical variety of the metal oxalate species detected seems to be limited to calcium, copper and, much less abundantly, zinc oxalates. Although a wide variety of other metal cations are typically found in historical paint layers (*e.g.* K^+, Na^+, Pb^{+2}, $Fe^{+2}/^{+3}$, Mn^{+2}, Co^{+2}, etc.) no other type of metal oxalate was found in any of the investigated cross-section samples or historical paintings. Such a limited range of cationic compositions might be due to the fact the paint materials studied during the MetOx project are several centuries old. Thus, it is highly possible that the observed trends reflect either the most thermodynamically stable or kinetically favored chemical configurations, towards which paint systems tend over time. Investigations on early stages of oxalate anion formation in the presence of mixtures of metal cations typically found in historical paint layers are nonetheless needed to test this hypothesis.

Furthermore, it seems that the metal oxalate compositions identified are intimately related to the palette of pictorial materials employed during the timeframe on which this study focused (*e.g.* 15th to 17th centuries). As shown in **Table 11** and **Figure 13** recurrent observations linking certain types of metal oxalates with specific paint materials were found. In that sense, previous studies have indeed shown that different metal oxalates types (*e.g.* cadmium, zinc and cobalt oxalates) are found in 19th and 20th century paintings in which other paint materials, not found in oil paintings produced in earlier centuries, have been employed.

Table 11 – Correlation between the chemical composition of metal oxalates and certain paint materials as found in historical paint layers during the MetOx project

Cation	Pigments	Other paint materials	Chronology
Calcium	▪ Red lakes (*e.g.* madder, kermes or cochineal) ▪ Ultramarine ▪ Smalt	▪ Natural resin varnishes ▪ Calcite-based materials (extenders or ground fillers).	15th to 17th centuries
Copper	▪ High occurrence when verdigris was employed ▪ Seldomly observed in the presence of malachite ▪ Very rarely observed when azurite was used	-	15th to 17th centuries
Zinc	-	Suspected zinc vitrol drier	Mostly 15th century paintings

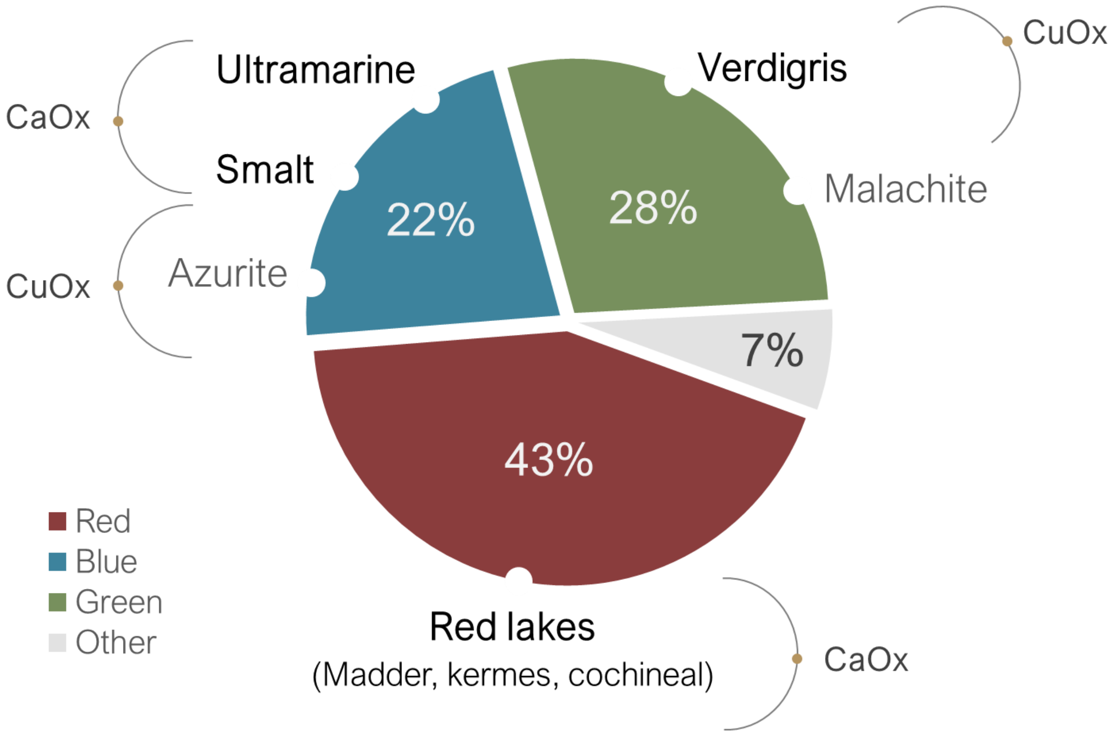


Figure 13 – Distribution statistics of positive metal oxalate cases found in historical cross-sections analysed by ATR-mFTIR. For each surface paint layer colour, the correspondence between pigments and related metal oxalates compositions are indicated. Given all surface colours are equally represented in the sample set, differences observed in positive metal oxalate cases are indicative of the involved pigments’ reactivity. Metal oxalates were also found in subsurface pictorial layers with colours “other” than green, red or blue. In those cases, metal oxalate composition depended on the pigments found in such layers, following the same trends indicated for the surface paint layers.

Where calcium oxalate was present, weddellite ($CaC_2O_4.2H_2O$) was systematically detected during the MA-XRPD analyses of the historical paint surfaces but also in those samples investigated with SR-m-XRPD. Traces of whewellite, a calcium oxalate monohydrate ($CaC_2O_4.H_2O$), were detected in a single historical painting, *The Knights* panel by Michiel Coxie. Whewellite is known to be the most stable form for calcium oxalate under environmental conditions, with weddellite spontaneously dehydrating into its monohydrate counterpart in a few hours after its synthesis [40]. Nonetheless, *in vivo* scientific investigations of renal calculi [41], mainly composed of calcium oxalate, have found that weddellite becomes the predominant form at higher calcium concentrations, while weddellite stabilization seems to be dependent on the oxalate anion concentration. Further studies in material systems similar to those found in historical paint layers are required to determine if the concentration of the calcium and oxalate ions yield similar trends in terms of the most favorable calcium oxalate crystalline form.

Weddellite was found in all red paint layers employing mainly an aluminum-substrate red lake as the main pigment, independent of the nature of the lake colorant (*e.g.* madder, kermes or cochineal). This metal oxalate was also found in blue paint layers when ultramarine or smalt were employed as the main blue pigments. Finally, it was found in green paint layers when these either contained calcite (*e.g.* employed as an extender or as substrate of a lake pigment) or verdigris as the main green pigment. In this last case, weddellite was commonly found mixed with copper oxalates within the paint layer (see **Figure 14** and **Figure 18**).

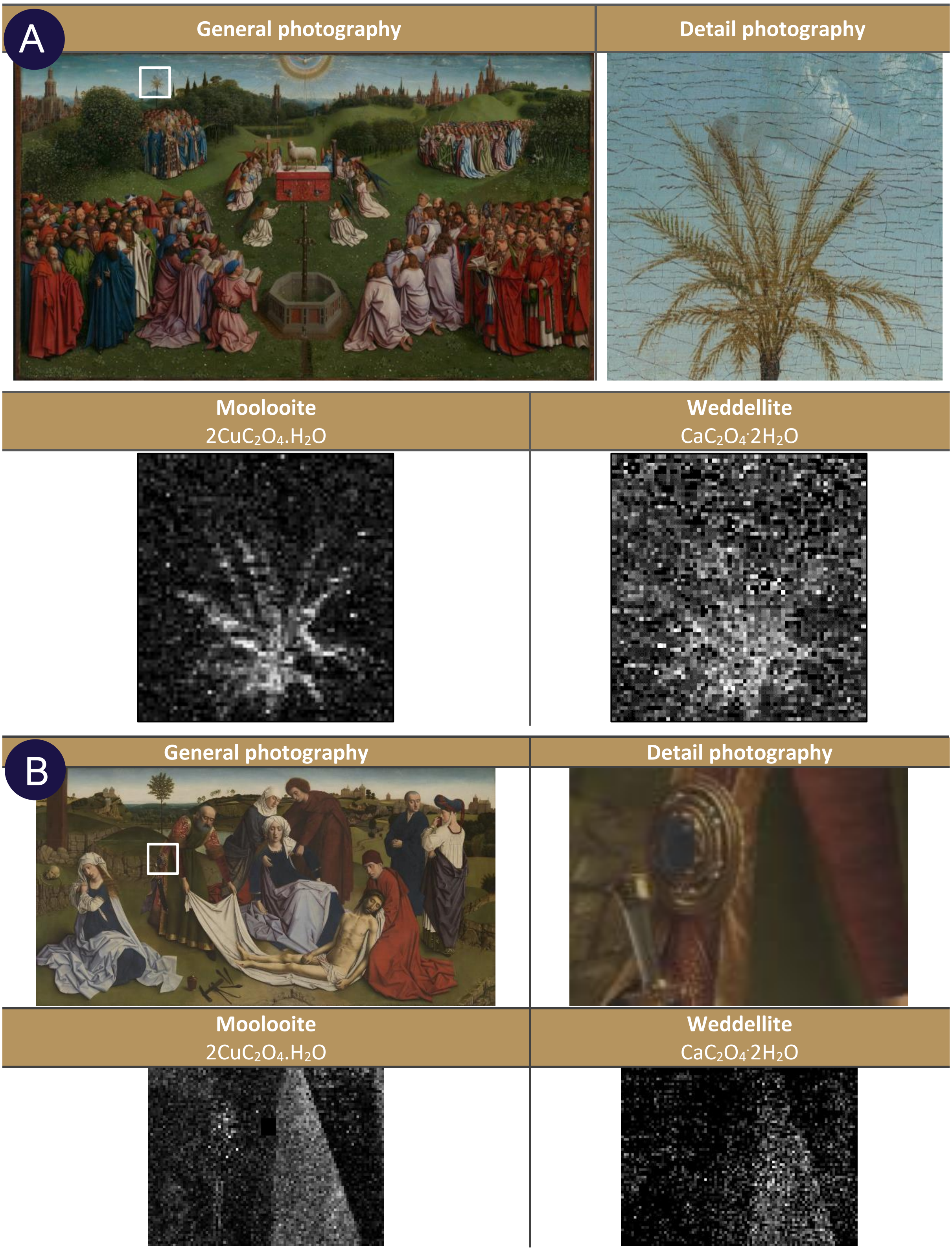


Figure 14 – MA-XRPD results obtained for Hubert and Jan Van Eyck's *Adoration of the Lamb*(A) and Petrus Christus' *Pietà* (B) panels. The scanned zones are indicated with a white square. In both panels, a spatial co-localization of moolooite and weddellite oxalates was detected in verdigris-containing areas. Brighter zones indicate higher relative concentrations of the selected species in the different mappings.

Likewise, weddellite was repeatedly found associated with natural resin varnishes, either at their surface or within such layers. In the MA-XRPD mappings, faint varnish-related weddellite diffraction signals were often found to be distributed over the entire analyzed paint surface. An increase in the relative intensity of such signals became apparent when certain areas of the scanned surface contained one of the pigments or paint materials described in **Table 9** (see **Figure 15**), suggesting that in such zones weddellite is also found within the paint layer itself.

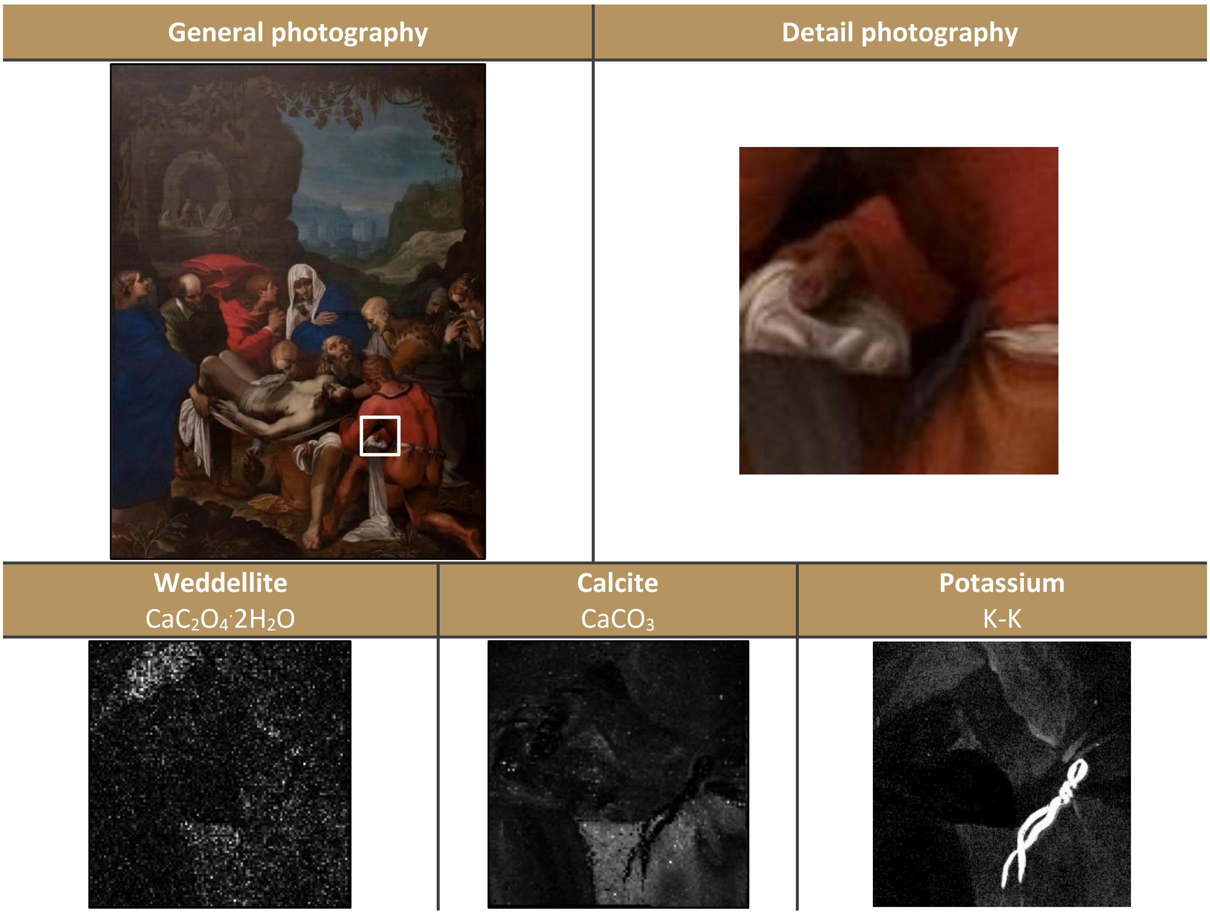


Figure 15 – MA-XRPD results obtained for Wenceslas Coebergher's *The entombment*. The scanned zones is indicated with a white square. Weddellite signals are detected over the entire scanned surface, indicating it is possibly localized in the surface varnish. Nonetheless, brighter zones, indicating higher relative concentrations of this calcium oxalate phase, are found in calcite or potassium-rich areas, the latter element suggesting the possible use of a lake pigment or ultramarine.

The microanalytical investigation of paint samples using ATR-mFTIR revealed that calcium oxalates were indeed found either at the surface or within the topmost natural resin varnish layers. Interestingly, they were also found in intermediary varnish layers, such as those found as an interlayer between original paint layers and subsequent overpaints (see **Figure 16**). It was also observed that while mixtures of metal oxalates (*e.g.* copper and calcium oxalates) could be spatially co-located in the paint layers, calcium oxalate would be the sole species to be found on the surface varnish (see **Figure 17**), as also observed in Hans Memling's *Christ surrounded by singing and music-making angels* retable [20]. Such a compositional transition is also clearly illustrated in **Figure 18**.

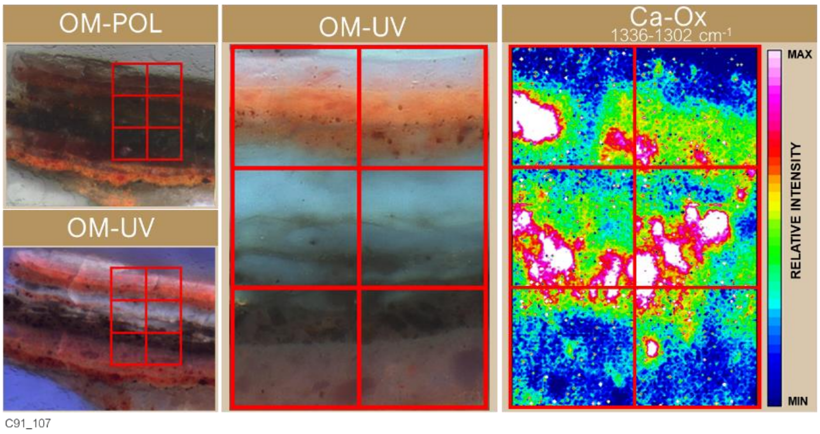


Figure 16 – ATR-mFTIR results obtained on a cross-section (KIK-IRPA number C91.107) extracted from Jan and Hubert Van Eyck's *Joos Vijd* panel (XVII) of the Ghent altarpiece. Calcium oxalates are highly concentrated in an intermediate varnish, detected as a white fluorescent layer in the OM-UV microphotograph.

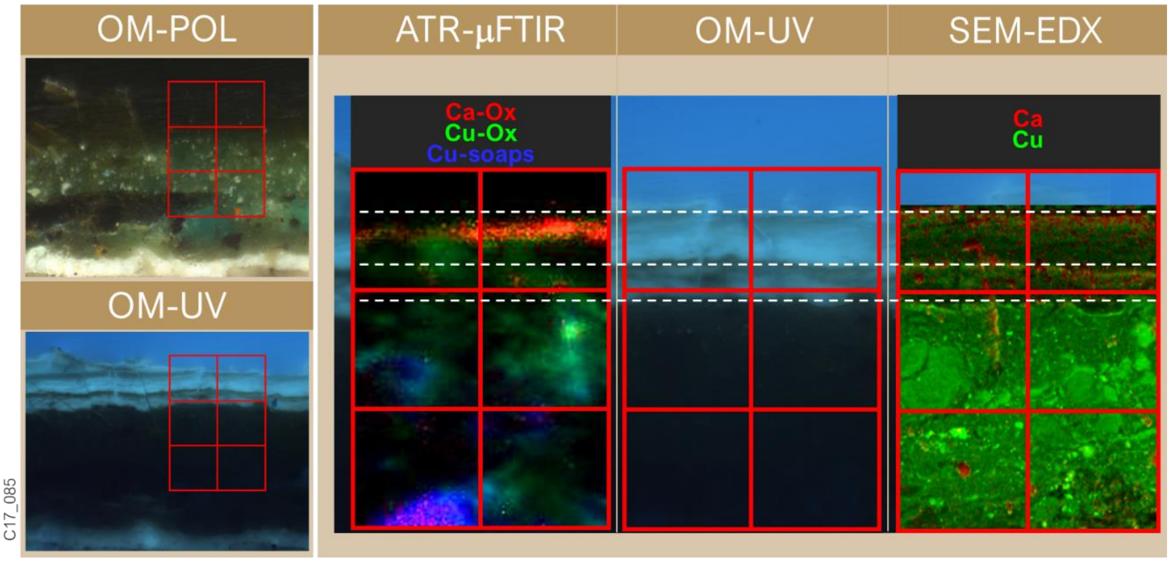


Figure 17 – ATR-mFTIR results obtained on a cross-section (KIK-IRPA number C17.085) extracted from Petrus Christus *Pietà* panel. Copper oxalates and soaps as well as calcium oxalates are co-localized in the verdigris-based paint layer. SEM-EDX results show that the varnishes, detected as white fluorescent layers in the OM-UV microphotograph, are enriched with copper. Nonetheless, only calcium oxalate is found at the sample's topmost surface.

Regarding copper oxalates, all of the verdigris-containing paint surfaces or microsamples that were investigated yielded positive results for this type of metal oxalate. Such a trend might be due to verdigris' acetato ligand lability, resulting in high ligand exchange rates when in contact with other carboxylate anions typically found in an oil-based paint layer (*e.g.* fatty acids, oxalates and formates) [42, 43]. Whenever MA-XRPD or SR-m-XRPD were employed for the analysis of paint surfaces or microsamples, respectively, a moolooite ($CuC_2O_4.H_2O$) crystalline phase was repeatedly identified. Interestingly, in all the investigated verdigris-based paint layers, copper oxalates were found in close spatial association with other copper-containing alteration products, mainly copper soaps and, in some cases, copper formates (see **Figure 18**).

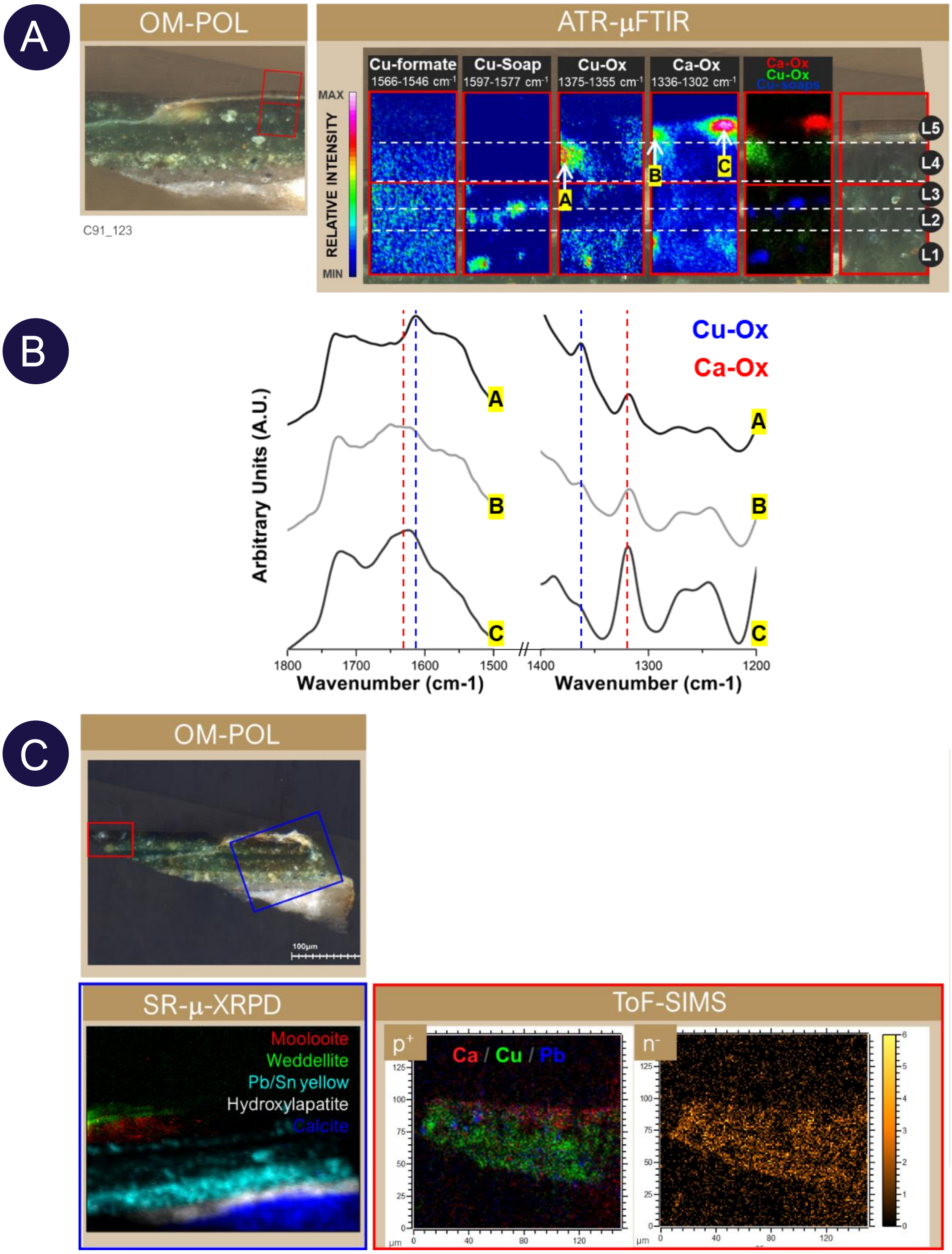


Figure 18 – ATR-mFTIR results obtained on a cross-section (KIK-IRPA number C91.123) extracted from Jan and Hubert Van Eyck's *The Virgin Annunciate* panel (XVI) of the Ghent altarpiece. (**A**) ATR-mFTIR results showing that copper oxalates (Cu-Ox), formates (Cu-formate) and soaps (Cu-Soap) are co-localized in the verdigris-based paint layer, mixed with calcium oxalates (Ca-Ox). (**B**) Spectra extracted from points A, B and C in the Cu-Ox and Ca-Ox ATR-mFTIR mappings show how the metal oxalate composition gradually changes from a copper and calcium oxalate mixture towards a single calcium oxalate phase in the surface varnish. **(C)** SR-m-XRPD (blue square) and TOF-SIMS (red square) positive mode (p^+) mappings confirm results shown in (A) and (B). The negative mode (n^-) TOF-SIMS mapping shows the distribution of copper oxalate ionized moieties ($CuC_2O_4^-$) in the verdigris paint layer. No calcium oxalates could be detected using this technique.

Unlike verdigris, the use of malachite and azurite seem to be much less correlated to the presence of copper oxalates, similar to what has been previously found [24, 36]. For instance, no correlation was found between a moolooite phase and the use of azurite or malachite in any of the historical oil paintings scanned using MA-XRPD. Likewise, during the microanalysis of historical cross-sections, copper oxalates were found in only ~5% of the cross-sections containing azurite as the main copper pigment while, in those containing malachite, the occurrence was of ~50%. Nonetheless, in those malachite-containing pictorial layers where copper oxalates were found, the green pigment was found mixed with other copper-based materials such as verdigris or posnjakite. Considering these pigment mixtures, establishing a direct correlation between the occurrence of copper oxalates and the use of malachite is not straightforward. In any case, the lower relative reactivity of malachite and azurite towards carboxylate ligand exchange has already been noted [42], attributed to the higher stability of the carbonato and/or hydroxo ligands that surround the copper(II) ion in such pigments.

Traces of zinc oxalates were detected using ATR-mFTIR in cross-sections belonging to the *Ghent Altarpiece* panel paintings included in the MetOx project. Their presence, alongside that of other zinc-containing species such as zinc soaps, was identified in paint layers containing poorly drying pigments (*e.g.* red lakes, carbon black, etc.), a trend confirmed by the systematic MA-XRF studies performed during the polyptych's ongoing restoration process. The presence of these zinc carboxylates, likewise attested in other paintings by Van Eyck [44,45] and several mid-fifteenth-century Cologne paintings [46], are now interpreted as transformation products of zinc vitriol (zinc sulfate-based), believed to have been employed as a drier mainly during the 15th century [47]. It is important to mention that zinc oxalates, only found in minor proportions, were always observed in mixtures with other metal oxalates (or soaps), depending on the paint layer composition and following the trends outlined above.

4.2.2 Trends in spatial distribution in the paint layer system

As demonstrated above, the MetOx macro-to-micro multi-analytical approach allowed trends in metal oxalate composition in relation to particular paint materials found in historical oil paintings to be successfully identified. However, only the microanalytical investigation of the historical cross-sections sample set, belonging to the NGL and KIK-IRPA's sample archives, was able to offer a clear overview of the spatial location of the different metal oxalates within the paint structure. It is noteworthy to mention that the large number of cross-sections that were investigated (*e.g.* 107) and the even wider range of analysis zones (*e.g.* 215) ensures that the results obtained are representative of the phenomenon under study, notwithstanding the micron-based observation scale.

Figure 19 shows the spatial distribution of all the different types of metal oxalates detected during the historical cross-section analyses. Independent of surface color of the samples, the metal oxalates are found predominantly within the oil paint layers themselves. After the paint layers, the strata that were most commonly found to contain metal oxalates were the surface varnish layer(s) or intermediate varnish layers within the paint stratigraphy. Surface degradation crusts or inner degradation layers constituted of metal oxalates were not commonly observed in the analyzed microsamples. Finally, the surface of calcium carbonate-containing grounds contained calcium oxalates in a few cases.

Interestingly, up to today, a significant number of scientific reports investigating the metal oxalate phenomenon in cultural heritage objects described it as a surface phenomenon, occurring in layers at the interphase with the external environment. Such reports thus suggested that the as-found metal oxalates, mostly of the calcium type, were probably produced either by deposition of air-suspended calcium oxalate (or oxalate anions) or the action of surface microorganisms. In light of these previous reports, the spatial distribution trends emerging from the MetOx results are highly relevant to the understanding of the formation mechanism of metal oxalates within oil paint layers. Indeed, they suggest that the chemical processes involved are happening within the paint film itself with the paint materials acting as the main reactants. Further insights on these issues will be discussed in the following section.

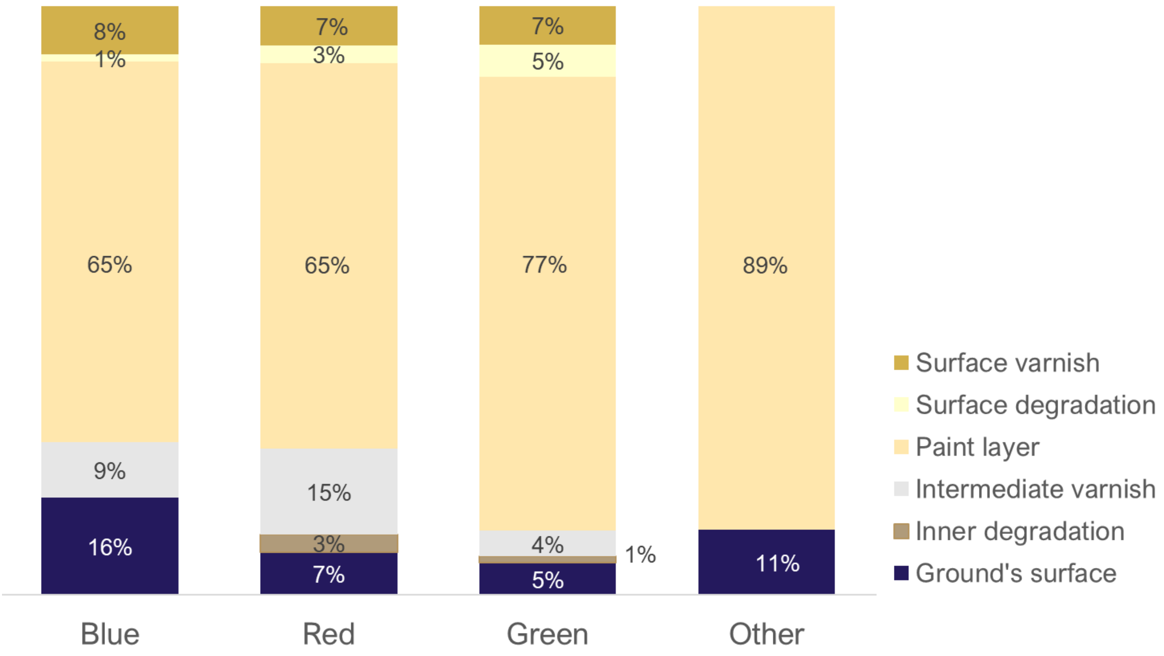


Figure 19 – Spatial distribution statistics of metal oxalates found in historical cross-sections analysed by ATR-mFTIR. Subsurface pictorial layers with colours "Other" than green, red or blue are also included.

4.3 New insights on the mechanism of formation of metallic oxalates in historical oil paintings

Describing and understanding chemical processes in historical oil paintings is a challenging endeavour. Besides being composed of mixtures of numerous materials, these paint systems have aged over time under varying environmental conditions which greatly influence the end-states that are investigated today. Nonetheless, as illustrated in the previous section, the MetOx research methodology has provided a successful approach to investigating the metal oxalate formation in historical oil paint layers, in spite of their inherent complexity. Thus, it was possible to identify clear trends relating specific paint materials to the presence of certain metal oxalates. Likewise, it was also clearly determined that these oxalates tend to concentrate in the oil paint layers themselves.

However, to deepen our understanding of the metal oxalate formation process, it was necessary to create simplified model systems in which both the materiality and artificial ageing conditions could be controlled in order to identify which material and environmental factors influence the production of metal oxalates within the oil paint layers. As mentioned in section 3.3, three different model paint sample-sets were investigated during the MetOx project: a) Mock-up stratigraphic oil paint systems; b) individual paint swatches; and c) zinc-based oil paint swatches.

By merging the results obtained from the investigation of the three different model systems, it was possible to refine the understanding of the mechanism through which metal oxalates are formed within the oil paint layer systems. More specifically, it was possible to infer the existence of specific pigment-binder interactions which are responsible for the formation of the oxalate anion inside the paint layers. The emerging trends resulting from these analyses will be discussed in the following subsections.

4.3.1 A summary of identified chemical reactivity trends retrieved from the model paint systems

By investigating the different model paint systems described in Sections 3.3.1 to 3.3.3, it was possible to identify reactivity trends concerning the formation of metal oxalates within paint layers. Thus, a series of pigments, binders and environmental aging conditions (*e.g.* temperature, relative humidity and exposure to ultraviolet/visible light) were found to promote the formation of metal oxalates in the associated oil paint systems, as summarized in **Table 12**. Noticeably, the chemical composition of the produced metal oxalate is entirely dependent on the employed pigment material.

Table 12 – General overview of tested (A) pigments; (B) binders; or (C) environmental conditions that were correlated to the formation of metal oxalates in model paint systems

A		B		C	
Metal oxalate composition correlated to specific pigments		**Binders**		**Environmental conditions**	
Calcium oxalate	▪ Red lakes ▪ Ultramarine ▪ Calcium carbonate	**Linseed oil**	▪ Cold-pressed raw with Harlem, cobalt or manganese siccatives. ▪ Stand-oil (heated) ▪ Boiled with minium (Pb_3O_4) ▪ Oleoresinous admixtures with natural resins (colophony, dammar, shellac).	**Light**	▪ UV-A (340-500 nm, 160W/m^2) ▪ UV-A (340-500 nm, 80W/m^2) + VIS (400-800 nm, 800W/m^2) ▪ UV-A (340-500 nm, 30W/m^2) + VIS (400-800 nm, 1250 lux)
Copper oxalate	▪ Verdigris ▪ Malachite	**Proteins**	▪ Animal glue ▪ Egg tempera	**% RH**	~ 0, 10, 32 and 80%
Zinc oxalate	▪ Zinc white ▪ Zinc yellow	**Polysaccharides**	▪ Gum Arabic	**T**	▪ 30ºC ▪ 40ºC

Abbreviations:
% RH = Relative humidity; T = Temperature; UV-A = ultraviolet type "A" light; VIS = visible light

As the mock-up stratigraphic oil paint systems results will be described in more detail in the next section, the following discussions in this section will focus on the trends observed in the two other model systems. For instance, the observations made from historical oil paintings regarding the presence of certain pigments and specific metal oxalate compositions matched well those found in these model systems. Thus, pigments such as madder lake, ultramarine or verdigris, were clearly associated with the presence of calcium or copper oxalates, following the patterns described in Section 4.2 and **Table 12**.

It is worth noticing that in the model samples exposed to accelerated ageing regimes copper oxalate formation was observed in malachite-containing oil and gum Arabic paint layers, indicating that this pigment can play a role in the formation of such metal oxalates under certain conditions. This is an important observation because, as mentioned in Section 4.2.1, no clear correlation between the presence of malachite and the formation of copper oxalates could be established during the analysis of historical oil paint layers, considering malachite was found admixed with other copper-containing materials in the analysed historical samples.

Regarding zinc oxalates, no investigation of the use of zinc vitriol was possible during the span of the MetOx project in order to verify whether it promoted the formation of zinc oxalates. However, in the experiments using zinc-based oil paint swatches, two zinc-containing pigments (*e.g.* zinc white, ZnO, and zinc yellow, $KZn_2(CrO_4)_2(H_2O)(OH)$) were tested. Even though these pigments are anachronic to the timeframe set for the MetOx project, it was decided to include them in the study given zinc compounds are highly reactive with fatty acids from oils, forming metal carboxylates such as zinc soaps. In the specific case of zinc white, it is currently being researched for its capacity to reduce atmospheric CO_2 into the oxalate anion, *via* a semiconductor-mediated photoreduction process [48]. As shown in [49], the MetOx research proved that such zinc pigments readily form zinc oxalates. However, this study also demonstrated that the origin of the oxalate anion in these paint films is not due to a CO_2-reduction process but rather involves the oil binder itself.

Indeed, in all of the model paint swatches investigated, the linseed oil binder was found to be prone to form metal oxalates, regardless on the binder's siccative composition or preparation recipe. Likewise, animal glue or egg-based proteins and polysaccharides (*e.g.* gum Arabic) also seem to favour the formation of metal oxalates. Unfortunately, the zinc-containing oil paint models did not allow any correlation of the particular type of natural resin (*e.g.* colophony, dammar or shellac) added to the oil paint with the formation of zinc oxalates. Indeed, no significant difference was observed between those paint films where these resins were admixed with linseed oil to create an oleoresinous media and those bound solely with the oil.

Regarding the different environmental ageing conditions explored, the model systems clearly showed that UV-A light and high relative humidity conditions promote the formation of metal oxalates. For instance, no oxalate formation was observed in highly reactive systems (*e.g.* zinc white) at ~ 0 %RH, even when the paint samples were exposed to UV-A irradiation (see **Figure 20**, left). Likewise, the results obtained indicate that the rate of formation of metal oxalates tends to increase as relative humidity increases, if there is exposure to light (see **Figure 20**, right). Unfortunately, based on the range of ageing conditions employed for the model systems, it was not possible to establish any trends regarding the effect of temperature or visible light exposure (*e.g.* 400-800 nm) in the formation of metal oxalates.

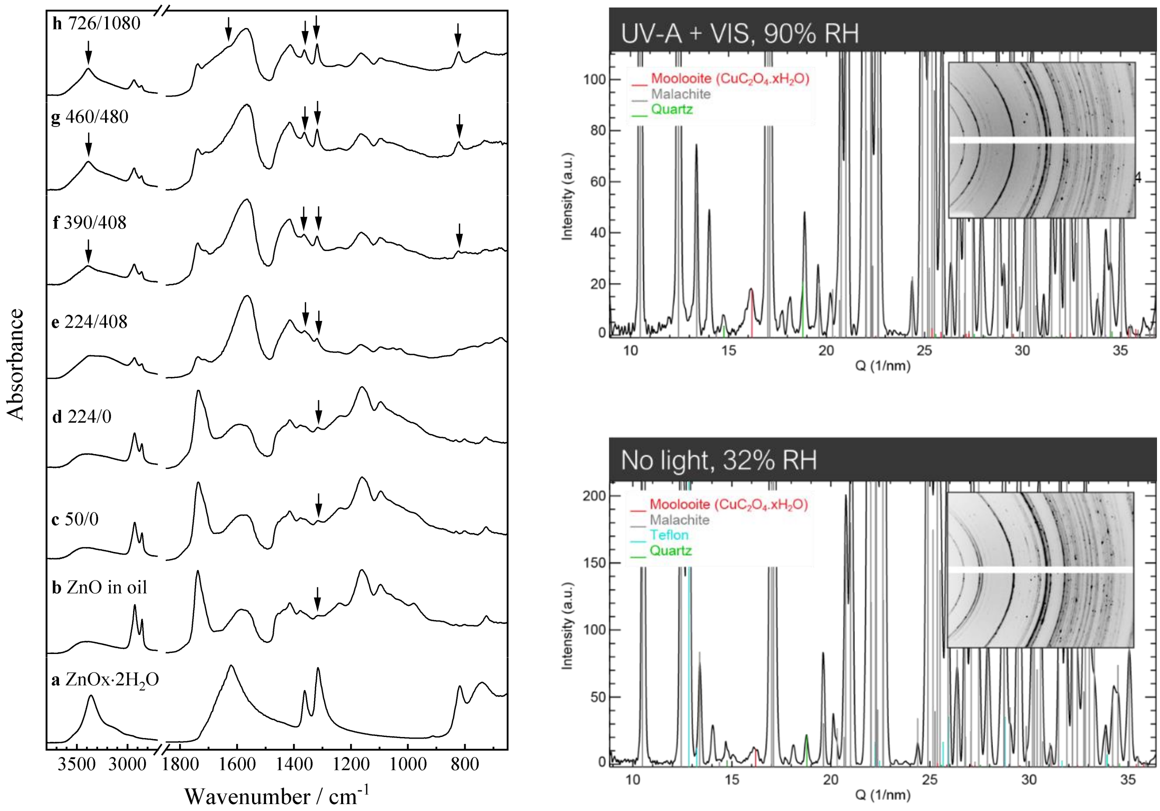


Figure 20 – Effect of light and humidity exposure on the formation of metal oxalates in oil paint films. **LEFT:** ATR-FTIR spectrum of zinc white in linseed oil with *Siccative de Haarlem* are shown as a function of UV-A / %RH treatment time together with the reference spectrum of zinc oxalate (a), and the paint film after drying in the dark (b). The treatment, in hours, given to the sample is shown in the spectra (c–h). The first number indicates UVA exposure hours and the second hours in the desiccator filled with water. The arrows indicate the appearance of zinc oxalate's characteristic IR bands. Notice the development in the spectrum for (e) 224/408 compared to (d) 224/0. Figure taken from [46] **RIGHT:** MA-XRPD diffractograms show that the formation of a copper oxalate moolooite phase is accelerated when a malachite linseed oil paint film with a cobalt siccative is exposed to higher relative humidities, if there is exposure to daylight-like illumination.

4.3.2 The role of binder-pigment interactions and environmental conditions on the formation of the oxalate anion

A more refined understanding on the role played by pigment-oil binder interactions in the formation of metal oxalates was obtained through the analysis of the mock-up stratigraphic oil paint systems. As summarized in **Figure 21**, these model systems were firstly artificially aged for 10 weeks in conditions that were shown to be favourable to the formation of metal oxalates in the other two model systems. Afterwards, they were naturally aged at constant temperature and relative humidity, in the dark, for three years.

As with the other model systems described above, the analysis of these mock-ups revealed patterns in the chemical compositions for the metal oxalates formed matching those found in historical oil paintings. For instance, a mixture of weddellite and whewellite calcium oxalates were found to be readily formed in paint swatches containing madder lake or ultramarine as well as in the presence of chalk white. This result was rather surprising, considering the pervasive presence of weddellite found, as only crystalline calcium oxalate phase, during the analysis of historical oil paintings and their cross-sections. Regarding copper oxalates, they were only found in the verdigris-based samples, while the azurite paint swatches remained seemingly unreactive throughout the ageing process. Interestingly, no significative differences were found between the two linseed oil binders employed (*e.g.* purified or mucilage-containing cold-pressed linseed oil). Thus, these results suggest that the origin of the as-detected metal oxalates within these paint layers is to be found in chemical interactions between the oil binder and the above-cited pigments.

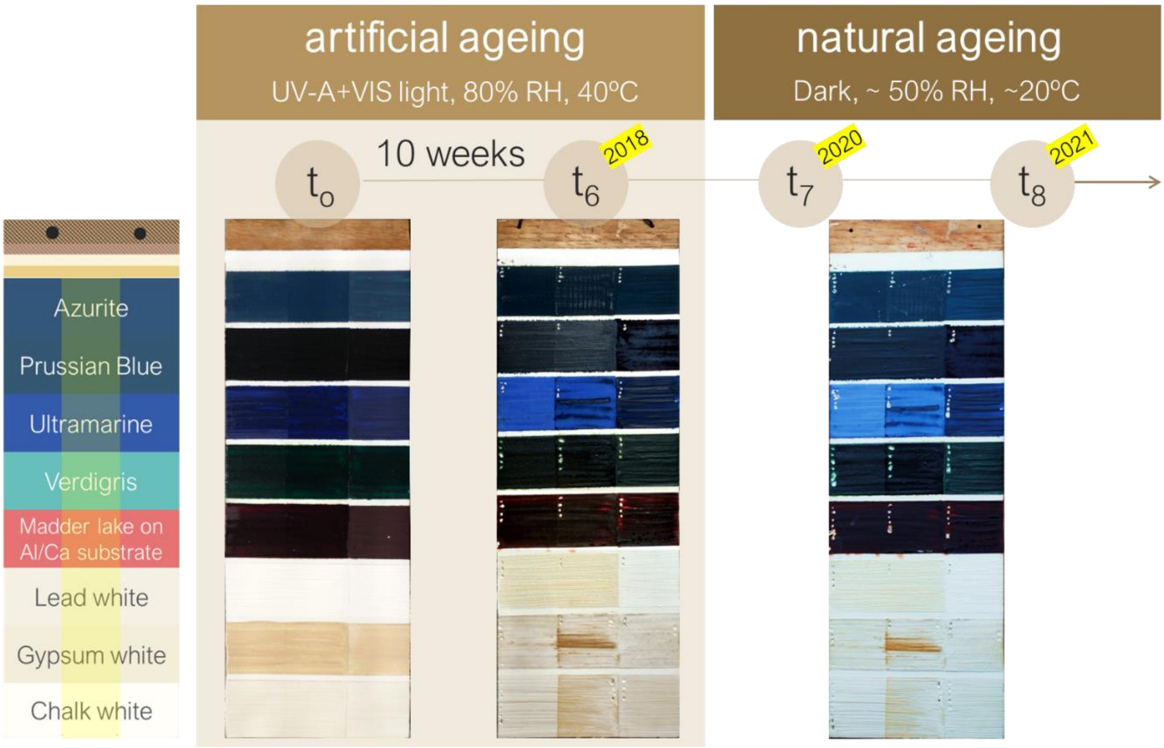


Figure 21 – Mock-up stratigraphic oil paint systems under artificial and natural ageing conditions. Characterisation measurements were undertaken at different *"t"* time intervals (see section 3.3.1). The years in which these measurements were performed are highlighted in yellow.

In these stratigraphic mock-ups, two types of material systems had been specifically designed to test the influence of colophony on the formation of metal oxalates. As described in Section 3.3.1, a colophony solution was either admixed to the oil binder in order to create an oleoresinous media (denoted "br" paint films in in **Figure 1**) or was applied as a varnish on top of the oil paint layer system (denoted as "v" paint films). However, in the "v" paint swatches, the colophony varnish fused into the paint layers during its application. Thus, under these conditions, the "v" paint swatches were materially very similar to the oleoresinous "br" ones. In any case, no significative difference in metal oxalate formation was observed either between the "v" and the "br" paint films or with those in which linseed oil was used as the only binder.

Thus, as previously discussed for the zinc-based oil paint systems, the stratigraphic mock-ups did not help to clarify if colophony influences the formation of metal oxalates within an oil paint layer. The potential effect of natural resins on metal oxalate formation is an important subject for future investigations, particularly given the MetOx findings concerning historical paint cross-sections demonstrated that calcium oxalates form in varnish layers. Furthermore, previous research [26] has demonstrated that such materials can foster the formation of metal oxalates in photo-oxidative environmental ageing conditions similar to the ones used in the MetOx study.

Interestingly, the ATR-mFTIR microanalytical investigation of cross-sections taken from the stratigraphic mock-ups showed that metal oxalates tend to form mainly at the surface of the paint films (see **Figure 22**), independently of their binder composition. The oxalate moieties seem to be concentrated in regions of similar thickness (~20-30 mm) in the case of the madder lake, ultramarine and chalk white paint swatches. In the verdigris paint films, the copper oxalate-containing region is thicker (~50 mm), possibly due to the fact that metal oxalates are mixed with other copper-based alteration species such as copper soaps and formates, in a manner similar to what was observed in historical oil paint samples (see **Figure 18**).

The fact that the metal oxalates species are mostly localized in the topmost section of the paint films suggests that their formation involves a humidity-mediated, photochemical process in which the oil binder is most probably the oxalate anion’s carbon source while pigments, extenders or ground fillers supply the metal cation. Indeed, the paint surface was the most intensely exposed both to light and to ambient humidity during the artificial ageing process. These two environmental factors are known to induce photooxidative processes in oil binders. For instance, it has been shown that high relative humidity conditions favour oxidation in paint films [15,50] and that light-induced oxidative degradation of the fatty acid chains produces a variety of small oxidised molecules upon evolution of peroxyl moieties [9]. Indeed, such peroxides will react further with time, undergoing scission and forming alkoxyl radicals which will eventually lead to the formation of low molecular weight oxidation products [4]. In turn, these products may further oxidize, ultimately leading to the formation of acidic moieties. To the best of the author’s knowledge, no study has experimentally documented the chemical pathways through which these oxidative processes in an oil binder eventually lead to the formation of the oxalate anion. Nonetheless, it has been hypothesized that this diacid can be formed by either methyl or methylene oxidation, hydrogen abstraction as well as hydroxylation at the a position to carbonyl groups of glycerides and acids [4].

Likewise, besides providing the metal cation necessary to oxalate formation, certain pigments used in this study are known to play a role in the oil binder oxidation process. For instance, it has recently been shown [51] that, under exposure to UV light, ultramarine induces a photocatalytic degradation of oil paints via a free radical process. In the case of verdigris, also known to catalyse the oxidative degradation of linseed oil [42, 52, 53], this reaction seems to involve copper in Cu(I) and Cu(II) oxidation states during redox cycles [52].

Otero *et al.* [21] have also proposed another potential mechanism to the formation of the oxalate anion from calcium carbonate, a material that was shown to readily form calcium oxalates in this study. These authors hypothesize that as ester triglycerides are hydrolysed and the oil film is locally acidified, $CaCO_3$ is converted into H_2CO_3 or CO_2, depending on the pH of the medium. The oxalate anion is then formed through a redox reaction involving CO_2 and radical species excited by light absorption. Nonetheless, no experimental proof has yet been given for this specific reaction pathway.

Finally, it is important to notice that it is not yet known how red lake pigments based on madder, kermes or cochineal dyestuffs either influence the oxidation process of the oil binder or promote the formation of the oxalate anion by means of another chemical pathway. This aspect must be addressed in future research considering that these pigments have been clearly shown to readily promote the formation of calcium oxalates in this study, both during the investigations of historical oil paintings and in the different model systems.

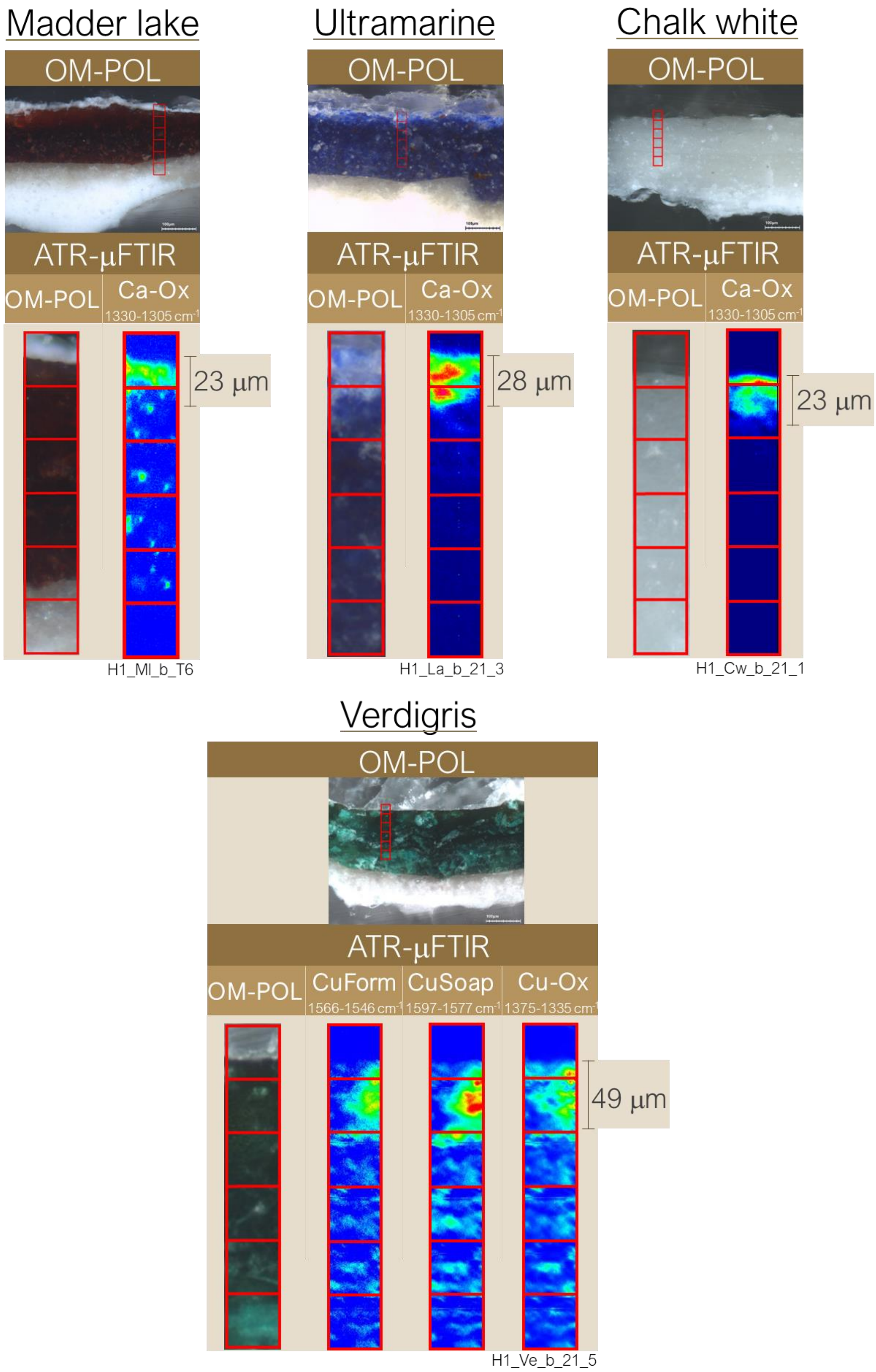


Figure 22 – ATR-mFTIR results obtained at the end of the natural ageing process (t_8, 2021) from refined linseed oil paint swatches containing madder lake, ultramarine chalk white and verdigris. Spatial distributions are shown for calcium or copper oxalates (Ca-Ox or Cu-Ox, respectively) as well as for copper formates (CuForm) and copper soaps (CuSoap). The thickness of the paint layer in which the different alteration products concentrate is indicated.

The study of these model systems also allowed a time-domain evolution of the formation of the metal oxalate species at both the macro and the microlevels to be observed. Indeed, as described in Section 3.3.1, the different paint swatches were analysed throughout their artificial and natural ageing, using either MA-rFTIR and MA-XRPD, directly on the mock-ups, or by OM-VIS/UV and ATR-mFTIR on extracted microsamples prepared into cross-sections.

The results obtained prove that the concentration of metal oxalates at the surface of the paint film increases as the latter is exposed to light and high relative humidity levels during the artificial ageing process. For instance, **Figure 23**, shows the evolution of calcium oxalate formation in a paint film composed of madder lake and purified linseed oil, as observed by MA-rFTIR and ATR-mFTIR. In both cases, the intensity of calcium oxalate's characteristic infrared vibrations increase as the artificial ageing process takes place. Moreover, the ATR-mFTIR mapping results make it possible to observe that the calcium oxalate concentration builds up in the topmost region of the paint film as the artificial ageing process advances.

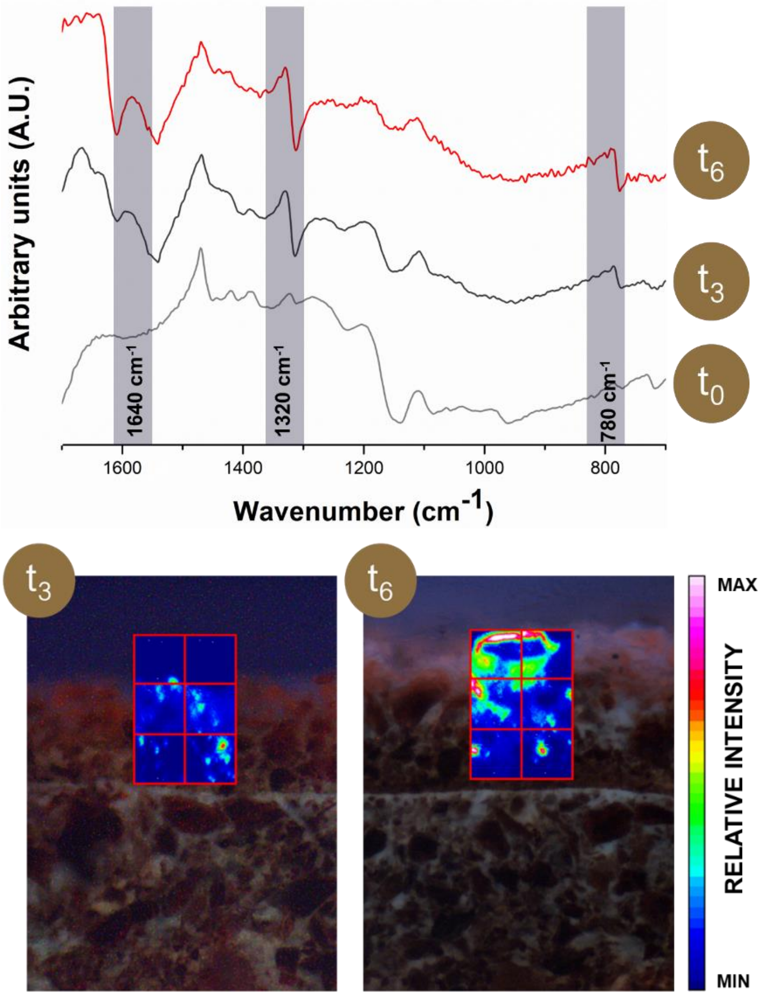


Figure 23 – MA-rFTIR (top) and ATR-m-FTIR results (bottom) obtained for a madder lake and purified linseed oil paint layer show how characteristic calcium oxalate IR bands increase in intensity as the artificial ageing process advances (t_0=beginning of the ageing process; t_3=4 weeks; t_6=10 weeks). The calcium oxalate mappings were obtained by integrating the 1330-1305 cm^{-1} IR region.

Likewise, by applying a semi-quantitative whole pattern refinement approach to the accumulated MA-XRPD diffractograms, it was possible to observe changes in the compositional profile of calcium oxalates in the same paint film discussed above, as it underwent both artificial and natural ageing.

As shown in **Figure 24**, the differences observed between the artificial and the natural ageing processes are striking. For instance, at the beginning of the artificial ageing process, no weddellite is present in the paint layer while minor amounts of whewellite were detected. This latter form of calcium oxalate is not due to an alteration of the paint film but rather to its presence in the raw plant materials used for the production of the lake, as confirmed by the XRPD and t-mTIR analysis of a root sample provided by the pigment producer.

However, after just two weeks of artificial ageing, the concentration of both, whewellite and weddellite, increased dramatically, suggesting that both calcium oxalate crystalline phases are being simultaneously formed during the artificial ageing process. After three weeks, the whewellite concentration decreases and this trend continues until the end of the artificial ageing process, resulting in a final whewellite concentration that is 20% below that of weddellite. The opposite trend is observed for weddellite, for which the concentration increases until the end of the artificial ageing phase. These results seem to indicate that whewellite is interconverting, in time, into its dihydrate counterpart, possibly explaining why weddellite is the most abundant calcium oxalate phase found nowadays in centuries-old historical oil paintings.

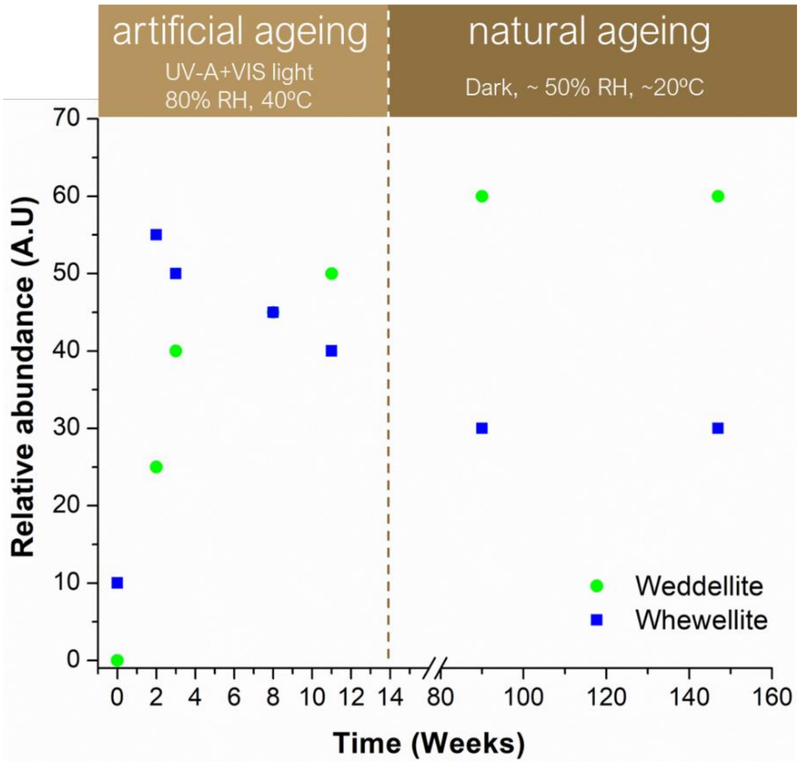


Figure 24 – Changes in weddellite and whewellite concentration in a madder lake and pure linseed oil paint swatch, tracked by MA-XRPD during the artificial and natural ageing processes.

Towards the end of the period of artificial ageing, the formation of the calcium oxalate phases appeared to slow down and their concentrations eventually reach a plateau as the paint film naturally ages. It thus seems that at lower relative humidity and temperature, in the absence of light, the chemical processes involved in the formation of weddellite and whewellite slow down, or even stop. Thus, these observations further confirm that the formation of metal oxalates is a humidity-mediated, photochemical process. Likewise, considering that both the concentrations of whewellite and weddellite reach a plateau-like state at lower relative humidity values, during the natural ageing phase, it seems that the whewellite-weddellite interconversion process is also humidity-driven.

4.4 Concluding remarks & recommendations

4.4.1 The MetOx project: contributions to the understanding of the metal oxalate phenomenon in historical oil paintings

One of the main objectives of the MetOx project was to develop a macro-to-micro analytical methodology allowing to characterise the metal oxalate phenomenon in historical oil paintings at different length scales. Highly successful results were obtained by combining state-of-the-art non-destructive and non-invasive macroanalytical techniques, applied on selected areas of historical oil paintings and model systems, with a large array of microanalytical techniques employed on cross-section samples obtained from the investigated objects.

On one hand, the combination of the three selected macroanalytical imaging techniques offered both, a representative overview of the metal oxalate composition found at the surface of historical oil paintings, and a visualisation of their two-dimensional distribution in representative, centimetre-scale areas. Nonetheless, these techniques are not able to extract layer-by-layer chemical information and thus do not allow to precise the localization of where, within the paint structure, metal oxalates are found. Likewise, even though MA-rFTIR was highly sensitive to metal oxalate detection regardless of their solid state, the use of this technique proved to be limited to unvarnished surfaces. Indeed, spectral features specific to the varnish's natural resins tend to hinder the identification of metal oxalates in underlying paint layers. MA-XRPD proved to be a powerful tool to localize metal oxalates, for instance allowing to differentiate weddellite from whewellite phases given slight differences in their crystalline structures. Nonetheless, the presence of amorphous oxalate phases remained undetected, possibly underrepresenting the extent of the oxalate phenomena in the investigated surfaces. As for MA-XRF, it offers relevant supporting information aiding the MA-XRPD or MA-rFTIR data analysis procedure (*e.g.* to identify original pigments, restored areas, etc.). However, it cannot directly identify the presence of metallic oxalates as they share the same elemental composition as the pigments they originate from.

On the other hand, microanalytical tools offered an in-depth comprehension of both, the metal oxalate composition and their spatial distribution within the paint stratigraphy. They also allowed to undoubtfully find correlations between such metal oxalate composition and specific paint materials (*e.g.* pigments, extenders, ground fillers or driers) composing the paint strata, as summarized in **Tables 11** and **12**. Furthermore, thanks to the research fostered by the MetOx consortium, a fast, reliable and reproducible ATR-mFTIR methodology was developed to identify and locate oxalate species in historical oil painting cross-sections, including an evaluation of the technique's limit of detection for metal oxalates. Similarly, it was possible to fine-tune the ToF-SIMS analytical protocol in order to detect metal oxalate moieties. Nonetheless, its use was limited to the detection of copper oxalates, given calcium oxalate's low ionisation probability of calcium oxalate. Likewise, the use of SR-m-XRPD to detect and localize crystalline metal oxalates in the paint strata allowed to complement the ATR-mFTIR and MA-XRPD investigations, refining the interpretation of the obtained results. Nonetheless, microanalytical results are usually considered unrepresentative of the large-scale paint structure given the extracted cross-section is only a few millimetres large. During the MetOx investigation of historical oil paintings, this drawback was overcome by analysing several areas of a very large number of cross-section samples, providing a statistical significance to the obtained results on the metal oxalates composition and spatial distribution or on their correlation to specific paint materials.

The application of such an analytical methodology to numerous historical oil paintings and model oil paint systems produced a considerably large results dataset. Clear trends related to the genesis of the metal oxalate phenomenon in historical oil paintings emerged from the meticulous analysis of the obtained results, thus achieving the MetOx project's second objective. Besides correlating specific paint materials to certain metal oxalate types, as described above, we were also able to demonstrate that a combination of UV-A light and ambient humidity are required to trigger metal oxalate formation in oil paint films, the process accelerating at higher relative humidity rates. Likewise, it has been clarified that atmospheric CO_2 reduction cannot be considered as a significant source of the oxalate anion, even in the presence of semiconductor pigments such as zinc oxide. Instead, we have proven that such an anion is produced by a humidity-mediated, photocatalytic oxidation of the oil binder itself and that other historically representative binders (*e.g.* animal or egg proteins and gum Arabic) can also promote oxalate formation. By elucidating these novel pigment-binder interaction trends for the first time, the MetOx project strongly contributes to our refined understanding of the metal oxalate alteration phenomenon of historical oil paintings.

4.4.2 Recommendations and perspectives for future research

Based on our results, we suggest that in order to slow down the formation of metal oxalate species, oil paintings should be the least exposed to UV radiation or high humidity rates. Fortunately, current preventive conservation guidelines for oil painting collections already match our recommendations. For instance, the Canadian Conservation Institute expressly recommends to display paintings at the lowest light level allowing for proper appreciation, while avoiding UV radiation exposure through the use of filters, visible light-only illumination systems, etc. Likewise, they prone to obtain stable relative humidity values ranging between 40 and 60%. Thus, the mechanistic insights produced by the MetOx project offer new arguments supporting the reinforcement of such preventive conservation practices.

Even though our study did not specifically evaluate the effect of water in the development of metal oxalates, a precautionary principle derived from our results would be to control the use of this solvent when performing aqueous conservation-restoration treatments. For instance, replacing "free water" treatments by cleaning systems in which the water-based solution (*e.g.* buffer, surfactant or chelator solutions, to name a few) is retained by a gelling agent would help reducing the penetration and diffusion of water into the paint layers.

Nonetheless, in order to provide further guidelines to the conservation-restoration community, further research is needed. For instance, it would be necessary to determine how the metal oxalate phenomenon is affected not only by the light source type (*e.g.* visible light) but also by its intensity. Furthermore, an artificial ageing study employing constant as well as changing relative humidity values would allow finding a compromise between a painting's optimal conservation during storage or exhibition and the reduction of the oxalate formation speed. Finally, considering conservation-restoration processes aim at becoming more sustainable, it is possible that water-based treatments, besides those currently used for cleaning, will become increasingly common. Thus, it would be greatly beneficial to study how water, either free or retained by a gel system, influences the rate of formation of metal oxalates in paint oil films.

Likewise, we have identified certain unresolved aspects of the metal oxalate phenomenon that should be researched further. For instance, it would be necessary to verify if white vitriol promotes the formation of zinc oxalates, thus explaining the presence of such species in several 15th century Southern Netherlandish oil paintings. Also, it is required to further refine our understanding of the processes underlying the reduced palette of metal oxalate compositions found in historical oil paintings, particularly given that a wide diversity of metal cations are found in these oil paint films. Furthermore, the role of natural resins (*e.g.* pine resin and dammar) in the formation of metal oxalates should be clarified, especially when applied as varnishes. It should also be verified whether a correlation exists between the type of calcium oxalate (*e.g.* weddellite and whewellite) formed and the amount of available Ca^{+2} cation in an oil paint layer. Likewise, it is worth elucidating the chemical mechanisms through which red lakes (*e.g.* madder, kermes or cochineal) promote calcium oxalate formation in oil paint films.

Finally, we have considered further areas of research which would push our comprehension of the metal oxalate phenomenon forward and link it to the wider research area of metal soaps. Indeed, although metal soaps and oxalates are both forms of metal carboxylates, up to now, fundamental research devoted to understanding the degradation of oil paint layers has tended to focus either on one or the other type of these products separately and not considered whether these processes are interlinked. However, during the MetOx project, we repeatedly observed in mock-ups and historical paintings that both metal carboxylates types are chemically and spatially correlated within the paint layer, suggesting that they are produced from the same paint materials aged under similar conditions. Nevertheless, to date, we have not been able to prove whether the photochemical mechanism leading to the formation of the oxalate anion involves only one or several of the three typical components of an oil binder (e.g. glycerol, saturated and (poly)unsaturated fatty acids), and if it can thus potentially implicate a metal soap' fatty acid moiety. Furthermore, even though ionic exchange and migration processes concerning metal soaps have previously been reported, our latest results suggest that these processes also operate not only amongst oxalate anions but also between both types of carboxylate species. For instance, we have observed surface oxalate species coordinated to cations only found in underlying paint layers, indicating that cationic and/or anionic migration takes place across paint layers. These complex ionic phenomena could explain the chemical and spatial distributions of these metal carboxylates recurrently found in our analysis of historical paintings and mock-up samples.

5. DISSEMINATION AND VALORISATION

The dissemination and valorization of the findings of the MetOx project was actively performed in order to reach a wide-ranging audience range belonging to different disciplines that could directly benefit from our research. We thus prioritized conservators-restorers, heritage scientists and art historians audiences, students and professionals alike.

Consequently, a series of conferences highlighting the findings of the MetOx project were given to professional heritage scientists, conservators-restorers and art historians, both in Belgium and abroad:

- Mederos-Henry, F., Sanyova, J. Provenance, composition et distribution des oxalates métalliques dans les couches picturales à l'huile de la peinture flamande du 15e au 17e siècles : bilan du projet MetOx. Midis de l'IRPA · Middagen van het KIK. Royal Institute for Cultural Heritage: Brussels, Belgium. 27/09/2022
- Mederos-Henry, F. The MetOx project: exploring the phenomenon of metal oxalates in Southern Netherlandish oil paintings from the 15th to the 17th centuries. Rijksmuseum : Amsterdam, The Netherlands. 02/06/2020
- Mederos-Henry, F., Glaude, C., Stillhammerova, M., Sanyova, J. The MetOx project: towards a comprehension of the formation mechanism of metal oxalates in Southern Netherlandish oil paintings from the 15th to the 17th centuries. Midis de l'IRPA · Middagen van het KIK. Royal Institute for Cultural Heritage: Brussels, Belgium. 12/03/2020.

Likewise, three different seminars were given to students in conservation-restoration or heritage science, both in Belgium and abroad:

- Mederos-Henry, F., de Meyer, S., Higgitt, C., Vanmeert, F., Legrand, S., Spring M., Delcorte, A., Poleunis, C., Janssens, K., Sanyova, J. Trends emerging from the macro-to-microscale investigation of the metal oxalate phenomenon within Southern Netherlandish oil paint layers from the 15th to the 17th centuries: final conclusions of the MetOx project. Opificio delle pietre dure: Florence, Italy. 12/05/2023
- Mederos-Henry, F. A systematic study on the metal oxalate phenomenon in Southern Netherlandish oil paintings from the 15th to the 17th centuries. Laboratoire d'Archéologie Moléculaire & Structurale, Sorbonne Université : Paris, France. 07/12/2022
- Mederos-Henry, F., de Meyer, S., Legrand, S., Janssens, K., Sanyova, J. Le projet MetOx: vers une compréhension du mécanisme de formation des oxalates métalliques dans les peintures à l'huile flamandes du 15e au 17e siècles. École Nationale Supérieure des Arts Visuels de La Cambre : Brussels, Belgium. 25/11/2020

Nonetheless, conscious that heritage science research such as the one performed in the MetOx project must also become accessible to the general public, several communications addressing this audience were performed:

- Theunis, L. Mieux comprendre l'altération des peintures flamandes du 15e au 17e siècle. Available at: https://dailyscience.be/10/02/2023/lever-le-voile-grisatre-sur-les-peintures-flamandes-du-15-au-17e-siecle/ (Accessed: 14/03/2023).

- Theunis, L. Restauration d’art: la quête de l’éclat originel. Le mystère du vieillissement des couches picturales originales des maîtres flamands se lève. Le Vif – L’express. 23/02/2023. pp.75-78.
- Dutrieux, L. Mieux comprendre la formation des oxalates métalliques dans les couches picturales à l’huile avec le projet MetOx. Available at : https://www.kikirpa.be/fr/projets/projet-metox (Accessed, 14/03/2023).
- Mederos-Henry, F., Colignon, A. Les recherches aux laboratoire des polychromies: le projet MetOx. Royal Institute for Cultural Heritage Open house day: Brussels, Belgium. 02/03/2023.

6. PUBLICATIONS

Throughout the MetOx project, a series of peer-reviewed articles, book chapters, conferences and poster communications were presented, as shown below.

Peer-reviewed articles

- Mederos-Henry, F., de Meyer, S., Higgitt, C., Vanmeert, F., Legrand, S., Delcorte, A., Poleunis, C., Spring M., Janssens, K., Sanyova, J. A macro-to-microscale systematic investigation of the metal-oxalates phenomenon in Southern Netherlandish oil paintings from the 15th to the 17th centuries. *Manuscript in preparation*, 2023.
- Mederos-Henry, F., de Meyer, S., Vanmeert, F., Higgitt, C., Legrand, S., Spring M., Janssens, K., Sanyova, J. Novel insights into the mechanism of formation of metal oxalates in historical oil paintings: a study on oil paint model systems. *Manuscript in preparation*, 2023.
- Mederos-Henry, F., Colignon, A., Bah, H., Sanyova, J., A study of the limit of detection (LOD) of metal oxalates commonly found in historical oil paintings using Attenuated Total Reflectance Micro Fourier-transform Infrared spectroscopy (ATR-mFTIR). *Manuscript in preparation*, 2023.
- Simonsen, K.P., Niemann Poulsen, J., Vanmeert, F., Ryhl-Svendsen, M., Bendix, J., Sanyova, J., Janssens, K., Mederos-Henry, F., Formation of zinc oxalate from zinc white in various oil biding media: the influence of atmospheric carbon dioxide by reaction with $^{13}CO_2$. *Herit. Sci.*, 2020, 8: 126.

Book chapters

- Mederos-Henry, F., de Meyer, S., Vanmeert, F., and Sanyova J. A macro-to-microscale scientific investigation of *The Visitation* panel: insights into its materiality and metal oxalate alteration phenomenon, in V. Bücken (ed.), Le Maître à la Vue de Sainte-Gudule. Un retable pour les carmes. Royal Museums of Fine Arts of Belgium & Silvana Editoriale : Bruxelles – Milan, 2023. *In press.*
- Sanyova, J., Van der Snickt, G., and Mederos-Henry, F., The Ghent Altarpiece: the challenges of a complex stratigraphy from a chemical point of view, in G. Steyaert, M. Postec, J. Sanyova and H. Dubois (eds.), The Ghent Altarpiece: Research and Conservation of the interior: the Lower Register. Brepols: Brussels, Belgium, 2021. pp. 111-145.

Conference presentations

- De Meyer, S., Mederos-Henry, F., Legrand, S., Sanyova, J., Janssens, K. Uncovering the prevalence of metal oxalates in 15th-17th century oil paintings by means of macroscopic X-ray powder diffraction scanning. European Conference on X-ray Spectrometry (EXRS) 2022: Brugge, Belgium. 01/07/2022.
- Mederos-Henry, F., Glaude, C., Stillhammerova, M., Colignon, A., Sanyova, J. Novel insights on the mechanism of metal oxalate formation within Southern Netherlandish oil paintings from the 15th to the 17th centuries. 6th International Congress “Chemistry for Cultural Heritage” (CHEMCH-6): Ravenna, Italy: 06/07/2022

- Mederos-Henry, F., Possible future(s) for research on the metal carboxylates phenomena in historical oil paintings: (a few) novel insights and (many) open questions. Invited lecturer at the Molecular Transformations in Oil Paint symposium: Paris, France. 16/06/2022.
- Mederos-Henry, F., Delcorte, A., Janssens, K., Sanyova, J. The MetOx project: novel perspectives on the formation mechanism of metal oxalates in Southern Netherlandish oil paintings from the 15th to the 17th centuries. Desafíos ante el tiempo: 150 años de Conservación de pintura en México. Simposio Internacional: Mexico City, Mexico. 10/11/2021.
- Mederos-Henry, F., Glaude, C., Legrand, S., de Meyer, S., Van der Snickt, G., Janssens, K., Sanyova, J. Metal oxalates in Southern Netherlandish paintings from the 15th to the 17th centuries: a study on their formation mechanism based on pigment-binder-resin interactions. TechnArt 2019: Brugge, Belgium. 09/05/2019.

Poster communications

- de Meyer, S., Mederos-Henry, F., Legrand, S., Derks, K., Sanyova, J., Janssens, K. Metal oxalates in 15th-17th century oil paintings: A macroscopic approach. Gordon Research Conference (GRC) on Scientific Methods in Cultural Heritage Research: Les Diablerets, Switzerland. 10/07/2022.
- Glaude, C., Stillhammerova, M., de Meyer, S., Legrand, S., Mederos-Henry, F., Vanmeert, F., Janssens, K., Sanyova, J. Study of metal oxalate formation in stratigraphic oil paint model systems. 6th International Congress "Chemistry for Cultural Heritage" (CHEMCH-6): Ravenna, Italy: 06/07/2022
- Colignon, A., Bah, H., Mederos-Henry, F. Study of the limit of detection (LOD) of metal oxalates by Attenuated Total Reflectance Micro Fourier-transform Infrared spectroscopy (ATR-mFTIR). 6th International Congress "Chemistry for Cultural Heritage" (CHEMCH-6): Ravenna, Italy: 06/07/2022

PhD Theses

- Legrand, S. (2021) Advanced chemical imaging of artworks [Doctoral dissertation, University of Antwerp]. https://hdl.handle.net/10067/1763420151162165141
- De Meyer, S. (2023) Development of a mobile X-ray powder diffraction instrument for artwork imaging [Doctoral dissertation, University of Antwerp]. *To be defended in 2023.*

Master Theses

- Le Brun, H. (2021) Study of the formation of metal oxalates and soaps in oil paintings from the Southern Netherlands using ToF-SIMS [Master Thesis dissertation, UCLouvain]. https://dial.uclouvain.be/memoire/ucl/object/thesis:33157
- González Merino, S. (2023) Characterization of the metal oxalate phenomena in oil paintings from the Southern Netherlands using ToF-SIMS and XPS [Master Thesis dissertation, UCLouvain]. *To be defended in June 2023.*

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  - Sarah GONZALEZ-MERINO

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